SOLUTIONS OF POTASSIUM IN AMINES

AND ETHERS.

A Thesis

presented for the degree of Doctor of Philosophy in the Faculty of Science of the University of Leicester

by

John Slater

The University,
Leicester,
June, 1970.
STATEMENT.

The experimental work described in this thesis was carried out by the author in the laboratories of the Department of Chemistry of Leicester University, between September 1967 and February 1970.

This work has not been presented, and is not being concurrently presented, for any other degree.

June, 1970.

Slater
ACKNOWLEDGEMENTS.

It is with great pleasure that I record my thanks to my fellow members of the Physical Chemistry research group, who have helped to provide a stimulating and pleasant atmosphere in which to work.

My particular thanks are due to Professor M. C. R. Symons and Dr. R. Catterall, who supervised the present research, to Mr. J. A. Brivati for help with the practical aspects of ESR spectroscopy and to Dr. I. Hurley for much helpful discussion.
To my father and mother, without
whose understanding and encouragement,
at all stages in my education, this
thesis would not have been possible.
Solutions of potassium in ethylamine, tetrahydrofuran, diglyme and a series of solvent mixtures have been studied by electron spin resonance and optical spectroscopy.

Optical spectra consisted of a single maximum at 14,000 cm\(^{-1}\) for solutions prepared in pyrex vessels, at 14,000 cm\(^{-1}\) for solutions prepared in quartz vessels. Electron spin resonance spectra, in pure solvents and solvent mixtures, consisted of an equally-spaced quartet, attributed to the "monomer", \(K_{solv.}^+\), and a central singlet, attributed to the solvated electron, \(e_{solv.}^-\). For some solvent systems, a marked dependence of hyperfine quartet line-widths upon nuclear magnetic quantum number, \(m_I\), was observed.

The dependence of the optical spectrum upon vessel material and the magnitude of electron spin resonance line-widths have been discussed in terms of the steady-state composition of the solutions. On the basis of results obtained in pure solvents and solvent mixtures, it is proposed that the monomer, in amine and ether solvents, is best represented as a solvent-separated ion-pair whose structure is modified at higher temperatures.
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1. **Fundamental constants.**

<table>
<thead>
<tr>
<th>symbol</th>
<th>designation</th>
<th>magnitude</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_0$</td>
<td>Avogadro's number</td>
<td>6.02252 x 10^{23}</td>
<td>mole^{-1}</td>
</tr>
<tr>
<td>$g_e$</td>
<td>electron g-factor.</td>
<td>2.0023</td>
<td></td>
</tr>
<tr>
<td>$g_n$</td>
<td>nuclear g-factor.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g_{1H}$</td>
<td>proton</td>
<td>5.58436</td>
<td></td>
</tr>
<tr>
<td>$g_{14N}$</td>
<td>nitrogen-14</td>
<td>0.40358</td>
<td></td>
</tr>
<tr>
<td>$g_{15N}$</td>
<td>nitrogen-15</td>
<td>-0.56608</td>
<td></td>
</tr>
<tr>
<td>$g_{39K}$</td>
<td>potassium-39</td>
<td>0.26063</td>
<td></td>
</tr>
<tr>
<td>$g_{41K}$</td>
<td>potassium-41</td>
<td>0.14325</td>
<td></td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton</td>
<td>9.2732 x 10^{-21} ergs gauss^{-1}</td>
<td>(EMU)</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>nuclear magneton</td>
<td>5.0505 x 10^{-24} ergs gauss^{-1}</td>
<td>(EMU)</td>
</tr>
<tr>
<td>$\mu$</td>
<td></td>
<td>1.821</td>
<td></td>
</tr>
<tr>
<td>$I_n$</td>
<td>nuclear spin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_I$</td>
<td>nuclear spin quantum number.</td>
<td>$I_n, I_n - 1, \ldots, -I_n$</td>
<td></td>
</tr>
<tr>
<td>$S$</td>
<td>electron spin.</td>
<td>$\frac{1}{2} (\hbar)$</td>
<td></td>
</tr>
<tr>
<td>$M_S$</td>
<td>electron spin quantum number.</td>
<td>$\pm \frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>electronic charge.</td>
<td>$1.60210 \times 10^{-19}$ cm$^3$ gm$^{-1}$ sec$^{-1}$ (ESU).</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>symbol</th>
<th>designation</th>
<th>equation</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_m$</td>
<td>molar paramagnetic susceptibility.</td>
<td>$1.2$</td>
<td>3</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>equivalent conductance per mole of solute.</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$t_+, t_-$</td>
<td>Cationic (+) and anionic (-) transference numbers.</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$D_S$</td>
<td>static dielectric constant.</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$D_{OP}$</td>
<td>optical &quot;&quot;</td>
<td>Table 5.2. 115.</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity</td>
<td>$89,90.$</td>
<td></td>
</tr>
<tr>
<td>$D_X$</td>
<td>diffusion coefficient of species $X$</td>
<td>$89,90.$</td>
<td></td>
</tr>
<tr>
<td>$W$</td>
<td>molecular weight of solvent.</td>
<td>$4$</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of the solvent.</td>
<td>$4$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>fraction of unpaired spins in solution.</td>
<td>$80$</td>
<td></td>
</tr>
</tbody>
</table>
3. Inter-conversion of energy units.

<table>
<thead>
<tr>
<th>ergs</th>
<th>sec^{-1}</th>
<th>cm^{-1}</th>
<th>eV</th>
<th>kcal</th>
<th>mole^{-1}</th>
<th>gauss (ESR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.509 \times 10^{26}$</td>
<td>$5.034 \times 10^{15}$</td>
<td>$6.242 \times 10^{11}$</td>
<td>$1.438 \times 10^{13}$</td>
<td>$5.533 \times 10^{19}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6.626</th>
<th>1</th>
<th>$3.36 \times 10^{-11}$</th>
<th>$4.16 \times 10^{-15}$</th>
<th>$9.531 \times 10^{6}$</th>
<th>$3.568 \times 10^{-7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.986</td>
<td>2.998</td>
<td>1</td>
<td>$2.40 \times 10^{-4}$</td>
<td>$2.857 \times 10^{-3}$</td>
<td>$1.070 \times 10^{4}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-16}$</td>
<td>$1.0 \times 10^{10}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.602</td>
<td>2.148</td>
<td>8.066</td>
<td>1</td>
<td>$2.305 \times 10^{1}$</td>
<td>$8.627 \times 10^{7}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-12}$</td>
<td>$1.0 \times 10^{14}$</td>
<td>$1.0 \times 10^{3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.952</td>
<td>1.049</td>
<td>3.500</td>
<td>$4.339 \times 10^{2}$</td>
<td>1</td>
<td>$3.743 \times 10^{6}$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-14}$</td>
<td>$1.0 \times 10^{13}$</td>
<td>$1.0 \times 10^{2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.855</td>
<td>2.803</td>
<td>9.349</td>
<td>1.159</td>
<td>$2.667 \times 10^{-7}$</td>
<td>1</td>
</tr>
<tr>
<td>$1.0 \times 10^{-20}$</td>
<td>$1.0 \times 10^{6}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Concentration units.

Concentrations, represented by square brackets, $[ ]$, have been measured in moles $l^{-1}$ (molarity). In much previous work, a mole ratio, $R$ (see page 95) has been used.

The two are related by the equation,

$$\text{concentration (moles } l^{-1} \text{)} = \frac{1000 \rho \text{solution}}{WR + M}$$

where $\rho \text{ solution}$ is the density of the solution, $W$ is the molecular weight of the solvent and $M$ is the molecular weight of the metal.

The term mole fraction has been used in its normal sense.
i.e. for two solvents, A and B, with densities \( \rho_A \) and \( \rho_B \), volumes \( V_A \) and \( V_B \) and molecular weights \( M_A \) and \( M_B \), the mole fraction of A is given by the ratio

\[
\frac{\rho_A V_A M_A}{\rho_A V_A M_A + \rho_B V_B M_B}
\]

and similarly for B.

5. Optical, ESR, and NMR spectra.

<table>
<thead>
<tr>
<th>symbol</th>
<th>designation</th>
<th>equation</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu )</td>
<td>frequency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_{\text{max}} )</td>
<td>frequency at band maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta \nu/2 )</td>
<td>band-width at half-height.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D )</td>
<td>optical density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>molar extinction coefficient.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c )</td>
<td>total concentration of absorbing species associated with the 11,000 or 14,000 cm(^{-1}) bands.</td>
<td>(4.1)</td>
<td>72</td>
</tr>
</tbody>
</table>

IR—, R— and \( V— \) bands.

\( A_{\text{iso}}(X), A(X) \) isotropic hyperfine coupling or \( A_X \) constant to nucleus X (gauss).

\( \Delta H_{\text{ms}} \) natural line-width (gauss).

\( \Delta H_{\text{obs}}(m) \) observed singlet g-factor.

\( g_e, g_K \) observed monomer g-factor.
(xiv)

<table>
<thead>
<tr>
<th>symbol</th>
<th>designation</th>
<th>equation</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta g$</td>
<td>$e'_g - e'_M$</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>$I'_x$</td>
<td>intensity of derivative ESR signal from hyperfine coupling to nucleus X.</td>
<td>Table 5.1</td>
<td>108,109</td>
</tr>
<tr>
<td>$\frac{A_N}{A_B}$</td>
<td>relative amplitudes of the $m_\perp = \pm \frac{1}{2}$ and $m_\perp = \pm \frac{3}{2}$ lines of the $^{39}K$ or $^{41}K$ hyperfine quartets</td>
<td></td>
<td>133</td>
</tr>
<tr>
<td>$O(X)$</td>
<td>Overhauser shift of the electron ESR resonance position, arising from hyperfine coupling to nucleus X.</td>
<td>5.9.</td>
<td>117</td>
</tr>
<tr>
<td>$K(X)$</td>
<td>Knight shift for nucleus X.</td>
<td>1.5, 1.6, 5.8, 6.117</td>
<td></td>
</tr>
</tbody>
</table>

6. Theoretical description of systems.

<table>
<thead>
<tr>
<th>symbol</th>
<th>designation</th>
<th>equation</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{iso}(X)$</td>
<td>isotropic hyperfine coupling constant to nucleus X (ergs)</td>
<td>1.10</td>
<td>9</td>
</tr>
<tr>
<td>$</td>
<td>\psi(\omega)</td>
<td>^2_x$</td>
<td>unpaired electron contact spin-density at nucleus X (cm$^{-3}$)</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>electron-nuclear correlation time</td>
<td>Table 4.8</td>
<td>97,98</td>
</tr>
<tr>
<td>$\tau_M$ or $\tau_{M^+}$</td>
<td>electron-cation correlation time</td>
<td>49.</td>
<td></td>
</tr>
<tr>
<td>$\tau_D$</td>
<td>correlation time for Debye molecular rotation</td>
<td>Table 4.8</td>
<td>equation 4.18</td>
</tr>
<tr>
<td>$n$</td>
<td>number of molecules with which electron interacts.</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>$T_{1e}^{-1}$, $T_{2e}^{-1}$</td>
<td>electron relaxation rates.</td>
<td>8-11.</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>ion-size parameter.</td>
<td>1.17,</td>
<td>17,94</td>
</tr>
</tbody>
</table>

\[ 1e^2e^* \] molecular rotation.

\[ n-1 \] number of molecules with which electron interacts.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Designation</th>
<th>Equation</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_A$, $P_B$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_A$, $T_B$</td>
<td>parameters defining states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{2A}$, $T_{2B}$</td>
<td>A and B (two-state model).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_A$, $A_B$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$* \left[ T_2(m_I) \right]^{-1}$</td>
<td>electron transverse relaxation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>rate corresponding to $\Delta H(m_I)_{\text{obs.}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\left[ T_2(m_I) \right]^{-1}$</td>
<td>electron transverse relaxation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>rate corresponding to $\Delta H(m_I)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(see page 138)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(see page 138)
CHAPTER 1

METAL-AMMONIA SOLUTIONS.
INTRODUCTION.

Since their discovery by Weyl in 1664, fluid solutions of alkali metals in ammonia have been the subject of an intensive investigation using a wide variety of techniques. In this chapter some of the properties of dilute metal-ammonia solutions are discussed in terms of the models proposed. The nature of these solutions is discussed in some detail since they are by far the most extensively studied metal solutions and it is only by reference to metal-ammonia solutions that metal-amine and metal-ether solutions can be understood.

PROPERTIES OF METAL-AMMONIA SOLUTIONS.

Conductance.

The principal measurements of conductivity have been performed by Kraus and, more recently, at three temperatures, by Dewald and Roberts.

In the dilute region (0-0.04M), the equivalent conductance per mole of solute, $\Lambda$, decreased as the concentration of metal in the solution increased. Similar behaviour has been observed for salts e.g. sodium chloride in ammonia. Thereafter the equivalent conductance of metal solutions increased rapidly as shown in Figure 1.1.

At all metal concentrations, $\Lambda$ increased with increase in temperature i.e. $\frac{d\Lambda}{dT}$ is positive. The complete behaviour observed is shown in Figure 1.2.

Transference numbers.

Transference numbers have been measured by direct and indirect methods. In dilute solutions, $t_-$, the transference number of the negatively-charged species, was 0.85; $t_+$, the transference number of the positively-charged species (the cation), was 0.15. In more concentrated solutions, $t_-$ increased and $t_+$
Concentration-dependence of equivalent conductance, $\Lambda$, for solutions of sodium in ammonia at -37°C. (ref 7.)
Variation of the temperature coefficient of conductance, with change in concentration, for solutions of sodium in ammonia. \( \Delta \) (ref. 3); \( X \) (ref. 6); \( \square \) (ref. 5) and \( \circ \) (ref. 4).
decreased i.e. the proportion of current carried by the negatively-charged species increased. This result, together with the conductivity data, suggests that, as metal concentration increases, a complexing reaction occurs between the charged species so that the mobility of both decreases. The detailed nature of this complexing reaction will be discussed later.

**Magnetic susceptibility.**

Metal solutions have been found to be paramagnetic i.e. to contain unpaired electrons. Magnetic susceptibility measurements enable concentrations of unpaired electrons to be estimated.

The electron has both a paramagnetism and a diamagnetism associated with it. Magnetic susceptibility can be measured by two methods, a "static" method using a Gouy balance and a "dynamic" method using radiofrequency (rf) or microwave (mw) absorption.

\[ \chi_S, \text{ the "static" susceptibility,} \]

is a measure of the sum of the diamagnetism and paramagnetism of all species present, whereas \( \chi_{\text{esr}} \), the susceptibility measured by the intensity of the absorption mode in an electron spin resonance experiment, is related to the imaginary part, \( \chi'' \), of the complex paramagnetic susceptibility, \( \chi_p \).

\[ \chi_p = \chi' + i \chi'' \quad \text{(equation 1.1)} \]

\( \chi_p \) can be calculated from \( \chi'' \) using the Kramer-Krönig relationship.

Thus, even if \( \chi_S \) is corrected for the diamagnetism of solvent and cations, it is still not equal to \( \chi_p \) because of the diamagnetic contribution from the electron spin. At low metal concentrations, \( \chi_S \) and \( \chi_p \) have been found to be approximately equal since diamagnetic contributions are generally much smaller than are paramagnetic contributions. At higher concentrations, however, when electron spins are
predominantly paired, $\chi_S$ was greater than $\chi_p$.

At low metal concentrations, the paramagnetic susceptibility per mole, $\chi_m$, corresponded to an Avogadro number of unpaired electrons per gram atom of metal solute, viz.

$$\chi_m = \frac{L_\omega g^2 \mu_e^2 S(S + 1)}{3kT}$$  \hspace{1cm} (equation 1.2)

(symbols have been defined in the Fördand).

$\alpha$, the fraction of unpaired spins, defined by

$$\alpha = \frac{\chi_m \text{(observed)}}{\chi_m \text{(equation 1.2)}}$$  \hspace{1cm} (equation 1.3)

has been observed to decrease with increase in metal concentration (Figure 1.3) and decrease in temperature, i.e., spin-pairing is favoured by high metal concentration and low temperature.

Heats of solution.

Gunn and Green measured heats of solution, at 25°C, for solutions of lithium, sodium and potassium in ammonia. They found that the solution process was exothermic at all concentrations, the heat evolved decreasing in the order lithium $>$ potassium $>$ sodium. In a given system, the solution process was most exothermic at higher concentrations. More recent measurements by Gunn, at three temperatures, have confirmed that the heat of dilution is strongly dependent upon both concentration and temperature and appears to correlate closely with the magnetic susceptibility.

Optical Spectra.

The optical spectra of metal-ammonia solutions
Concentration-dependence of $\alpha$, determined by measurements of magnetic susceptibility (equation 1.3), for solutions of potassium in ammonia at $-33^\circ$C.

$\alpha$ (ref 11); $\chi$ (ref. 129).

The dashed line (- - -) represents corresponding values of $\alpha$ obtained by using

$$\alpha_{\text{calc.}} = \frac{[e^{-}] + [K]}{C}$$

(equation 4.4).

with the data in Fig. 4.11.
were found to consist of a single, broad band in the infrared
\( \nu_{\text{max.}} \sim 5,500 \text{ cm}^{-1} \) at room temperature, \( \Delta \nu_{h} \sim 3,500 \text{ cm}^{-1} \). The band was asymmetrically broadened on the high energy side, with a long tail extending into the visible and ultraviolet regions. The position of the maximum was markedly temperature-dependent, shifting to higher energies at lower temperatures \( \left( \frac{d \nu_{\text{max}}}{dT} = -20 \text{ cm}^{-1} \text{ deg}^{-1} \right) \). The band, however, was relatively insensitive to concentration, shifting to slightly lower energies as the concentration of metal increased (Figure 1.4). The band shift with concentration was much less than the band width and no significant changes in band shape or extinction coefficient with concentration have been detected.

There is some evidence for the existence of a second, and possibly a third, absorption band in the optical spectra of \( \sim 5 \times 10^{-3} \) m sodium-ammonia solutions containing 1.5 M sodium iodide. The additional weak bands have been observed at 12,500 cm\(^{-1}\) and, in one instance, \( 15,000 \text{ cm}^{-1} \). The latter band has also been observed in solid metal-ammonia solutions at very low temperature. Similar results have been reported for solutions of alkali metals in hexamethylphosphoramide (HMPA), where, in addition to the infrared band, a strong, metal-dependent band was detected at frequencies from 10,000 cm\(^{-1}\) to 13,500 cm\(^{-1}\). As will be discussed fully in Chapter 2, an analogous band has also been observed for metal-amine solutions.

**Nuclear magnetic resonance (NMR).**

In general, the presence of paramagnetic centres in a system leads to very broad NMR lines due to very rapid nuclear relaxation via coupled electron spins. For metal solutions, however, the cation-electron correlation time is very short (\( \sim 10^{-12} \text{ secs.} \)) and relaxation via the electron spin is no longer as effective. This obscures the information available from electron spin resonance (ESR) spectra but results
Fig 1.4
Concentration-dependence of the (infrared) band position for solutions of alkali metals in NH₃ and ND₃ at -65°C.

NH₃
- sodium (O)
- potassium (□)
- lithium (△)
- caesium (+)

ND₃
- sodium, lithium (ref. 130)
- and barium (X) (ref. 131).
in relatively-sharp NMR lines, which are shifted from their normal positions. This shift, the Knight shift ($K$), arises because the two spin-states for the electron are not equally populated (a Boltzmann distribution exists), resulting in a net local field from the electron at the nucleus. The Knight shift is measured as,

$$K = \frac{H_{\text{reference}} - H}{H_{\text{reference}}}$$  \hspace{1cm} (equation 1.4),

where $H$ is the field at which resonance occurs for the nucleus in the metal solution, $H_{\text{reference}}$ is the field at which the resonance of the same nucleus occurs in the absence of paramagnetic centres. The magnitude of the Knight shift is given for solvent nucleus (X) by equation 1.5 and for metal nucleus (M) by equation 1.6.

$$K(X) = \frac{-nAx}{3kT} \frac{S(S + 1)}{g_e \mu_B} \frac{C_x}{g_n \mu_n} \alpha$$  \hspace{1cm} (equation 1.5)

$$K(M) = \frac{-A_M}{3kT} \frac{S(S + 1)}{g_e \mu_B} \frac{[M^+e^-]}{[M^+]}$$  \hspace{1cm} (equation 1.6)

where $[M^+e^-]$ and $[M^+]$ represent the concentrations of ion-pair and total metal respectively (all other symbols are defined in the Forward). For a given concentration, if $K(X), K(M), \alpha$ and $k_1$, the ion-pairing formation constant, are known, then $nAx$ and $A_M$, the total contact hyperfine splitting constants to solvent and metal nuclei respectively, can be determined. For metal-ammonia solutions, these quantities cannot be evaluated by ESR, furthermore Knight shift measurements give the sign of the hyperfine coupling i.e. a positive hyperfine coupling constant leads to a downfield shift, a
negative hyperfine coupling constant leads to an upfield shift of the resonance position.

Knight shift measurements for the magnetic nuclei in metal-ammonia solutions have been performed by McConnell and Holm, Acivos and Pitzer, O'Reilly, and Hughes. A small downfield shift for the sodium nucleus, a large downfield shift for the nitrogen nucleus and a small upfield shift for the hydrogen nucleus were observed.

In dilute solutions of sodium in ammonia, there was an initial increase in $K(\text{Na})$ with increase in sodium concentration\(^2\). At higher metal concentrations, however, $K(\text{Na})$ was concentration-independent, until the onset of metallic character occurred (Figure 1.5). The nitrogen Knight shift, $K(N)$, was found to decrease with decrease in temperature i.e. it is clear from equation 1.5 that the temperature-dependence of $\alpha$ and possibly $nAx$, determine the temperature-dependence of $K(N)$. The sodium Knight shift, $K(\text{Na})$, also decreased with decrease in temperature. The analysis in terms of equation 1.6, however, is more complex since, although there is evidence from metal-amine and metal-ether results that $A_m$ decreases with decrease in temperature, the temperature-dependence of the factor $\left[\frac{M^+e^-}{M^+}\right]$ is the cause of some controversy, as will be discussed later.

**Electron spin resonance (ESR)**

The ESR spectrum of a sodium-ammonia solution was originally reported by Hutchison and Pastor and consisted of a single narrow line ($\Delta H_{ms} \sim 20$ milligauss), close to free-spin. Virtually no change in line-width was observed with change in metal, increase in metal concentration up to $0.5M$ or when $^{14}\text{ND}_3$ was used instead of $^{14}\text{NH}_3$ but there was a decrease in line-width of approximately...
Concentration-dependence of the sodium Knight shift, $K(\text{Na})$, for solutions of sodium in ammonia at room temperature (X: ref 23).

The dashed lines (---) represent attempts to fit the experimental data by varying $|\psi(o)|^2_{\text{Na}}$ (ref. 52), with values for $10^{-22}$ $|\psi(o)|^2_{\text{Na}}$ of 1.80 (I), 2.82 (II), 3.44 (III) and 4.29 (IV).
The Theory of Electron Relaxation.

Relaxation times.

After the absorption of energy by the spin-system, relaxation back to thermal equilibrium with the surrounding lattice must occur.

For the component of the spin along the axis of the applied magnetic field (the Z-axis), the rate of relaxation is given by,

\[
\frac{d \langle I_z \rangle}{dt} = -\frac{1}{T_1} \left( \langle I_z \rangle - I_o \right) \quad \text{(equation 1.7)}
\]

where \( I_z \) is the component of magnetisation along axis Z
\( \langle I_z \rangle \) is the ensemble average of \( I_z \) at time \( t \),
\( I_o \) is the equilibrium value of \( I_z \),
and \( T_1 \) is the spin-lattice relaxation time.

For the component of the spin perpendicular to the magnetic field i.e. along the x- and y-axes,

\[
\frac{d \langle I_{xy} \rangle}{dt} = -\frac{1}{T_2} \left( \langle I_{xy} \rangle - I_o \right) \quad \text{(equation 1.8)}
\]

where \( T_2 \) is the transverse or spin-spin relaxation time and governs the communication of spin energy between the individual units comprising the spin system.

Electron-nuclear interactions.

For electron-nuclear contact interactions with hyperfine coupling constant \( A \) and no modulation of the interaction, a mean-square "rigid-lattice" ESR line-width, \( \langle (\delta \omega)^2 \rangle \) can be defined.\(^{27}\)
where $A$, the hyperfine coupling constant, is defined by the Fermi contact expression,

$$A = \frac{8\pi}{3} g_\sigma g_n \mu_B \mu_n |\psi(0)|^2$$  (equation 1.10).

(see Forward for definitions of symbols).

and $m_I$, the nuclear spin quantum number, has values $I, \ldots, -I$. It can be shown that,

$$\langle m_I^2 \rangle = \frac{1}{3} I(I + 1)$$  (equation 1.11).

If the electron-nuclear interactions are modulated at a rate $\tau_c^{-1}$, such that

$$\left(\hat{\omega} \tau_c\right)^2 \ll 1$$

where $\hat{\omega}$ is the frequency of measurement, then motional narrowing occurs. The differentiation between the axes is lost, $T_1^{-1} = T_2^{-1}$ and the line-widths of the ESR lines are given by $T_1^{-1,2}$.

The contribution to the electron-spin relaxation rate arising from the rapid modulation of the electron-nuclear contact interaction is given by,

$$T_{1e}^{-1} (contact) = T_{2e}^{-1} (contact) = \frac{2 \langle (\delta \omega)^2 \rangle \tau_c}{\text{contact}}$$  (equation 1.12).

\[\langle (\delta \omega)^2 \rangle = \left(\frac{A}{\hbar}\right)^2 \langle m_I^2 \rangle\]  (equation 1.9).
Substituting for $\langle \Delta \omega \rangle^2$ (equation 1.9) and $\langle m_f^2 \rangle$ (equation 1.11) leads to,

$$T_{1,2e}^{-1} \propto \text{nucleus of type } Y$$

$$= \frac{2}{3} \left( \frac{A_Y}{\hbar} \right)^2 I_Y(I_Y + 1) \tau_c$$

For $n$ molecules, each with $x$ of nucleus $Y$, the total relaxation rate, $T_{1,2e}^{-1}$ (Contact) is given by,

$$T_{1,2e}^{-1} \propto \frac{2nx}{3} \left( \frac{A_Y}{\hbar} \right)^2 I_Y(I_Y + 1) \tau_c$$

Substituting for $A$ (equation 1.10) gives,

$$T_{1,2e}^{-1} \propto \frac{128n^2 g_e^2 \mu_B^2 \mu_n^2 \tau_c}{27 \hbar^2 n} \left[ \frac{g_n^2 I_Y(I_Y+1)x^2}{n|\psi(0)|_Y^2} \right]$$

Application of electron-relaxation theory to metal-ammonia solutions.

In metal-ammonia solutions, the magnetic nuclei are the metal, nitrogen and hydrogen nuclei i.e. equation 1.15 becomes,

$$T_{1,2e}^{-1} = \frac{C \tau_c}{n} \left[ g_N^2 I_N(I_N+1) \right] \{ n|\psi(0)|_N^2 \}^2$$

$$+ g_H^2 I_H(I_H+1) \{ n|\psi(0)|_H^2 \}^2 + C \tau_m \left[ g_M^2 I_M(I_M+1) \{ |\psi(0)|_M^2 \}^2 \right]$$

(equation 1.16)
where \( c = \frac{128 \pi 2g_e^2 \mu_B^2 \mu_n^2}{27 \hbar^2} \)

\( \tau_c \) and \( \tau_M \) are the correlation times for the electron-nuclear and the electron-cation interactions respectively. The mechanism of the modulation of these interactions is not defined.

**MODELS FOR METAL-AMMONIA SOLUTIONS.**

Several models have been proposed to explain the properties of metal-ammonia solutions. Models can broadly be divided into three main classes, depending upon whether they postulate the existence of cavities in the solvent, metal-based species, or electrostatic aggregates.

The first model for metal-ammonia solutions was that of Weyl, who proposed that the solutions were molecular compounds e.g. \( \text{NH}_3^+ \) and \( \text{NH}_3\text{Na} \) with tetrahedral co-ordination to the nitrogen.

Vapour pressure and conductivity measurements led Kraus to the conclusion that these simple molecular compounds did not exist. He postulated the existence of ions \( \text{Na}^+ \) and \( \text{Y}^- \) in equilibrium;

\[ \text{Na}^+ + \text{Y}^- \rightleftharpoons \text{Na} \]

and identified \( \text{Na} \) with the metal atom and \( \text{Y}^- \) as a new type of anion, the "negative electron". The "negative electron" was surrounded by weakly-interacting ammonia molecules, with little or no tendency for the formation of \( \text{NH}_3^- \).

The first cavity model was the square-well model of Ogg, who proposed that metal solutions were analogous.
to solid solutions of alkali metals in alkali halide crystals, with \( e^- \) and \( e_2^- \)-centres in the former corresponding to \( F^- \) and \( F^+ \) centres in the latter. \( F^- \) and \( F^+ \) centres consist, respectively, of a single electron and an electron pair trapped at an anion vacancy. Both \( e^- \) and \( e_2^- \) species were considered to be trapped in solvent cavities defining potential wells, the potential energy being due to electrical polarisation of the medium surrounding the cavity. Using the form of the Schrödinger wave equation applicable to this system, Ogg demonstrated \(^{34}\) that the optimum values of cavity radius, \( r_c \), and total energy, \( W \), for the \( e^- \) species, were 9.9 Å and -0.38 eV respectively. Application of the theory to the \( e_2^- \) centre, i.e. to two \( 1s^- \)electrons trapped in the same cavity, led to the conclusion that this centre was more stable than the \( e^- \) centre, a result which was confirmed by Kaplan and Kittel\(^{35}\) who, from a consideration of the temperature-dependence of the magnetic susceptibility, calculated that the \( e_2^- \) centre was more stable than the \( e^- \) centre by 0.2 eV. This somewhat surprising result was rationalised by assuming that the greater polarisation energy of the electron pair outweighed the unfavourable electrostatic repulsion term. This simple model was applied by Ogg to optical spectra and by Kaplan and Kittel\(^{35}\) and later Pollak\(^{26}\) to ESR spectra. These applications are discussed in more detail later.

The other principal cavity model is the polaron model, originally proposed by Landau\(^{36}\) for \( F^- \)-centres and applied to metal solutions by Jortner and co-workers\(^{37-39}\). The electron is bound in a spherical cavity, of radius \( 3 - 3.5 \AA \), by polarisation of the surrounding medium. The solvent is considered to be a continuous dielectric medium, characterised by macroscopic properties e.g. static and optical dielectric constants, \( D_s \) and \( D_{op} \) respectively. Very sophisticated
mathematical treatments e.g. Hartree-Fock self-consistent field analysis, have been applied to describe the interaction between the unpaired electron and the polarisation field of the dielectric medium.

In 1956, Becker, Lindquist and Alder[^1] argued that the cavity models could not predict the dependence of conductivity and magnetic susceptibility upon the metal used. They proposed that the solutions contained four species:

1. A neutral monomer, of stoichiometry $M$, consisting of an alkali metal cation surrounded octahedrally by ammonia molecules, with the negative (nitrogen) end of the dipole pointing towards the cation. The electron was assumed to circulate around this unit, with highest spin-density on the positive protons of the ammonia molecules.

2. A solvated cation, $M^+_{\text{solv.}}$ formed by

3. A solvated electron, $e^-_{\text{solv.}}$ dissociation of (1)

4. A dimer species, of stoichiometry $M_2$, in which two monomer species are held together by exchange forces.

Equilibria between the species were written,

$$M_{\text{solv}} \stackrel{K_1}{\rightleftharpoons} M^+_{\text{solv}} + e^-_{\text{solv}} \quad K_1 = \frac{[M^+] [e^-]}{[M]}$$

$$2M_{\text{solv}} \rightleftharpoons (M_2)_{\text{solv}} \quad K_2 = \frac{[M_2]}{[M]^2}$$

$K_1$ and $K_2$ being the ion-pairing and spin-pairing equilibria constants respectively.

his arguments upon the apparent lack of an electronic absorption resonance from the monomer, he proposed that the observed properties of dilute metal solutions could be explained using only two species, $e^-$ and $M_2$.

Evers\textsuperscript{42} analysed the conductivity data of Kraus\textsuperscript{2} and performed similar measurements on lithium-methylamine solutions. He concluded that, whereas the concentration of monomer species was small in ammonia solutions (6-7\%), it was much larger in the amine solutions ($\sim 25\%$) and was therefore clearly not negligible.

In 1964, Arnold and Patterson\textsuperscript{43} correlated conductivity and magnetic susceptibility data and pointed out that the data could not be accommodated using a single diamagnetic species, $M_2$, since the susceptibility fell much faster than the conductivity. They proposed a further, conducting diamagnetic species, $M'$, which they identified as an electron trapped in the field of an M- centre. The following equilibria between the species were written,

\[
M \xrightarrow{K_1} M^+ + e^- \quad K_1 = \frac{[M^+][e^-]}{[M]}
\]

\[
2M \xrightarrow{K_2} M_2 \quad K_2 = \frac{[M_2]}{[M]^2}
\]

\[
M + e^- \xrightarrow{K_3} M' \quad K_3 = \frac{[M']}{[M][e^-]}
\]

In order to elucidate the nature of the monomer or ion-pair species in metal-ammonia solutions, Catterall and Symons\textsuperscript{44,45} studied solutions of europium in ammonia. In dilute solutions,
the europium dissociates,

\[ \text{Eu} \xleftrightarrow{\text{Eu}_{\text{solv}}^{2+} + 2e_{\text{solv}}^\text{-}} \]

Separate ESR signals were observed from \( \text{Eu}_{\text{solv}}^{2+} \) and \( e_{\text{solv}}^- \), though both were broadened by spin-spin exchange.

There was no evidence, from either ESR or optical spectra, for the formation of the Eu\(^+\) species. They therefore concluded that the major form of cation-electron interactions in metal-ammonia solutions was best described as loose ion-pairing.

Golden, Guttman and Tuttle\(^{45-48}\), from a consideration of the electron affinities of the alkali metals in the gas phase, have proposed that the species \( M_{\text{solv}}^- \), the solvated alkali-metal anion, is a constituent of metal-ammonia solutions.

There is a formal resemblance between this model and that of Arnold and Patterson\(^{43}\). The latter authors, however, did not fully define the nature of the second diamagnetic species, furthermore there is no monomer species in the redox model of Golden, Guttman and Tuttle, for which equilibria were written,

\[ M^+ + 2S^- \xrightleftharpoons{K_1} M^- + 2S \]

and

\[ M^+ + A^- \xrightleftharpoons{K_2} M^+A^- \]

where \( S \) and \( S^- \) represent a solvent molecule and a solvent-electron complex respectively and \( A^- \) represents \( e^- \) or \( M^- \).

Gold, Jolly and Pitzer\(^{49}\) have proposed the existence of electrostatic aggregates with overall stoichiometry corresponding to \( M, M^-, M_2 \) etc. viz. \( M^+e^- \), \( e^-M^+e^- \), \( e^-M^+e^-M^+ \) respectively. This model has some success in interpreting null effects i.e. in explaining the concentration-independence of molar volumes, ESR and optical spectra.

As reported in a review to be published shortly, Catterall and Dye\(^{50}\), using the new conductivity data of Dewald and Roberts\(^3\),
have subjected a considerable amount of data to re-analysis in terms of the species $M^+$, $e^-$ and $M^+e^-$ only, with spin-pairing attributed to the formation of diamagnetic collision complexes. This very important model is discussed in detail later.

**SPECIFIC INTERACTIONS IN METAL-AMMONIA SOLUTIONS.**

**Electron-cation interactions.**

In relatively-dilute solutions, as metal concentration increases, the equivalent conductance and transference numbers decrease, while the metal Knight shift increases. These observations have been interpreted in terms of the equilibrium,

$$M^+ + e^- \rightleftharpoons M^+e^- / M$$

The conductivity data of Kraus\(^2\) (1921) has only recently been improved and extended, by Dewald and Roberts\(^3\) (1968). The data of Kraus, at one temperature only, led to an ion-pairing equilibrium constant similar to those of salts in ammonia and so the ion-pair $M^+e^-$ was described as being analogous to $M^+X^-$. Gunn and Green\(^{12}\), and later Gunn\(^{13}\), measured heats of solution and dilution which, with the conductivity data of Kraus, led to the conclusion that the ion-pairing reaction was endothermic ($\Delta H = +2.3$ kcal.) i.e. ion-pairing ought to be less pronounced at low temperatures. This result, which was adopted by Arnold and Patterson\(^{14}\) and Golden, Guttman and Tuttle\(^{15,16}\), is in accord with the observed behaviour of $M^+X^-$ and can be rationalised in terms of an increase in solvent dielectric constant with decrease in temperature, leading to increased stabilisation of the free ions and consequent reduction in the number of ion-pairs. The new conductivity data of Dewald and Roberts\(^3\) for sodium-ammonia and of Dewald\(^5\) for caesium-ammonia, has shown, however, that the
ion-pairing reaction is exothermic ($\Delta H = -2.4 \text{ kcales}$) and, therefore, that ion-pairing is more pronounced at low temperatures. In order to explain this, Dewald and Roberts have pointed out that a fundamental difference between $M^+e^-\text{ and } M^+X^-$ is that the anion of the former can undergo considerable change in size with change in temperature. Optical considerations, discussed later, have led to the conclusion that the effective ion-size of $e^-_{\text{solv}}$ increases with increase in temperature. Applying

$$K^{-1} = \exp \left( -\frac{e^2}{a^2 \kappa T} \right)$$

(equation 1.17),

where $K$ is the ion-pair dissociation constant and $a$ is the ionic separation in the ion-pair, it is clear that, for a normal ion-pair for which $a$ does not change significantly with temperature, the ion-pair dissociation constant increases with decrease in temperature. If, however, with decrease in temperature, $D_s$ increases and $a$ decreases, as suggested above for the solvated-electron anion, then the two factors act to change $K$ in opposite senses. Dewald has suggested that the effect of change in size outweighs that of change in dielectric constant.

Using either set of conductivity data, attempts to explain the variation of cation Knight shift with concentration (Figure 1.5) have been unsuccessful. It has not been found possible to reproduce the plateau observed, by substituting $K_1$ values from conductivity data in equation 1.6. Whatever the value of $A_{Na}$ employed, the calculated sodium Knight shift falls rapidly in intermediate concentration regions. O'Reilly has varied both $K_1$ and $A_{Na}$ and reproduced the plateau region up to $R \sim 10$, beyond which metallic character becomes evident. The value of $K_1$ required, however, is an order of magnitude greater.
than that observed from conductivity measurements. This apparent contradiction has not been satisfactorily explained.

**Electron-electron interactions.**

The observation that $\alpha$, the fraction of unpaired spins, fell as metal concentration increased, implied that spin-pairing was becoming progressively more important. 3 main types of spin-pairing have been postulated, viz.

\[ e^- + e^- \rightleftharpoons e^-_2 \]  
\[ M + M \rightleftharpoons M_2 \]  
\[ M + e^- \rightleftharpoons M^- \]

Freed and Sugarman\textsuperscript{10} and Ogg\textsuperscript{14,33,34} attributed spin-pairing to (1), Becker, Lindquist and Alder\textsuperscript{40} to (2), Arnold and Patterson\textsuperscript{43} and Golden, Guttman and Tuttle\textsuperscript{46,47} to a combination of (2) and (3). Catterall and Dye\textsuperscript{50} have shown, however, that the introduction of $e^-_2$, $M_2$ or $M^-$ in sufficient concentrations to explain the susceptibility data leads to a poor fit with a considerable amount of electrical data e.g. conductivity, transference numbers, ionic activity coefficients, and they have postulated that spin-pairing occurs without the formation of species subject to mass-action equilibria. For diamagnetic collision complexes of the type invoked\textsuperscript{50,53}, the correlation time expected ($\sim 10^{-12}$ secs.) agrees very poorly with that required for a narrow ESR line ($> 10^{-6}$ secs.) and it has been necessary to introduce spin-exchange reactions of type,

\[ e_i^\alpha + (\text{Diamagnetic cluster}) \rightleftharpoons (\text{diamagnetic cluster}) + e_i^\alpha \]

in which one electron from a singlet state pair is replaced.
by another of the same spin and whereby the effective correlation
time for the spin-spin interaction is increased.

Electron-solvent interactions.

(1) Nuclear magnetic resonance.

The results obtained for the Knight
shifts indicated that the electron had a large positive contact
spin-density at the nitrogen nucleus, a small positive spin-
density at the metal nucleus and a small negative spin-density
at the hydrogen nucleus. Similar upfield shifts of proton
resonance signals have been observed in lithium-amine$^{54}$ and
sodium-HIPAm$^{55,61}$ solutions. The sign of the coupling suggests
a spin-polarisation mechanism, but no convincing explanation
has yet been suggested. The above conclusions are confirmed
by results from isotopic substitution in ESR spectra, which
are discussed in (11).

(11) Electron spin resonance (ESR)

Kaplan and Kittel$^{35}$ assumed, in the
absence of NMR Knight shift data or ESR isotope substitution
data, that electron relaxation was dominated by modulation of
the hyperfine coupling to the protons of the ammonia molecules,
basing this assumption on the relative numbers and nuclear
magnetic moments of the nuclei present. They assumed that the
electron interacted with 50 equivalent protons and that the
source of rapid modulation of the electron-nuclear interactions
was rotation of the ammonia molecules with frequency $\omega_c$ given
by the Debye relation,

$$\omega_c = \frac{kT}{3\eta V} \quad \text{(equation 1.18)}$$

where $V$ was the volume of the molecule, which was assumed to
be spherical. This treatment led to a line-width of 30
milligauss, assuming that the interaction of the electron with the hydrogen atom was purely via the 1s - orbital of the latter. It has been shown, however, that Kaplan and Kittel made a mathematical error and that the true result obtained by their treatment is 90 milligauss.

Pollak, from the Knight shift data of McConnell and Holm, concluded that electron relaxation was dominated by modulation of the hyperfine coupling to the nitrogen nuclei, not the hydrogen nuclei as Kaplan and Kittel assumed. Employing a similar treatment to that of Kaplan and Kittel, assuming that the electron interacted with 17 equivalent nitrogen nuclei, Pollak obtained a value of $T_{1,2} = 2.9 \mu\text{secs}$ which agreed very well with the value of $3 \mu\text{secs}$ corresponding to a linewidth of 20 milligauss. More recent Knight shift data by O'Reilly and theoretical calculations by Abragam and Cutler and Powles have shown, however, that the Pollak treatment was in error and that the Debye rotation frequency is an order of magnitude too slow to explain the observed linewidth.

Catterall has subjected the system to a much more thorough investigation. By evaluating $\frac{n|\psi(0)|^2_N}{n|\psi(0)|^2_H}$ and $|\psi(0)|^2_M$ from Knight shift data, he has confirmed the conclusion of Pollak and O'Reilly that electron relaxation is dominated, at least in sodium - and potassium-ammonia solutions, by modulation of the hyperfine coupling to nitrogen. He has shown, moreover, that dipolar couplings to all solvent nuclei make a negligible contribution to electron relaxation (<0.1%) and that, in dilute solutions, the contribution from spin-orbit coupling is also negligible, though O'Reilly has suggested that, in a 0.06M sodium-ammonia solution,

$$T_{1,2e}^{-1} \text{ (spin-orbit)} \sim \frac{1}{5} T_{1,2e}^{-1} \text{ (observed)}$$
Thus, for dilute solutions of sodium or potassium in ammonia, equation 1.16 reduces to,

\[
T_{1,2e}^{-1} \text{(total)} = \frac{T_{1,2e}^{-1} \text{(contact)}}{c} \cdot \frac{g_n^2 I_N(I_N + 1)x_N}{n \left| \psi(0) \right|^2} \cdot \frac{\tau_c}{n}
\]

(equation 1.19)

**Isotope effects.**

The slight increase in ESR line-width from \( ^{14}\text{NH}_3 \) to \( ^{14}\text{ND}_3 \) is fully explained by the longer correlation time, \( \tau_c \), in \( ^{14}\text{ND}_3 \) due to its higher viscosity.

The change in ESR line-width from \( ^{14}\text{NH}_3 \) to \( ^{15}\text{NH}_3 \) is fairly well accommodated by the change in the factor \( g_n^2 I_N(I_N + 1) \). A decrease in line-width of approximately 35\% is expected, a decrease of 20\% has been observed, the discrepancy being attributed to incomplete isotopic substitution.

**Temperature-dependence.**

For dilute solutions of sodium in ammonia, the temperature-dependence of \( T_{1e}^{-1} \) is well accommodated by a constant \( n|\psi(0)|^2_n \) and \( \tau_c \propto \frac{T}{T} \), implying that the spin-orbit contribution to electron relaxation (for which \( \tau_c \propto \frac{T}{T} \)) is negligible. For concentrated solutions, however, \( T_{1e}^{-1} \) passes through a minimum at 40°C i.e. is represented by,

\[
T_{1e}^{-1} = C \frac{T}{T} + S \frac{T}{T} \quad \text{(equation 1.20)}
\]

where \( C \) and \( S \) are constants for the contact and spin-orbit...
contributions to electron spin relaxation.

**Calculation of $n$.**

Using equation 1.19 with Knight shift and electron relaxation data, $\frac{\tau_c}{n}$ (ammonia) has been assigned a value of $0.62 \times 10^{-13}$ secs. Comparison with $\tau_c$ values for a wide variety of processes in ammonia leads to $3 < n < 10$. Similarly, $\frac{\tau_c}{n}$ (HMPA) = $0.83 \times 10^{-11}$ secs.

(111) Optical spectra.

The first attempt to interpret the optical spectrum of metal-ammonia solutions was by Ogg. Due to instrumental limitations, he was unable to detect the peak of the absorption. As the temperature changed, he mistook the normal temperature movement of the band for the appearance of a second band. He concluded that there were two absorptions in the infrared, due to $e_-$ and $e_2^-$ centre species. As the temperature decreased, the "band at higher energy" appeared to grow. The susceptibility data of Freed and Sugarman showed that spin-pairing increased with decrease in temperature and Ogg therefore attributed the "band at higher energy" to $e_2^-$ species, the "band at low energy" to $e$ species, i.e.

$$\Delta E(e_2^-) > \Delta E(e).$$

This is in conflict with the observation that $\Delta E(F) > \Delta E(F')$ (Ogg correlated $e$- and $e_2^-$ centres with $F$- and $F'$- centres, respectively). This was explained by arguing that polarisation of the solvent was greater for $e_2^-$ than for $e$ with a consequently smaller cavity for the former. On the basis of the square-well model, the energy of the first transition is given by,

$$\Delta E = \frac{1.04 \hbar^2}{8mR_0^2} \quad (equation \, 1.21).$$
If the radius of the cavity containing the \( e^2 \) species is less than that containing the \( e^- \) species, then \( \Delta E(e^2) > \Delta E(e^-) \), as observed.

Equation 1.21, in conjunction with the observation that the band shifts to lower energies with increase in temperature, also predicts that, as temperature increases, the radius of the species responsible for the absorption increases.

A weakness of most of the models proposed has been their inability to explain the relative insensitivity of band position to concentration i.e. it is difficult to explain the lack of detectable absorptions from \( M, e^2_2, M_2^- \) etc.

On the basis of the aggregate model of Gold, Jolly and Pitzer\(^9\) the insensitivity was explained by assuming that aggregates such as \( M^+ e^- M^+ \) modify, but do not destroy, the character of the absorbing species, \( e^- \).

Catterall and Dye\(^5\), having proposed the presence of only three species in solution viz. \( M^+, e^- \) and \( M^+ e^- \), explained the infrared band as a combination of bands from \( M^+ e^- \) and \( e^- \). The shift to lower energies with increase in metal concentration was attributed to a slight perturbation in the character of \( e^- \) due to the "long-range" spin-pairing discussed earlier.
CHAPTER 2.

METAL-ALINE AND METAL-ETHER SOLUTIONS.
INTRODUCTION.

Just as in ammonia, alkali metals have been found to dissolve in amine and ether solvents to give conducting, paramagnetic blue solutions, stable in the absence of air and moisture. Metal solubility in these solvents has generally been found to be much lower than in ammonia. Thus saturated solutions of potassium in tetrahydrofuran, ethylamine and ammonia are approximately $10^{-6} \text{M}$, $10^{-5} \text{M}$ and $5 \text{M}$ in the metal, respectively. Because of the lower solubility and stability of metal-amine and metal-ether solutions, these have not been as extensively studied as have metal-ammonia solutions. Consequently, although much of the behaviour of metal-amine and metal-ether solutions differs significantly from that of metal-ammonia solutions, the observed properties of the former have generally been discussed in terms of the models proposed to describe the behaviour of the latter.
METAL-AMINE SOLUTIONS.

In 1918, Gibson and Arga\textsuperscript{63} reported the preparation and spectroscopic study of potassium-methylamine solutions. Since that time, metal-amine solutions have been prepared using both simple aliphatic amines, up to n-butylamine, and aliphatic di-amines, up to 1,2- and 1,3-propylene diamines. No metal solutions have yet been prepared using secondary or tertiary amines, or using cyclic or aromatic amines. In such cases, attempts to prepare metal solutions have resulted in chemical reduction of the solvent.

All the alkali metals have been found to be soluble in methylamine and ethylenediamine (H\textsubscript{2}N \cdot CH\textsubscript{2} \cdot CH\textsubscript{2} \cdot NH\textsubscript{2}), lithium being considerably more soluble than the others. In higher homologues, metal solubility has been found to be considerably lower and metal solutions are formed with increasing reluctance. Thus, for example, pure ethylamine will not dissolve sodium to form a metal solution.

PROPERTIES OF METAL-AMINE SOLUTIONS.

1. Solubility and Stability.

For simple amines, the metal solubility was markedly dependent upon both metal and solvent, varying from 5 \cdot 29\textsuperscript{M} for lithium-methylamine\textsuperscript{64} to approximately 10^{-5}\textsuperscript{M} for solutions of potassium in ethylamine or iso-propylamine\textsuperscript{65}.

For solutions in ethylenediamine, metal solubility varied from 0 \cdot 28\textsuperscript{M} for lithium to 2 \cdot 4 \times 10^{-3}\textsuperscript{M} for sodium\textsuperscript{66}.

Metal-amine solutions were somewhat less stable than the corresponding solutions in ammonia. The metal ethylamide and hydrogen were identified as principal decomposition products, the overall reaction occurring being represented by
2. Conductance and Transference numbers.

The conductivity of 0.03 - 5M lithium-methylamine solutions was measured by Evers, who observed similar behaviour to that of metal-ammonia solutions, with a minimum in the equivalent conductance, $\Lambda$, at 0.1M lithium.

For lithium concentrations less than 0.3M, $\Lambda$ was an order of magnitude lower than that for lithium-ammonia solutions, indicating that aggregation reactions involving the solvated electron were more important in the amine solvent than in ammonia.

At a given lithium concentration, the plot of $\Lambda$ against temperature displayed a maximum, the maximum occurring at higher temperatures for higher lithium concentrations.

At room temperature, the ratio $\frac{t_-}{t_+}$, where $t_-$ and $t_+$ represent the transference numbers of the anion and cation respectively, was found to be approximately 9, similar to the value observed for metal-ammonia solutions. With increase in temperature, transference numbers changed as expected, i.e. there was an overall equalization of the cation and anion mobilities, so that $\frac{t_-}{t_+}$ decreased.

By analogy with results for normal electrolytes e.g. potassium iodide in pure amine solvents, the maximum in the plot of $\Lambda$ against temperature was explained by Panson and Evers as a combination of the normal increase in ionic mobilities with increase in temperature and a simultaneous progressive removal of the conducting species by mass-action effects e.g. by ion-pairing.
3. Optical Spectra.

(A) Ethylenediamine (1) lithium.

Optical spectra of lithium-ethylenediamine solutions have been recorded by Windwer and Sundheim and by Dewald and Dye. The former reported a single maximum at 15,000 cm\(^{-1}\); the latter observed two bands, at 7,800 cm\(^{-1}\) and 15,100 cm\(^{-1}\). Freshly-prepared solutions contained both bands, of varying relative intensities. Decomposition of the solution led to the 15,100 cm\(^{-1}\) band only.

(B) sodium.

A single band only, at 15,000 cm\(^{-1}\), has been observed. Any infrared absorption must have had absorbance less than 0.03 when the absorbance of the 15,000 cm\(^{-1}\) band was approximately 2.

(C) potassium.

Fowles, McGregor and Symons observed a single band at 14,900 cm\(^{-1}\). The same band was observed by Windwer and Sundheim with an occasional shoulder at 12,200 cm\(^{-1}\). Three bands were detected by Dewald and Dye, at 7,800 cm\(^{-1}\), 11,800 cm\(^{-1}\) and 15,100 cm\(^{-1}\). The 7,800 cm\(^{-1}\) band was present at all concentrations. High metal concentrations were found to favour the 11,800 cm\(^{-1}\) band, whilst dilution or decomposition led to a relative increase in the 15,100 cm\(^{-1}\) band, so that, in very dilute solutions, the 11,800 cm\(^{-1}\) band was observed only as a shoulder.

(D) rubidium.

Two bands, at 11,000 cm\(^{-1}\) and 14,200 cm\(^{-1}\), were observed by Windwer and Sundheim, whereas Dewald and Dye observed principal bands at 7,800 cm\(^{-1}\) and 11,200 cm\(^{-1}\), with a shoulder at 15,100 cm\(^{-1}\).

The 11,100 cm\(^{-1}\) band was originally more intense than the
The 14,200 cm\(^{-1}\) band but decayed more quickly as the solution decomposed, so that ultimately only the 14,200 cm\(^{-1}\) band was observed.

(V) Caesium.

Two bands were observed, at 7,800 cm\(^{-1}\) and 9,700 cm\(^{-1}\). In concentrated solutions, the 9,700 cm\(^{-1}\) band was favoured. Dilution or decomposition of the solution led to the 7,800 cm\(^{-1}\) band only.

(VI) Mixtures of Metals.

Addition of a dilute caesium-ethylenediamine solution, displaying a 7,800 cm\(^{-1}\) absorption only, to a decomposed lithium-ethylenediamine solution, with 15,100 cm\(^{-1}\) band only, resulted in an optical spectrum with bands at both 7,800 cm\(^{-1}\) and 15,100 cm\(^{-1}\).

A mixture of a rubidium-ethylenediamine solution (with bands at 7,800 cm\(^{-1}\), 11,200 cm\(^{-1}\) and a shoulder at 15,100 cm\(^{-1}\)) and a decomposed lithium-ethylenediamine solution, with 15,100 cm\(^{-1}\) band only, showed strong bands at 7,800 cm\(^{-1}\), 11,200 cm\(^{-1}\) and 15,100 cm\(^{-1}\).

(VII) Kinetics of Decay.

In a decomposing sodium-ethylenediamine solution, decay was found to be first-order for the 15,100 cm\(^{-1}\) band. For solutions of the other alkali metals in ethylenediamine, study of the kinetics of decay was complicated by overlapping bands, but it was noted that all bands in a given spectrum did not decay at the same rate.

(B) Methylamine (1) Lithium and Calcium.

A single infrared band, at 7,000-8,000 cm\(^{-1}\), was observed by Blades and Hodgins\(^{15}\) for lithium- and calcium-methylamine solutions. For lithium-methylamine solutions, a band at 14,100 cm\(^{-1}\) has also been reported\(^{70}\).
(11) sodium.

A single band was observed at 15,700 cm\(^{-1}\) (-50°C),\(^{15}\) and the band shifted to lower energies with an increase in temperature (\(\frac{d \lambda_{\text{max}}}{dT} = -13 \text{ cm}^{-1} \text{ deg}^{-1}\)).

Similar temperature-dependence of the band position was observed for metal-ammonia solutions.

(111) potassium.

Two bands, at 12,100 cm\(^{-1}\) and 15,100 cm\(^{-1}\) (-67°C), have been reported.\(^{15}\)

(c) Ethylamine (1) lithium.

A single infrared band, at 7,000 cm\(^{-1}\), has been reported, though some workers have also observed a band at 14,700 cm\(^{-1}\).

(11) sodium.

It has generally been stated that sodium is insoluble in pure ethylamine.\(^{65,72,73}\) Hohlstein and Wannagat\(^{70}\), however, detected a band at 14,700 cm\(^{-1}\) for sodium-ethylamine solutions. Their analyses, however, showed the presence of traces of ammonia impurity in the ethylamine.

(111) potassium.

Potassium-ethylamine solutions have been extensively studied by optical spectroscopy,\(^{15,74-76}\) and conflicting results have been obtained.

Blades and Hodgins\(^{15}\) reported a single band at 15,500 cm\(^{-1}\). Ottolenghi et al.\(^{76}\) observed two bands, at 11,800 cm\(^{-1}\) and 15,400 cm\(^{-1}\). In a decomposing solution, the 11,800 cm\(^{-1}\) band was observed to decay with a first-order rate constant, at double the rate for the 15,400 cm\(^{-1}\) band. Catterall and Symons\(^{74}\) reported a principal band at 14,800 cm\(^{-1}\), with a shoulder at 11,500 cm\(^{-1}\).
Recently, Hurley, Tuttle and Golden\textsuperscript{75} have demonstrated that the nature of the optical spectra observed for solutions of potassium in ethylamine or ethylenediamine was dependent upon the method of solution preparation. For solutions prepared in pyrex vessels, two bands were observed, at 11,500 cm\textsuperscript{-1} and 15,100 cm\textsuperscript{-1} whereas, for those prepared in quartz vessels, the former band only was observed. It was argued that the 15,100 cm\textsuperscript{-1} band is characteristic of sodium species and is observed only when there is a possibility of sodium contamination i.e. of extraction of sodium ions from the pyrex, either by the metal solution itself or during sublimation of added salts e.g. potassium iodide.

To some extent, this conclusion was anticipated by Ottolenghi et al.\textsuperscript{76} who observed that addition of small amounts of sodium chloride to rubidium-ethylamine solutions caused an increase in the intensity of the 15,400 cm\textsuperscript{-1} band, from which they argued that the non-reproducibility of optical spectra of metal-amine solutions was probably due to contamination by low atomic-number alkali metals e.g. lithium and sodium.

The possibility of sodium contamination, for samples prepared or studied in pyrex vessels, is very important and is discussed later in this chapter and, more fully, in Chapter 4.

(IV) rubidium.

In freshly-prepared solutions, the dominant band was at 10,700 cm\textsuperscript{-1}, with a shoulder at 14,800 cm\textsuperscript{-1}. In very dilute, or partially-decomposed, solutions the 14,800 cm\textsuperscript{-1} band predominated.

(V) caesium.

In freshly-prepared solutions, at room temperature, the most intense band was at 9,600 cm\textsuperscript{-1}, a shoulder being observed at 13,300 - 14,700 cm\textsuperscript{-1} and a broad infrared band at 7,000 - 8,000 cm\textsuperscript{-1}. As observed for the
corresponding rubidium solution, the 14,500 cm\(^{-1}\) band was most important in dilute or decomposed solutions.

\begin{enumerate}
\item[(V1)] \textit{Flash photolysis.}
\end{enumerate}

Ottolenghi, Bar-Eli and Linschitz\(^{74}\) studied the effect of high-energy flash photolysis on lithium-, potassium-, rubidium- and caesium-ethylamine solutions, at several temperatures and metal concentrations.

(a) potassium, rubidium and caesium.

Prior to flash photolysis, three bands were observed; an infrared band at approximately 7,000 cm\(^{-1}\), a metal-dependent band at 10,000-12,000 cm\(^{-1}\) and a high-energy band at approximately 14,500 cm\(^{-1}\). These bands were referred to as the IR-, R- and V- bands respectively.

Initially flash photolysis, at energies greater than 20,000 cm\(^{-1}\), caused a decay of the V- band, a growth of the IR- band. This was followed by a growth of the R- band, with decay of the IR- band. These two changes, however, occurred at different rates and, to explain this, a precursor X of the R- transient was proposed. The R- band finally reverted back to the V- band in a first-order process. The ratio of the yields of the species responsible for the IR- band and the R- transient, X, was observed to be constant, independent of excitation energy or metal concentration.

Direct reversible photolysis of the original R- band led to a transient IR- band which decayed back to the R- band in a second-order process.

The overall reactions occurring are represented by the scheme,
where $V$ represents the species responsible for the original $V$-band, etc.

(b) **lithium.**

Prior to flash photolysis, IR- and $V$- bands were observed. Flash photolysis led to IR- band enhancement, followed by direct reaction back to the $V$- band with no intermediate $R$- transient i.e.

(D) **Mixed solvents.**

(1) **ammonia-methyamine mixtures.**

Blades and Hodgins\textsuperscript{15} found that a solution of sodium in a 1:1 ammonia-methyamine solvent mixture had an optical spectrum consisting of bands at 7,500 cm\textsuperscript{-1} and 14,700 cm\textsuperscript{-1} i.e. bands characteristic of sodium solutions in both pure solvents were observed. The optical spectrum of a solution of potassium in a 1:1 ammonia-methyamine solvent mixture, however, consisted of a single band at 7,500 cm\textsuperscript{-1}.

(11) **ammonia-ethylamine mixtures.**

Dalton et al\textsuperscript{73} recorded the optical spectra of a series of solutions of potassium
in ammonia-ethyamine mixtures and, in general, observed three bands, at 14,000 - 15,000 cm\(^{-1}\) (the V- band), 11,000-11,400 cm\(^{-1}\) (the R- band) and at 7,500 cm\(^{-1}\) (the IR- band), the relative intensities of the bands depending on the ammonia concentration and temperature.

At low ammonia concentrations (< 6 mole %), the V- band was dominant at all temperatures, with no IR- band. Even at high temperatures, the R- band was observed only as a shoulder.

At intermediate ammonia concentrations (7-14 mole %), all three bands were observed, with intensities dependent upon temperature. Low temperatures favoured the V- band, high temperatures the R- and IR- bands. This behaviour is the reverse of that reported by Blaas and Hodgins\(^{15}\) for a solution of sodium in a 1:1 ammonia-methylamine mixture, for which the V- band was found to be more prominent at high temperatures.

At high ammonia concentrations, the IR- band was dominant at all temperatures. For solutions containing more than 33 mole % ammonia, only the IR- band was observed.

In decomposing solutions, the V- and R- bands were found to decay at the same rate, not in the ratio 1:2 as reported by Ottolenghi et al. for potassium-ethylamine solutions\(^76\).

4. **Electron Spin Resonance (ESR).**

(A) **Ethylenediamine.**

ESR signals have been observed\(^{68,77}\) from solutions of sodium, potassium and rubidium in ethylenediamine. In each case, the spectrum consisted of a single line (\(g = 2.0015 \pm 0.0002\)) with line-width decreasing in the order rubidium (approximately 6.5 gauss) > sodium (0.75 gauss) > potassium (\(< 0.15\) gauss). No changes in line-width or \(g\) - factors were observed upon decomposition.
35.

(B) Methylamine.

Vos and Dye recorded the ESR spectra, at several temperatures, of solutions of all the alkali metals in methylamine. In the cases of rubidium and caesium, hyperfine splitting to the metal nucleus was observed, resulting in 6- and 8-line hyperfine spectra respectively, from coupling to the $^{85}\text{Rb} (I = 5/2)$ and $^{133}\text{Cs} (I = 7/2)$ nuclei. In addition a single broad line, whose intensity increased rapidly with decrease in temperature, was observed at $g = 2.0018$.

The total hyperfine separation for both nuclei was found to be very temperature-dependent, decreasing, in the case of caesium, from 320 gauss at 5°C to 90 gauss at -95°C.

(c) Ethylamine (1) lithium.

For dilute solutions, Bar-Eli and Tuttle observed a single line whose width increased with decrease in temperature, from 0.3 gauss at 28°C to 2.5 gauss at -80°C.

For very dilute solutions, a different spectrum was observed, consisting of a 7- or 9-line hyperfine pattern ($A_{iso} = 2.45 \pm 0.2$ gauss), the central line being most prominent, particularly at low temperature and low lithium concentration.

Bar-Eli and Tuttle attributed the hyperfine coupling to interaction with four equivalent nitrogen nuclei in a centrosymmetric monomer, Li(EtNH$_2$)$_4$.

Catterall, Symons and Tipping have studied solutions of both $^6\text{Li}$ and $^7\text{Li}$ in ethylamine and of $^7\text{Li}$ in ethylamine - $d_2$ (EtND$_2$). They found that the ESR spectrum was changed little by these isotopic substitutions, confirming the assignment of the hyperfine pattern to coupling to nitrogen nuclei. Although no hyperfine coupling attributable to lithium nuclei or amine protons was observed, analysis of line-widths enabled upper limits to be placed on the respective
hyperfine coupling constants, viz.

\[ |A_{iso}(^7\text{Li})| \leq 0.05 \text{ gauss.} \]

and \[ |A_{iso}(\text{H})| \leq 0.10 \text{ gauss.} \]

For solutions of \(^6\text{Li}\) and \(^7\text{Li}\) in \(n\)-butylamine \(^{54}\) or \(n\)-propylamine \(^{76}\), \(A_{iso}(^4\text{H})\) was approximately 4.0 gauss and no central singlet was observed.

The low hyperfine coupling to the lithium suggests that the species present is best described as an ion-pair, more closely analogous to the ion-pair species in ammonia than to the monomer species in amine solutions of higher alkali metals. The presence of resolved hyperfine coupling to the nitrogen implies a relatively long electron-nitrogen correlation time \(> 10^{-7} \text{ secs.}\) i.e. a long-lived ion-pair. The absence of such coupling for the corresponding potassium solution leads to the conclusion that the cation is important in "tying down" the solvent. The structure of the species is therefore written as \([\text{LiSi}]^+ \times [\text{e S}]^-\), where S represents an ethylmimino molecule. The strong central line observed is composite, comprising the central line of the hyperfine pattern and the signal from \(\text{eS}^-\).

(11) sodium.

All attempts \(^{65,72,73}\) to prepare solutions of sodium in ethylamine have resulted in crumbling of the metal surface, without formation of a metal solution.

(111) potassium.

Hyperfine coupling in potassium-ethylamine solutions was first reported by Bar-Eli and Tuttle\(^{72}\) who observed four equally-spaced lines from coupling to the \(^{39}\text{K}\) nucleus \((I = 3/2)\). As observed for caesium-methylamine
solutions, the hyperfine coupling constant, $A_{iso}(^{39}K)$, was markedly temperature-dependent, decreasing smoothly from 13 gauss at 48°C to 4 gauss at -36°C. The hyperfine quartet line-widths were 0.5 gauss at room temperature and decreased slightly upon cooling. The outer ($m_I = \pm 3/2$) lines of the hyperfine quartet were broader than the inner ($m_I = \pm 1/2$) lines, as gauged by their relative amplitudes.

Catterall and Symons observed two quartets ($A_{iso} = 9.85$ and 5.4 gauss, at room temperature; $g = 2.0014 \pm 0.0002$; $\Delta H_{ms} \sim 0.2$ gauss), the quartet with the smaller splitting being only 7% of the intensity of that with the larger splitting and being assigned to hyperfine coupling to the $^{39}K$ nucleus ($I = 3/2$). They also observed a weak central singlet ($g = 2.0019 \pm 0.0002$; $\Delta H_{ms} \sim 0.2$ gauss).

Dilution with pure solvent resulted in a growth in amplitude of the central singlet relative to the hyperfine quartet, with no apparent change in $g$-factors, line-widths or $A_{iso}$ values.

Excess potassium ions, added as the ethylamide ($K^+EtNH^-$) by decomposition or as the bromide ($KBr$) by direct addition, produced a broadening of the hyperfine quartet (up to 3 gauss) but not of the central singlet. This broadening was attributed by Catterall and Symons to rapid electron-exchange between the monomer, $^*K$, and normal cations having different nuclear-spin configurations, viz.

$$^*K + K^+ \leftrightarrow ^*K^+ + K.$$

such that the mean lifetime of a given electron-potassium nucleus interaction was of the same order of magnitude as the inverse of the hyperfine separation i.e. $\sim 10^{-7} - 10^{-8}$ secs.

In a later study of the same system, Catterall, Tipping and Symons confirmed the observation of Ottolenghi et al. that the spectroscopic properties of solutions of metallic
potassium in ethylamine were identical with those prepared by
32,000 cm$^{-1}$ photolysis of ethylamine solutions of potassium
ethylamide. They found that solutions of potassium in very
pure ethylamine had hyperfine quartet line-widths of approximately
0.25 gauss, but that the presence of excess potassium cations,
produced by the reaction of metallic potassium with impurity
species, led to electron-exchange reactions of the type
discussed above and thereby to hyperfine quartet line-widths
of up to 0.5 gauss.

The hyperfine quartet line-widths were independent of metal
concentration but decreased slightly on cooling. For a dilute
potassium-ethylamine solution, however, the singlet line-width
was found to increase by a factor of two for a 60 Centigrade
degree decrease in temperature, which is similar to the
behaviour observed for metal-ammonia solutions.

For fairly dilute potassium-ethylamine solutions ($< 10^{-4}$
M in metal), the ratio $\frac{[\text{singlet}]}{[\text{quartet}]}^2$, where $[\text{singlet}]$ and
$[\text{quartet}]$ represent the intensities of the singlet and hyper-
fine quartet respectively, was found to be independent of metal
concentration, whilst for solutions saturated with potassium
bromide, the ratio $\frac{[\text{singlet}]}{[\text{quartet}]}$ was found to be constant.\textsuperscript{65}

These results are discussed fully in Chapter 4.

Dye and Dalton\textsuperscript{80} obtained a temperature-dependence of
$A_{iso}(^{39}\text{K})$ which differs in form from that of Bar-Eli and Tuttle\textsuperscript{72}
and Catterall and Symons\textsuperscript{74} and also reported temperature-
independent g-factors. Both these observations are discussed
fully in Chapter 4.

(IV) caesium.

The ESR spectrum of caesium in ethylamine,
at $-10^\circ$C, consisted\textsuperscript{81} of a hyperfine octet due to coupling
to the $^{133}$Cs$(I = 7/2)$ nucleus, with a superimposed central singlet slightly shifted to the high-field side of the centre of the hyperfine octet, though the application of second-order corrections leads to the conclusion that the $g$-factor of the species responsible for the hyperfine pattern is less than that of the species responsible for the singlet, as observed in potassium-ethylamine solutions. The central singlet was found to be more prominent at low temperatures.

A marked line-width effect was observed for the components of the hyperfine octet, such that the hyperfine lines nearest to the centre were narrower, and therefore of greater amplitude, than the outer lines. A similar, though considerably less marked, effect has been noted for potassium-ethylamine solutions. For caesium-ethylamine solutions, this $m_I$-dependence of the line-widths has been found to be more marked at low temperatures.

(v) rubidium.

The earliest ESR spectra of rubidium-ethylamine solutions were rather poorly-resolved i.e. the signal-to-noise ratio was low, but they appeared to consist of a hyperfine sextet, from coupling to $^{85}$Rb$(I = 5/2)$, with a central singlet similar to that observed for caesium-ethylamine solutions. More recently, an additional quartet, arising from hyperfine coupling to the $^{87}$Rb$(I = 3/2)$ has been detected.

(d) Higher amines.

Catterall, Symons and Tipping prepared solutions of potassium in higher primary aliphatic amines e.g. $n$-propylamine, iso-propylamine, $n$-butylamine and $s$-butylamine. Metal solubility and solution stability decreased with increasing complexity of the alkyl group. The $^{39}$K hyperfine coupling constant, $A_{iso}(^{39}$K), increased with increasing
complexity of the alkyl group and with increase in temperature. For the amine solvents studied, $A_{iso}^{(39\text{K})}$ values appeared to approach a common value of 2.5 gauss at -80°C.

Mixed solvents (1) Ethylamine-methylamine mixtures.

ESR spectra of solutions of potassium in ethylamine-methylamine mixtures were recorded by Bar-Eli and Tuttle. As the concentration of methylamine in the solvent mixture increased, the $A_{iso}^{(39\text{K})}$ value decreased and the line-widths of the hyperfine quartet increased such that, at approximately 40 mole % of methylamine, a single broad line only was observed. Further addition of methylamine resulted in a narrowing of this singlet.

The temperature-dependence of $A_{iso}^{(39\text{K})}$, for a solution of potassium in a 0.9 mole fraction of ethylamine : 0.1 mole fraction of methylamine solvent mixture, was found to parallel that for a solution of potassium in pure ethylamine. Hyperfine line-widths were virtually independent of temperature (0.9 gauss at 27°C to 0.8 gauss at -25°C).

For a solution of potassium in a 1:1 ethylamine-methylamine mixture, cooling led to a change in the ESR spectrum from a broadened hyperfine quartet (\( \Delta H_{ms} \sim 2 \) gauss at room temperature) to a single broad line and ultimately to a relatively narrow line (\( \Delta H_{ms} \sim 0.5 \) gauss at -65°C).

For a solution of potassium in an ethylamine-methylamine mixture showing partially-resolved hyperfine splitting, addition of potassium iodide resulted in collapse to a single narrow line (\( \Delta H_{ms} \sim 0.3 \) gauss at room temperature).

Ethylamine-isopropylamine mixtures.

A solution of potassium in 1:3 ethylamine-isopropylamine had $A_{iso}^{(39\text{K})}$ intermediate between those of potassium solutions in the pure solvents. No broadening of the hyperfine lines, such as
reported for ethylamine-methylamine mixtures, was observed. 

Ethylamine-ammonia mixtures.

Dalton et al. recorded ESR spectra of solutions of potassium in ethylamine-ammonia mixtures and found similar behaviour to that for solutions of potassium in ethylamine-methylamine mixtures. Thus an increase in ammonia concentration produced a decrease in $A_{iso}(^{39}K)$ and an increase in hyperfine quartet line-widths. In the plot of $A_{iso}(^{39}K)$ against temperature, however, they observed a "plateau" i.e. a region of relative insensitivity of $A_{iso}(^{39}K)$ to temperature. This anomalous behaviour will be discussed in detail in Chapter 4.

At low ammonia concentrations, the ESR spectrum consisted of a hyperfine quartet alone. At intermediate concentrations, a broad singlet, underlying the hyperfine quartet, was observed. The singlet was much more prominent at high ammonia concentrations and was therefore assigned to the solvated electron.

In one case, for a solution of potassium in a 1.2 mole % ammonia-ethylamine mixture allowed to stand for 9 months, a second singlet species was observed, of intensity $\sim 0.003$ times that of the hyperfine quartet, with different $g$-factor and line-width. In contrast with the behaviour of solutions of lithium, rubidium and caesium in methylamine or ethylamine, there was no detectable increase in the intensity of this singlet at low temperatures and it was therefore assumed to be due to decomposition products, an assumption which is discussed in Chapter 4.

Catterall, Symons and Tipping prepared a solution of sodium in ethylamine - 40 mole % ammonia mixed solvent and obtained a hyperfine quartet, attributed to coupling to the
$^{23}\text{Na}(I = 3/2)$ nucleus, $(A_{1s0}(^{23}\text{Na}) \sim 7.5 \text{ gauss}; g = 2.0019 \pm 0.0002; \Delta H_{ms} = 0.5 \text{ gauss})$, together with a central singlet $(g = 2.0019 \pm 0.0002)$. The behaviour of $A_{1s0}(^{23}\text{Na})$ and linewidths, with increase in ammonia concentration, was identical to that observed for potassium in the same solvent mixture.

5. **Nuclear Magnetic Resonance (NMR)**

Very little NMR work has been performed on metal-amine solutions and conflicting results have been reported.

Catterall et al. measured proton Knight shifts for lithium-methylamine and lithium-ethylamine solutions and found a small upfield shift, implying a negative unpaired electron spin density at the amine protons. Similar behaviour was observed for metal-ammonia solutions.

Evers and Haynes reported lithium Knight shifts which led to the conclusion that $|\psi(0)|^{2}_{\text{Li}}$ was considerably greater for lithium-methylamine solutions than for lithium-ammonia solutions which is in disagreement with the observation of Catterall et al., based upon $^{6}\text{Li}$ and $^{7}\text{Li}$ ESR isotopic substitution results, that $A_{1s0}(^{7}\text{Li})$ was an order of magnitude lower in the former case. Hurley has recently performed lithium Knight shift measurements on lithium-ethylamine solutions and has confirmed the observations of Catterall et al.

Tuttle has observed a large downfield shift for $^{14}\text{N}$ nuclei, of much the same magnitude as observed for metal-ammonia solutions.

**MODELS PROPOSED TO DESCRIBE OPTICAL SPECTRA.**

In 1955, Blades and Hodgins proposed a model to explain the observation of an infrared band for solutions of lithium and calcium in methylamine, a visible band for solutions of sodium...
and potassium in methylamine. They postulated the existence of two types of trap for the solvated electron, an amine-type trap, with nitrogen atoms of the methylamine lining the cavity boundary and an aliphatic-type trap, with methyl groups lining the cavity boundary. The former, by analogy with ammonia, was assumed to be responsible for the infrared absorption, the latter for the visible absorption. The metal ion was presumed to have a relatively long-range effect on solvent orientation and thereby to govern the type of trap formed. It has been suggested\textsuperscript{59}, however, that intermediate orientations of the methylamine molecule around the cavity should be just as likely as the two extremes i.e. on the basis of this model a whole range of absorption bands ought to be observed.

The cavity model of Ogg\textsuperscript{44,33,34}, developed for metal-ammonia solutions, was applied to metal-amine solutions by Fowles, McGregor and Symons\textsuperscript{69} who assigned the IR- and V- bands in metal-methylamine solutions to e- and e\textsubscript{2}- centres respectively. In solvents of high dielectric constant e.g. ammonia, formation of the e- centre was favoured irrespective of the metal. In amine solvents, however, the e- centre was formed only if the metal ion had a high surface-charge density, e.g. Li\textsuperscript{+} or La\textsuperscript{2+}, which suggests ion-pair formation, a strong cation-electron interaction favouring the formation of the e- centre.

In a later publication\textsuperscript{67}, Symons assigned the IR- and visible (\( \sim 14,000 \text{ cm}^{-1} \)) bands of metal-amine solutions to e- and M\(_2\), respectively and, from a comparison with the gas-phase optical spectra of the alkali metal free atoms, suggested that the monomer was not a major component under any conditions.

For either model\textsuperscript{69,67}, paramagnetism was associated with the IR- band, diamagnetism with the visible band.

The conductivity data of Evers\textsuperscript{64,67}, however, led him to
the conclusion\textsuperscript{42} that the monomer was the major constituent of lithium-methylamine solutions but he was unable satisfactorily to explain the lack of detectable absorption from the monomer.

Windwer and Sundheim\textsuperscript{68}, from optical-conductivity correlations for metal-ethylenediamine solutions, argued that the species responsible for the V- band is more highly associated than the conducting species, $e^-$. They suggested that the former species was the monomer, M and that the intermediate $11,000 \text{ cm}^{-1} (R)$ band observed for solutions of rubidium in ethylenediamine, methylamine, ether solvents and occasionally for solutions of potassium in ethylamine, was due to dimer species, $M_2^+$.

From the optical results of Dewald and Dye\textsuperscript{82} for metal-ethylenediamine solutions, Dye and Dewald\textsuperscript{82} postulated the existence of 3 distinct species to account for the 3 optical absorption bands observed.

(1) The infrared (IR) band ($\sim 7,800 \text{ cm}^{-1}$).

This band was assigned to the solvated electron, both alone and in ionic aggregates. Evidence for this assignment was provided by good correlations of this absorption with conductivity and the observation that the IR- band was enhanced by the addition of ammonia, in which the presence of such species is well established.

(11) The intermediate (R) band ($\sim 9,700 - 11,800 \text{ cm}^{-1}$)

The position of the R-band has been shown\textsuperscript{74} to be metal-dependent, occurring at $11,800 \text{ cm}^{-1}$, $11,200 \text{ cm}^{-1}$ and $9,700 \text{ cm}^{-1}$ for potassium, rubidium and caesium respectively.

Dye and Dewald\textsuperscript{82} assigned this band to covalent metal dimers. They explained the metal-dependence of band position by comparison with metal dimers in the gas phase, for which the energy of the transition $\Sigma_g \rightarrow \Sigma_u$ is metal-dependent,
in the same sense as observed for the R- bands.

It has been pointed out\textsuperscript{73}, however, that the energy of the above gas-phase transition is relatively insensitive to temperature, whereas the R- band shifts to lower energies with increase in temperature. If the species \( \text{H}_2 \) is to be retained as the species responsible for the R- band, the transition must be of the \( \Sigma_g^+ \rightarrow \Pi_u^+ \) type, whose temperature-dependence is in the same sense as that of the R-band.

In Table 2.1, the energies of both these transitions, for \( \text{K}_2(g) \), \( \text{Rb}_2(g) \) and \( \text{Cs}_2(g) \)\textsuperscript{88} are compared with observed R-band energies for potassium-, rubidium- and caesium-ethylenediamine solutions.

<table>
<thead>
<tr>
<th></th>
<th>( \Sigma_g^+ \rightarrow \Sigma_u^- )</th>
<th>( \Sigma_g^+ \rightarrow \Pi_u^+ )</th>
<th>R-band</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K}_2 )</td>
<td>11,670</td>
<td>15,369</td>
<td>11,800</td>
</tr>
<tr>
<td>( \text{Rb}_2 )</td>
<td>11,190\textsuperscript{89}</td>
<td>12,700</td>
<td>11,200</td>
</tr>
<tr>
<td>( \text{Cs}_2 )</td>
<td>10,100</td>
<td>11,452</td>
<td>9,700</td>
</tr>
</tbody>
</table>

(All energies are in wave-numbers, cm\(^{-1}\)).

Both gas-phase transitions correlate qualitatively with R-band positions. Quantitative correlations are of little use since little is known about the effect of solvation on band positions.

(111) The high-energy (V) band (13,400 - 15,400 cm\(^{-1}\))

This band, the V-band, was formed most readily for lithium- and sodium-ethylenediamine solutions, being prominent in the corresponding potassium and rubidium solutions only after decomposition or dilution\textsuperscript{66}. Although the formation of the V-band was strongly metal-dependent, once formed its position and width appeared to be independent of metal.

Dye and Dewald\textsuperscript{82} suggested that the V-band was due to a
species with a covalently bonded $M_2^+$ core, with the solvated electron trapped by the core in the same manner as in the cation-centred monomer of Becker, Lindquist and Alder. The resulting species, written as $M_2^+ \cdot e^-$, was termed the "ionic-covalent dimer". The slow conversion of the $V$-band into other bands was attributed to the $M_2^+$ core, whilst the lack of metal-dependence of the band position was rationalized by assuming that the nature of the electron, though of course modified by the electrostatic influence of the core, is insensitive to its detailed composition.

Ottolenghi et al.\textsuperscript{76} attributed the $V$-band to $M$ and the $R$-band to $M_2^+$, basing their argument upon the observation, for potassium-ethylamine solutions, that the $R$-band decayed at twice the rate of the $V$-band.

Not only has this result been shown to be non-reproducible,\textsuperscript{73} but correlations of optical and ESR spectra, which are discussed in detail later, have shown that the monomer cannot be responsible for the $V$-band.

**Flash Photolysis.**

Ottolenghi et al.\textsuperscript{71} discussed their flash-photolysis results using a combination of previous models. Thus the IR-band was attributed to the solvated electron and its ionic aggregates,\textsuperscript{69,82,87} the $V$-band was attributed to a cation-centred monomer of the Becker, Lindquist and Alder type,\textsuperscript{40} and the $R$-band to an "ionic-covalent dimer".\textsuperscript{82}

Although they were thus able to rationalize their observations, more recent results\textsuperscript{65,73,75} have shown that their assignments of $V$- and $R$-bands were in error. Unfortunately their results cannot be interpreted in the light of later models because Hurley et al.\textsuperscript{75} have shown that the rate of interconversion of $R$- and $V$-bands is strongly dependent upon the concentration of
sodium ions in solution i.e. to interpret any kinetics measured in pyrex vessels it is necessary to know the ratio $\frac{[Na^+]}{[M^+]}$ where $[M^+]$ represents the concentration of cations produced by ionization of the metal M and $[Na^+]$ represents the concentration of sodium cation impurity extracted from the pyrex by the metal solution.

**Pulse Radiolysis.**

The most recent results for pulse-radiolytic generation of free electrons in ethylenediamine have suggested that the infrared absorption is probably due to the solvated electron, as has been generally assumed. The absorption was found to increase continuously down to the photomultiplier cut-off at 8,900 cm$^{-1}$, the shape of the absorption closely following that of the high-energy tail of the infrared absorption in metal-ethylenediamine solutions. The maximum reported at 10,900 cm$^{-1}$ by earlier workers was shown to be spurious.

**Discussion.**

The study of the optical spectra of metal-amine solutions has been complicated by non-reproducibility, particularly of band intensities. It has generally been observed, however, that one, or more, of 3 bands, previously designated as the IR-, V- and R- bands, is present. The assignment of the IR- band to the solvated electron has been fairly well agreed but the R- and V- bands have defied satisfactory interpretation.

Hurley et al. have proposed, simply, that the so-called V- band is merely the sodium R- band, produced by extraction of sodium impurity from the pyrex, as discussed in an earlier section of this chapter. Thus positions of R- band maxima, for metal-ethylenediamine solutions, are,
Cs(9,700 cm\(^{-1}\)) < Rb(11,200 cm\(^{-1}\)) < K(11,800 cm\(^{-1}\)) < Na(\sim 14,000 cm\(^{-1}\)) and instead of two high-energy bands there is only one.

This idea offers possible explanations of several hitherto inexplicable observations e.g.

(a) The irreproducibility observed is attributed to the fact that almost all optical studies reported have been for solutions allowed to come into contact with pyrex, i.e. apparently identical solutions could easily contain vastly different amounts of sodium impurity.

(b) It has frequently been observed that a freshly-prepared metal solution displayed an R- band and/or an IR- band, whereas the V- band only was observed on standing. This is rationalized as a progressive extraction of sodium cations from the pyrex by the metal solution, leading to a growth in the sodium R- band, at 14,000 cm\(^{-1}\).

(c) The fact that the problem of sodium contamination is most serious for potassium, whose R- band reverts to V- band very quickly, must be due to a size factor. The extraction of sodium ions from the pyrex must, presumably, be accompanied by the reverse reaction, the incorporation of metal ions, from the metal solution, into the vacancies in the pyrex. This process is apparently easiest for potassium ions. Lithium cations are presumably too small, rubidium and caesium cations too large, to fit very easily into the vacancies in the pyrex. Thus, for these metals, the growth of the V- band is considerably slower than for potassium.

There is, therefore, only one high-energy band to assign. The species responsible, however, for reasons which will be discussed later in this chapter, must be diamagnetic. Metal dimers, \(M_2^+\), and metal anions, \(M^-\), have been proposed. It has
been one of the aims of the present work, by performing joint ESR and optical measurements on solutions prepared in both pyrex and quartz vessels, to determine the species responsible for the \( R \)-bands. A theory has been developed and will be advanced in Chapter 4.

**DISCUSSION OF ESR SPECTRA.**

**Electron-cation interactions.**

Analysis of conductivity data \(^{64,67}\) for lithium-methylamine solutions has demonstrated the importance of cation-electron interactions in amine solvents i.e. reactions of the type,

\[
\text{M}^+ \text{solv.} + e^- \text{solv.} \xrightarrow{\frac{1}{2}} X \text{solv.}
\]

occur, just as in ammonia. Species \( X \text{solv.} \) may represent either an ion-pair, \( \text{M}^+ \text{solv.} e^- \text{solv.} \), or a monomer, \( (\text{M}^+e^-) \text{solv} \) or \( \text{M} \text{solv.} \). In either case, cation-electron interactions are important and the rate at which these interactions are modulated governs the appearance of the ESR spectrum.

For reactions 1 and 2 fast, the rate at which cation-electron interactions are modulated is much faster than the hyperfine separation of \( X \text{solv.} \) (in radians/sec) and no hyperfine structure is observed. A single line is observed, an average of the two signals from \( X \text{solv.} \) and \( e^- \text{solv.} \). Examples of this situation are solutions of alkali metals in ammonia, ethylenediamine and of lithium, sodium and potassium in methylamine.

As reactions 1 and 2 slow down, the cation-electron correlation time, \( \tau_{\text{M}^+..e^-} \) increases, when \( \tau_{\text{M}^+..e^-} \) is of the same order of magnitude as the inverse of the hyperfine separation for \( X \text{solv.} \) i.e. \( \sim 10^{-7} \) secs, separate, but broadened, signals are observed from \( X \text{solv.} \) and \( e^- \text{solv.} \), as in solutions of rubidium and caesium in methylamine and of potassium in 1,2-
and 1,3- propylenediamines.

For $\tau_{M^+e^-}$ long compared with the inverse of the hyperfine separation, as in potassium-ethylamine solutions, separate narrow signals are observed from $X_{\text{solv}}$ and $e^-_{\text{solv}}$, the centre of the hyperfine pattern being at higher field than the singlet, i.e. of lower $g$-value, due presumably to spin-orbit coupling of the electron to the cation, in species $X_{\text{solv}}$.

The Nature of the Monomer Species.

With the exception of lithium$^{54}$, whose solution in ethylamine has been discussed previously, alkali metals dissolve in amines to give resolved metal hyperfine splitting. The magnitude of the hyperfine splitting observed has been taken as evidence against the existence of species $M^+_{\text{solv}}e^-_{\text{solv}}$ and for the existence of $(M^+e^-)_{\text{solv}}$, i.e. $M_{\text{solv}}$, the so-called monomer.

Two of the most interesting features of the ESR spectra of metal-amine solutions are the dependence of hyperfine splitting constant upon temperature and the dependence of line-width of the hyperfine multiplet upon nuclear magnetic quantum number, $m_I$. Several models for the monomer species have been advanced to explain either or both of these observations. Such models can be divided into 2 classes,

1) the "static" or continuum models of Bar-Eli and Tuttle (1964)$^{72}$, O'Reilly and Tung Tsang (1965)$^{92}$ and of Dye and Dalton (1967)$^{80}$ in which continuous changes in structure of a single monomer species are invoked to explain the observations and

2) the "dynamic" or multi-state model of Catterall et al (1966)$^{65}$ and Dalton et al (1966)$^{73}$ in which two or more monomeric species, with distinct magnetic properties, are in rapid equilibrium with one another. These models will be discussed in turn.
argued that the rigid monomer of Becker, Lindquist and Alder\(^{40}\) could not accommodate the temperature-dependence of the hyperfine splitting constant. They therefore defined the monomer framework to include several concentric shells of solvent molecules. The unpaired electron density on the molecules in a given shell was presumed to be determined by the binding energy of that shell to the metal nucleus. With increase in temperature, \(B_n\), the average binding energy per molecule in the \(n\) th shell of the monomer was assumed to decrease i.e. the unpaired electron has a smaller framework over which to spread and the unpaired electron spin density at the metal nucleus increases i.e. \(\Delta_{iso}(M)\) increases. This behaviour is analogous to that of a diatomic molecule for which, as temperature increases, there is an increase in the population of excited vibrational states, with equilibrium distances greater than that in the ground-state.

Arguing by analogy with transition metal ions e.g. \(\text{Mn}^{2+}\), in which ligands produce an asymmetric environment for the ion \(93,94\) with a consequent long-lived \(g\)- and \(\Delta\)- anisotropy and \(m_I\)- dependent line-widths, Bar-Eli and Tuttle have postulated\(^{51}\) that a long-lived, non-spherical distribution of the unpaired electron spin density about the metal nucleus leads to an \(\Delta\)- anisotropy and that the \(m_I\)- dependence of the line-widths of the hyperfine multiplet arises from modulation of the \(\Delta\)- anisotropy via tumbling of the monomer unit. Rapid modulation of \(\Delta\)- anisotropy, with an isotropic \(g\)- factor, leads to a line-width effect of the type observed i.e. symmetrical about the centre of the hyperfine pattern, with line-width proportional to \(m_I^2\).
Modulation of both $g$- and $A$- anisotropy, or of $g$-anisotropy alone, could not produce this behaviour. The former case leads to an $m_1$-dependent line-width effect which is asymmetric with respect to the centre of the hyperfine pattern, while the latter produces no $m_1$-dependence of line-widths at all. These effects are illustrated diagrammatically in Figure 2.1.

O'Reilly and Tsang, by analogy with the cavity model of Ogg for $e_-$ and $e_2$- centres in metal-ammonia solutions, have proposed that polarization of solvent around the cation defines a potential square-well for the cation, the inverse of that for $e_-$ or $e_2$ species. The effect of electrostatic attraction between the solvated electron and metal cation was represented as a "hole" in the inverted potential square-well as illustrated diagrammatically below (1). A similar diagrammatical representation of the $e_-$ cavity is included for comparison (11).

O'Reilly and Tsang defined the monomer in terms of a cation, $M^+$, surrounded octahedrally by 6 solvent molecules at distance $a$, the remainder of the solvent being treated as a dielectric medium i.e. in contrast to the monomer of Bar-El.
Fig 2.1

Diagrammatic representation of the effect of

(a) rapid modulation of an anisotropic $A$-value with isotropic $g$-factor.

(b) rapid modulation of both anisotropic $A$-value and $g$-factor.

(c) rapid modulation of an anisotropic $g$-factor, with isotropic $A$-value ($A_{\parallel} = A_{\perp}$).

(narrow, broad and very broad lines are designated $N$, $B$ and $VB$ respectively).
and Tuttle, only a single shell of solvent molecules was considered. O'Reilly performed quantum-mechanical calculations to formulate the various interactions as a function of $g$ and found that the temperature-dependence of the hyperfine splitting constant could be accommodated by an expansion of the monomer unit, i.e. an increase in $g$, of $+0.02\%$ per °C.

On the basis of the simple diagram (1) above, position A represents low-temperature conditions. As temperature increases, $g$ increases i.e. lone-pair donation by the nitrogen nuclei into the empty $n_s$ orbital of $M^+$ decreases, so that these orbitals become more available to the electron. The high-temperature conditions are therefore represented by B and correspond to increased cation-electron interactions i.e. to increased $A^-$ value.

$m_1^*$-dependent line-widths have been observed in the hyperfine lines of alkali metals trapped in inert and polar matrices and were attributed to the existence of a range of trapping sites for the alkali metal atoms. Dye and Dalton have proposed a model in which the $A^-$ value of the monomer is modulated between limits $A-8A$ and $A+8A$ by fluctuations in the solvent structure, with a fairly long correlation time for a given monomer-solvent interaction ($>10^{-7}$ secs). Thus, on the ESR time-scale, the monomer units are, in effect, contained in a range of trapping sites, defined by given arrangements of solvent molecules. The situation is analogous to that of the trapped atoms and line-widths proportional to $m_1^*$ are predicted.

2) The "dynamic" or multi-state model for $M_{\text{solv}}$.

The multi-state model was developed by Hirota et al. to explain the $m_1^*$-dependent line-widths of cation hyperfine lines in ion-pairs of type $M^+ R^-\cdot$, where $R^-$ represents an organic radical. Dye and Dalton have attempted to apply this type of model to
metal solutions.

On the basis of a multi-state model, the ESR spectra are explained by assuming the existence of two or more monomeric states, with distinct magnetic properties, interconverting rapidly, such that the lifetime of each state is short compared with the inverse of the difference in hyperfine separation between the states. Thus none of the states can be detected separately by ESR and the observed properties are an average of those of the individual states, weighted by their relative populations and modulated by the rapid interconversions.

For 2 such states, A and B, equation 2.1 can be derived:

\[ \frac{1}{T_{2(m_I)}} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} + \frac{P_A^2}{T_{2B}} \frac{P_B^2}{T_{2B}} \left( \tau_A + \tau_B \right) \]

\[ \left( \omega_A^{(m_I)} - \omega_B^{(m_I)} \right)^2 \]

where \( T_{2(m_I)} \) is proportional to the line-width of the \( m_I \)-component of the hyperfine spectrum.

\( P_A \) and \( \tau_A \) represent the fraction and mean lifetime respectively, of A (similarly for B).

\( T_{2A} \) is the exchange-independent transverse relaxation time of A (similarly for B).

\( \omega_A^{(m_I)} - \omega_B^{(m_I)} \) represents the difference in hyperfine separations (in radians/sec) of the \( m_I \)-component of the hyperfine spectrum, for the two states A and B.

For rubidium and caesium solutions, because of the large hyperfine splitting constants involved, it is necessary to correct the observed transition frequencies, \( \omega_A^{(m_I)} \) and \( \omega_B^{(m_I)} \), to third-order in \( m_I \).

The transition frequency in the absence of hyperfine interactions, \( \omega_0 \), is given by equation 2.2:
where $a_A$ is the contact hyperfine splitting constant for A.

Substitution of $\tilde{\omega}_A^0$ and $\tilde{\omega}_B^0$ from equation 2.2 into equation 2.1 leads to,

$$\left[T_2(m_I)e^{-1}\right] = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} + \frac{P_A^2 P_B^2 T_A T_B}{T_{2A} T_{2B}}$$

$$= (\alpha + \beta m_I + \gamma m_I^2 + \delta m_I^3 + \ldots)$$

(equation 2.3)

For a dilute caesium-ethylamine solution, Dye and Dalton observed, with increase in temperature, a smooth increase in $A_{iso}^{133Cs}$. The $g$-factor for the centre of the hyperfine octet, $g_M$, however, decreased in approximately linear manner from $-100^\circ C$ to $0^\circ C$ and thereafter remained constant. This behaviour is shown in Figure 2.2. Dye and Dalton, considering only the data up to $0^\circ C$, applied a 2-state model with high- and low-temperature species characterised by $A$- and $g$-values at $0^\circ C$ and $-100^\circ C$ respectively. On this basis, coefficients
Fig 2.2
Temperature-dependence of $A_{iso}(^{133}_{133}Cs)$ (O) and $g_{^{133}_{133}Cs}$ (X),
corrected to second-order, * for solutions of caesium in
ethylamine (refs. 80 and 88)
* see foot-note, page 56.
Temperature-dependence of \( A_{\text{iso}}(^{133}\text{Cs})(0) \) and \( g_{133}\text{Cs} (X) \) for solutions of caesium in ethylamine. The data on Fig. 2.2 have been corrected (ref. 78) by a full Breit–Rabi treatment. The \(^{133}\text{Cs}\) hyperfine splitting constant has been expressed in energy units in order to avoid the non-linearity of the same function expressed in gauss, which is observed under conditions for which the high-field approximation does not hold i.e. for which the applied magnetic field, \( H_0 \gg A_{\text{iso}}(M) \).

The lines drawn through the data points represent attempts to fit the data for \( A- \) and \( g- \) values using,

\[
X_{\text{calc}} = \frac{X_1}{1 + X} + \frac{X_2}{1 + X^{-1}}
\]

where \( X \) represents \( A_{\text{iso}}(^{133}\text{Cs}) \) and \( g_{\text{Cs}} \) and \( K = e^{-\Delta G/RT} \approx \frac{1}{e^{\Delta H/RT}} e^{\Delta S/RT} \); \( \Delta G, \Delta H \) and \( \Delta S \) are the free energy, enthalpy and entropy changes between the two states 1 and 2.

Varying \( X_1, X_2 \) and \( \Delta H \) to give the least mean square deviation of the calculated points from the experimental data leads to:

1. For \( X = A_{\text{iso}}(^{133}\text{Cs}) \), \( A_1 = 0.814 \times 10^9 \text{ radians sec}^{-1} \), \( A_2 = 203.3 \times 10^9 \text{ radians sec}^{-1} \) (cf. \( A_{\text{free atom}} = 14.44 \times 10^9 \text{ radians sec}^{-1} \)), \( \Delta H = 2.43 \text{ kcals. mole}^{-1} \), \( \Delta S = 1.57 \text{ entropy units (e.u.)} \)

2. For \( X = g_{\text{Cs}} \), \( g_1 = 1.99866, g_2 = 1.99310 \) (cf. \( g_{\text{free atom}} = 2.00258 \)), \( \Delta H = 3.57 \text{ kcals. mole}^{-1}, \Delta S = 1.552 \text{ e.u.} \)

(N.B. the lack of agreement of \( \Delta H \) and \( \Delta S \) values, together with the fact that \( A_2 > A_{\text{free atom}} \) indicates that a two-state model is inadequate to describe this system.)
Fig 2.3

(Caption on previous page).
The deviation between lines $\overline{I}$ and $\overline{II}$ is a measure of the failure of a two-state model to describe the caesium-ethylamine system.
gaseous free atom \(^{101}\), whereas the properties \(^{102}\) of silver atoms produced by \(\gamma\) - irradiation of frozen solutions of silver cations, differed markedly from those of the gaseous free atom. In particular, the \(g\) - factor for the former was considerably lower than that for the latter. Solvation is not possible for the silver atoms prepared by matrix isolation, whereas those prepared by irradiation will be solvated just as were the silver cations prior to irradiation. In this case, therefore, as for state A, the effect of solvation is to produce a negative \(g\) - shift.

The nature of the low-temperature monomeric state, C, was not defined but the value of \(A_{iso}(^{39}K)\) associated with C was very small ( \(\sim 1-2\) gauss). It has been suggested \(^{80}\) that species C could be the ion-pair, \(K^+\text{solv.}e^-\text{solv.}\). Such a species would be expected to have a low value of \(A_{iso}(^{39}K)\) and to be favoured at low temperature, as observed for metal-ammonia solutions (Chapter 1).

Although A, B and C, with mean life-times \(< 10^{-7}\) secs, could not be separately observed in an ESR experiment, they might, in theory, be separately observed in an optical experiment, for mean life-times greater than \(10^{-12} - 10^{-13}\) secs. It has been shown earlier, however, that no optical band attributable to the monomer has been observed and it is generally assumed that such bands, if they exist, are hidden under bands due to diamagnetic species.

Electron Spin Resonance line-widths.

Catterall et al \(^{103}\) have observed that, for a given concentration of paramagnetic species, the singlet line-width in potassium-ethylamine solutions was governed by the concentration of diamagnetic species. They postulated that this was due to the equilibrium,
where $D$ and $D'$ represent distinct diamagnetic species. The predicted broadening of the hyperfine lines was not observed.

**Attempted optical-ESR correlations.**

Attempts to correlate ESR and optical data have been generally unsuccessful due to the fact that the principal species responsible for the optical absorption bands are diamagnetic.

The earliest attempt to correlate optical and ESR data was by Symons et al., who assigned the infrared band to $e$ and the visible band to $e'$. They suggested that there ought to be a correlation between the strength of the infrared absorption and the degree of paramagnetism exhibited. Such a correlation has, in fact, been observed. Thus a solution of lithium in methylamine displays a very intense infrared band and the solution is strongly paramagnetic, whereas no infrared band has yet been observed for a solution of potassium in tetrahydrofuran and the paramagnetism is so weak as to have remained undetected until the present work.

More recent measurements on solutions of caesium in ethylamine and of potassium in ethylamine-ammonia mixtures have shown, however, that, in these systems at least, the infrared band was too strong to be assigned to paramagnetic species alone and must contain some contribution from spin-paired species.

Ottolenghi et al.

assigned the $V$- and $R$- bands to monomer, $M$ and dimer, $M_2$, respectively, basing their assignations upon the observations that the $V$- band and hyperfine quartet lines decayed in parallel manner and that the $R$- band decayed at double the rate of the $V$- band. This interpretation does not accord with the following observations for solutions of
potassium in ethylamine - ammonia mixtures

(1) Increase in temperature resulted in an increase in intensity of the hyperfine quartet, a decrease in intensity of the V- band.

(II) Experimental determinations of ESR and optical concentrations showed that the species responsible for the V- band was present in concentrations at least an order of magnitude greater than that responsible for the ESR hyperfine quartet.

(III) With increase in ammonia concentration, the intensity of the hyperfine quartet increased steadily, whereas the intensity of the V- band passed through a maximum.
Although solutions of alkali metals in ethers are in many ways analogous to the corresponding amine solutions, the former have been much less extensively investigated. This is due to the lower metal solubility in ether solvents, the lower stability of metal-ether solutions and the very weak paramagnetism generally associated with these solutions.

**PROPERTIES OF METAL-ETHER SOLUTIONS.**

1. **Solubility and Stability.**

   Down et al. studied solutions of potassium and sodium-potassium alloy in several ethers. Blue solutions were formed with poly-ethers e.g. 1,2-dimethoxyethane (CH₂OCH₂CH₂OCH₃) and diethylene glycol dimethyl ether (diglyme; CH₂OCH₂CH₂OCH₂CH₂OCH₃) but not with simple aliphatic mono-ethers. The intensity of the blue colour was critically dependent upon steric factors, thus 1,2- dimethoxyethane dissolved sodium-potassium alloy readily to give a deep-blue solution, whereas 1,2- diethoxyethane did not dissolve the alloy at all.

   Pale blue colours have been observed for solutions of potassium, lithium and rubidium in tetrahydrofuran. These are the only metal-monoether solutions known.

   Solubilities of potassium in tetrahydrofuran, 1,2- dimethoxyethane and tetraglyme have been given values 5×10⁻⁴M, 1×10⁻³M and 1×10⁻²M respectively.

2. **Conductance.**

   The equivalent conductances, $\Lambda$, of 0.001 M solutions of lithium, sodium and potassium in 1,2- dimethoxyethane, at -75°C, have values $6\times10^{-6} \Omega^{-1} \text{cm}^{-1}$, $2\times10^{-6} \Omega^{-1} \text{cm}^{-1}$ and
$4 \times 10^{-6} \, \text{L}^{-1} \text{cm}^{-1}$ respectively. Similar values have been reported by other workers. For solutions of potassium in 1,2-dimethoxyethane, $\Lambda$ decreased with increase in metal concentration and with decrease in temperature, as observed for metal-ammonia solutions.

The data, limited though it is, implies that there is considerable ion-pairing, even at low concentrations.

3. Optical Spectra.

(A) 1,2-dimethoxyethane (1) lithium, sodium and potassium.

A single band at 14,200 cm$^{-1}$ has generally been observed, though, for potassium, a second band at 10,000 cm$^{-1}$ has been reported.

(11) rubidium and caesium.

Single bands, at 11,000 cm$^{-1}$ and 14,000 cm$^{-1}$, respectively, were observed for solutions of rubidium and caesium in 1,2-dimethoxyethane.

(111) mixed metals.

Addition of a rubidium-1,2-dimethoxyethane solution, showing an 11,000 cm$^{-1}$ band only, to a potassium-1,2-dimethoxyethane solution, with 14,200 cm$^{-1}$ band only, yielded bands at both 11,000 cm$^{-1}$ and 14,200 cm$^{-1}$.

(B) Tetrahydrofuran (1) potassium.

Bands at either 11,000 cm$^{-1}$ or 14,000 cm$^{-1}$ have been reported.

(11) rubidium.

A single band at 10,300 cm$^{-1}$ has been observed.

(C) Tetraglyme. Cafasso and Sundheim have recorded optical spectra for metal-tetraglyme solutions and obtained;
for (1) potassium a single band at 14,500 cm$^{-1}$
for (11) rubidium, a single band at 11,200 cm$^{-1}$, and
for (111) caesium, two bands, at 14,500 cm$^{-1}$ and 10,000 cm$^{-1}$

**Flash Photolysis.**

When a solution of potassium in tetrahydrofuran was subjected to flash photolysis $^{111}$, the single band originally at 11,000 cm$^{-1}$ was shifted to lower energies ($<10,000$ cm$^{-1}$). There was then a fast conversion to a band at 11,000 cm$^{-1}$, more intense than the original band, followed by a slow first-order decay back to the original band. These observations were explained by the reaction scheme,

\[ \text{flash} \quad e^1_2 \rightarrow e^1_1 \rightarrow e^3_2 \quad \text{recombination.} \]

\[ \text{slow, first-order} \]

\[ k \approx 13 \text{ sec}^{-1} \]

where $e^1_2$ and $e^3_2$ represent electrons trapped in singlet- and triplet-state pairs respectively and $e^1_1$ represents a singly-trapped electron.

4. **Electron spin resonance (ESR)**

The only reports of an ESR signal from metal-ether solutions are of a moderately-intense single line ($\Delta H_{ms} \sim 5$ gauss) from potassium-tetraglyme$^{109}$, and of a single line ($\Delta H_{ms} \sim 2$ gauss) from a potassium - 1,2 dimethoxyethane solution at low temperature $^{112}$. 
MODELS FOR METAL-ETHER SOLUTIONS.

Since there is so little reliable data on metal-ether solutions, models have been proposed by analogy with metal-amine and metal-ammonia ether solutions.

Dainton et al.\textsuperscript{107} attributed the 14,000 cm\textsuperscript{-1} band observed for solutions of lithium, sodium, potassium and caesium in 1,2-dimethoxyethane to expanded metal dimers. For solutions of potassium in 1,2-dimethoxyethane and in tetrahydrofuran, a band at 10,000 - 11,000 cm\textsuperscript{-1} has been observed.\textsuperscript{107,110,111} Dainton mistook this band for a shifted ammonia-like infrared band and attributed it to the solvated electron. If this assignment were valid, these solutions ought to be strongly paramagnetic\textsuperscript{69} whereas they are, in fact, very weakly paramagnetic.

Cafasso and Sundheim\textsuperscript{109} pointed out that the lack of metal-dependence of the 14,000 cm\textsuperscript{-1} band for solutions of lithium, sodium, potassium and caesium in 1,2-dimethoxyethane was in conflict with the idea of Dainton\textsuperscript{107} that it was due to a metal dimer. Cafasso and Sundheim suggested that this band was due to the \(e_2\) species. Like Dainton\textsuperscript{107}, they assigned the 10,000-11,000 cm\textsuperscript{-1} band to the solvated electron.

Cafasso and Sundheim realized that the critical factor governing the formation of a metal solution was solvation of the cation. Thus diglyme forms cavities suitable for solvating both cation and solvated electron, whilst tetrahydrofuran forms cavities suitable for solvating the cation only but, nevertheless, has been observed to form pale-blue solutions with potassium and rubidium.
CHAPTER 3.

AN INTRODUCTION TO THE PRESENT WORK.
The object of the previous chapters has been to give a brief outline of the past and present states of knowledge and opinion in the field of metal solutions, with particular reference to the spectroscopic properties which are the object of the present study.

In the present work, some previous results have been extended or modified and some new data have been obtained.

In Chapter 4, the results of an intensive investigation into the properties of the potassium-ethylamine system are reported. This system has been the subject of several investigations, principally by optical spectroscopy but, in spite of this, there are a great many points of disagreement and several very basic properties of the system have been completely without rationalization. In the present work, by performing complementary quantitative optical and ESR experiments, information about the stoichiometry of species present in solution, both paramagnetic and diamagnetic, and the equilibria relating them has been obtained and has been applied successfully to explaining the spectroscopic properties of the system.

In Chapter 5, new data are reported for solutions of potassium in ether solvents viz tetrahydrofuran, diglyme and triglyme. Prior to the present work, very little data have been available for such systems (Chapter 2), principally because of the low metal solubility and low concentrations of paramagnetic species. The improved sensitivity of the Varian E-3 spectrometer employed in the present work has enabled well-resolved ESR signals to be obtained from such systems for the first time. The observation of hyperfine splitting to the metal nucleus has enabled a direct comparison with the corresponding amine solvents. The resemblance of
metal-ether to metal-amine (but not to metal-ammonia) solutions has been established.

The results in Chapters 4 and 5, together with results for related systems, suggest that the structure of the monomer species, M, is dependent upon the solvent to such an extent that the monomeric unit must be defined to include the solvating molecules i.e. the interaction between the metal ion and solvent is considerably stronger than can be explained by a simple ion-dielectric interaction. In Chapters 6-9, an attempt is made to probe the nature of the metal-solvent interaction i.e. the nature of the monomer, by studying the change in properties of the monomer with change in bulk solvent composition. In order to do this, the monomer has been generated in binary ether-ether, ether-amine and amine-amine solvent mixtures for which subtle changes in the environment of the monomer were possible, rather than the dramatic change incurred by a complete change of solvent. Although the behaviour of the monomer under such conditions has been satisfactorily interpreted in terms of a two-state model, it has not been found possible to differentiate unequivocally between such a model and a continuum model.
CHAPTER 4.

POTASSIUM-ETHYLAMINE SOLUTIONS.
**INTRODUCTION.**

The aims of the present research on potassium-ethylamine solutions have been indicated in Chapter 3. The potassium-ethylamine system was chosen as a model metal-amine system since metal solubility is reasonably high, solution stability is good and resolved hyperfine splitting to the potassium nucleus is detected and is sufficiently small as to render corrections to $A$- and $g$- values unnecessary.

The spin-count data obtained has been used to investigate the equilibria established and the stoichiometry of species present, for solutions prepared in both pyrex and quartz vessels and thereby to explain the concentration-dependence of the line-widths of the singlet and hyperfine components of the ESR spectrum and the dependence of optical spectrum upon cell material.

**EXPERIMENTAL.**

**Purification of ethylamine.**

Two samples of ethylamine, differing in purification technique, were used in the present work. The first was purified by rapid transfer of the anhydrous ethylamine, as supplied by BDH in sealed containers, on to clean lithium in a solvent-storage vessel attached to a high-vacuum line of standard design \(^{18,65}\). The lithium-ethylamine solution was thoroughly out-gassed by repeated freeze-pump-thaw cycles, until a deep-blue coloration spread throughout the whole of the ethylamine solution and all the hydrogen generated by the reaction,

\[
e^- + \text{EtNH}_2 \rightarrow \text{EtN}^- + \frac{1}{2} \text{H}_2^+\]

had been removed. The out-gassed lithium-ethylamine solution was maintained at \(-78^\circ\text{C}\) in a Drikold-acetone bath.

The second ethylamine sample, supplied by Dr. J.R. Hurley,
was freed from ammonia by fractional distillation. The ammonia concentration was estimated, by vapour-phase chromatography, to be less than one part in $10^4$. This sample of ethylamine was used without further purification.

**Solution preparation.**

Solution preparation was by standard high-vacuum technique $^{18,65}$. Ethylamine (b.p. 19°C at 760 mm.) was carefully distilled from an ice-cooled storage vessel on to a thin potassium film deposited on the walls of a vessel, which was cooled in a Drikold-acetone mixture and fitted with a narrow side-arm suitable for insertion into the microwave cavity of an ESR spectrometer. Samples of ethylamine stored over lithium were thoroughly outgassed immediately prior to solution preparation, in order to remove any hydrogen evolved during storage. In cases where this simple precaution was neglected, quite serious explosions have occurred.

Solutions were prepared in both pyrex and quartz vessels. Solutions prepared in quartz vessels were at no time allowed to come into contact with pyrex glass, either during preparation or study.

**ESR spectroscopy.**

Once prepared, the pale-blue potassium-ethylamine solution was carefully tipped into the ESR side-arm, which was of small bore (3-4 mm.) so that insertion into the microwave cavity was possible, without serious microwave power damping. If required, dilution of the metal solution with pure solvent was effected by cooling the ESR side-arm, containing some of the metal solution, and distilling over pure solvent from the metal solution contained in the main limb of the solution-preparation vessel.
Measurements at 9500 Mc sec$^{-1}$ were taken on a Varian Associates E-3 spectrometer, with 100 kc sec$^{-1}$ modulation frequency and a 9" magnet. A conventional variable-temperature unit was used for temperature control and measurement. "Natural" line-widths, $\Delta H_{ms}$, were measured under conditions of low modulation amplitude ($\leq \frac{1}{10} \Delta H_{ms}$) and low microwave power ($\leq$ 1 milliwatt). For the E-3 spectrometer, the contribution to $\Delta H_{ms}$ arising from inhomogeneity of the applied magnetic field was found to be approximately 0.06 gauss. Values of $\Delta H_{ms} \leq$ 0.1 gauss were therefore determined on a Varian Associates Vh502-03 spectrometer with a 12" magnet. For this spectrometer, with superheterodyne detection, the resolution limit was approximately 0.02 gauss. In general, however, ESR spectra were recorded on the E-3 spectrometer because of its greater sensitivity.

Spin-concentrations associated with the paramagnetic constituents of the potassium-ethylamine solutions were determined by comparing the intensity of the ESR signal from the particular paramagnetic species with that from a $1 \times 10^{-3}$M aqueous solution of manganous (II) sulphate, $\text{Mn}^{11} \text{SO}_4 \cdot 5\text{H}_2\text{O}$. In practical terms, the amplitudes of the derivative signals from sample and standard were compared at a given microwave power and a given ratio of modulation amplitude to natural line-width, the latter being determined in each case prior to the actual spin-count. Corrections were applied for differences in signal amplification factor and for differences in microwave power saturation characteristics of the two signals.

From such comparisons, the spin-concentration associated with any particular paramagnetic species in the solution was compared with that of the standard
(1.10^{-3} M), after correcting for differences in spectral hyperfine composition between sample and standard. Changes in cavity Q were found to be negligible.

Optical spectroscopy.

Optical spectra of solutions contained in both pyrex and quartz cylindrical vessels (8-10 mm in diameter) were recorded over the range 5,000 cm^{-1} - 30,000 cm^{-1}, using a Unicam SP700 recording spectrophotometer, with air in the reference beam.

RESULTS.

1. Stability.

Saturated potassium-ethylamine solutions prepared in pyrex and quartz vessels had half-lives of approximately three hours and half-an-hour respectively, at room-temperature and up to 40°C. Stability was better at low temperatures. At no time was photolysis used to regenerate paramagnetic species.

2. Optical spectra.

Room-temperature optical spectra were recorded for saturated potassium-ethylamine solutions prepared in both pyrex and quartz vessels and stored for some hours at -78°C.

For solutions prepared in pyrex vessels, a single band at 14,000 cm^{-1} was observed, whilst for those prepared in quartz vessels, a single band at 11,000 cm^{-1} was observed. Both bands had width at half-height, \( \Delta \nu/2 \), of approximately 4,000 cm^{-1} and were asymmetrically broadened on the high-energy side, as has been observed for many instances of electron trapping and solvation.

For a cell thickness t, total concentrations of absorbing species in solution, C, were calculated from the optical density at the band maximum, D_{\text{max}}2, assuming Beer's law.
to hold and using an extinction coefficient, \( \varepsilon \), for either band, of \( 5 \times 10^{-6} \). Values of \( c \) thus determined for saturated potassium-ethylamine solutions prepared in pyrex and quartz vessels were \( 3.3 \times 10^{-5} \) and \( 3.2 \times 10^{-5} \) respectively.

3. **Electron spin resonance (ESR)**

(a) **Hyperfine splitting constants.**

For saturated solutions prepared in either pyrex or quartz vessels, ESR spectra consisted of two quartets (\( A_{iso} = 9.29 \) gauss and \( 5.21 \) gauss at \( 23^\circ C \)), the quartet with the smaller splitting being approximately 7\% of the intensity of the other. A weak, broad central singlet was observed, superimposed on the hyperfine spectrum, slightly displaced to low-field of the centre of the hyperfine quartets. The effect of dilution with pure solvent i.e. of decreasing \( C \), the overall concentration of species in solution, was to cause an apparent increase in the intensity of the central singlet relative to that of the hyperfine quartet. In very dilute solutions (\( \sim 5 \times 10^{-7} \) M in potassium), only the central singlet was observed. These effects are shown in Figure 4.1. The relative splittings and intensities of the two quartets agreed well with those expected on the basis of coupling to \( ^{39}K \) and \( ^{41}K \) nuclei. (Table 4.1).

Hyperfine splitting constants were independent of metal concentration, spin-concentration, line-widths, nature of vessel (pyrex or quartz), solution decomposition or purification of solvent but were markedly dependent upon temperature, increasing steadily with increase in temperature for samples prepared in either pyrex or quartz vessels (Figure 4.2).
ESR spectra of solutions of potassium in ethylamine at room temperature.

(a) saturated solution \((4.3 \times 10^{-5} \text{ moles l}^{-1})\)
(b) dilute \((4.3 \times 10^{-6} \text{ moles l}^{-1})\)
(c) very dilute \((4.3 \times 10^{-7} \text{ moles l}^{-1})\).
**Table 4.1**

**ESR hyperfine structure.**

<table>
<thead>
<tr>
<th></th>
<th>PYREX</th>
<th>QUARTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{iso}^{39K}$ (gauss)</td>
<td>9.29</td>
<td>9.33</td>
</tr>
<tr>
<td>$A_{iso}^{41K}$ (gauss)</td>
<td>5.21</td>
<td>5.12</td>
</tr>
<tr>
<td>$A_{iso}^{39K}$</td>
<td>1.78</td>
<td>1.82</td>
</tr>
<tr>
<td>$A_{iso}^{41K}$</td>
<td>(1.82)</td>
<td>(1.82)</td>
</tr>
<tr>
<td>$100I_{41K}'$</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>$I_{39K}' + I_{41K}'$</td>
<td>(6.9)</td>
<td>(6.9)</td>
</tr>
</tbody>
</table>

(the figures in parentheses are calculated values, based upon the relative magnetic moments and abundances of the two isotopes).

**Table 4.2**

**Concentration dependence of line-widths.**

<table>
<thead>
<tr>
<th>$10^7$C (moles l$^{-1}$)</th>
<th>vessel material</th>
<th>$\Delta H_{ms}$ (hyperfine quartet) (gauss)</th>
<th>$\Delta H_{ms}$ (singlet) (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>P</td>
<td>0.37</td>
<td>0.84</td>
</tr>
<tr>
<td>320</td>
<td>Q</td>
<td>0.22</td>
<td>0.54</td>
</tr>
<tr>
<td>43</td>
<td>P</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>15</td>
<td>Q</td>
<td>0.13</td>
<td>0.075</td>
</tr>
<tr>
<td>4</td>
<td>P</td>
<td>0.11</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Fig 4.2

Temperature-dependence of $A_{1\text{so}}^{(39K)}$.

In pyrex; + (present work), □ (J.W. Tipping, Leicester, 1967)

$\triangle$ (ref. 72), X (ref 80.)

In quartz; o (present work).
(b) Line-widths.

(1) Dependence upon solvent purity.

Line-widths of the hyperfine quartet, though not of the central singlet, were significantly greater for solutions prepared using samples of ethylamine not purified over lithium prior to solution preparation than for those thus purified (in saturated solutions, $\Delta H_{\text{ms}} \sim 0.4-0.5$ gauss and $0.25$ gauss, respectively). This behaviour is similar to that observed upon the addition of excess potassium cations to the potassium-ethylamine solution (page 37). In the present case, the excess potassium cations were presumably produced by reaction of the potassium with impurities, particularly traces of water, in the ethylamine.

Very broad lines ($\Delta H_{\text{ms}} \sim 4$ gauss) have been observed when the solvent is out-gassed with nitrogen prior to solution preparation and have been attributed to the formation of a surface layer of the nitride on the potassium metal, leading to line-broadening by excess potassium cations as above.

(11) Dependence upon metal concentration.

Line-widths of freshly-prepared, saturated potassium-ethylamine solutions and of potassium-ethylamine solutions diluted with pure solvent are given in Table 4.2. Line-widths of both singlet and hyperfine quartet lines increased with increase in concentration. In a previous study, the smaller concentration-dependence of the hyperfine quartet line-widths was not detected.

This marked concentration-dependence of the singlet line-width is responsible for the growth in amplitude, $A$, of the singlet upon dilution of a saturated potassium-ethylamine solution with pure solvent (Figure 4.1).
A similar effect has been observed when saturated potassium-ethylamine solutions decompose (Figure 4.3). The singlet line-width, $\Delta H_{ms}$, decreased continuously, from $\sim 0.8$ gauss in saturated solution to 0.06 gauss in almost completely-decomposed solution. Initially, however, the area under the singlet i.e. the intensity $I'$, given by

$$I' = A \left( \Delta H_{ms} \right)^2$$

remained constant and only decreased significantly when the decay was well-advanced. The singlet amplitude, $A$, showed an initial slow increase, followed by a rapid increase and then a rapid decrease as the solution decomposed.

These results are in conflict with those of Catterall et al.\(^{63}\) who observed an initial rapid decrease in $I'$. The results of these authors can probably be attributed to poor solution stability (photolysis was frequently necessary to regenerate paramagnetic species) and to a lack of awareness of the importance of microwave power saturation effects, such effects becoming progressively more important as the singlet narrowed.

(III) Temperature-dependence.

In saturated solutions, the line-widths of the hyperfine quartet showed little dependence upon temperature, whereas the width of the central singlet increased with increase in temperature (Table 4.3), in contrast to the narrowing which has been observed in dilute solutions.\(^{65}\)

(IV) Microwave power-dependence.

In the absence of incident microwave power, the two spin-states of the electron are populated according to Boltzmann distribution, i.e.
Changes in singlet line-width ($X$), amplitude ($o$) and intensity ($\square$) with decay of a saturated potassium-ethylamine solution. The amplitude and intensity are in arbitrary units.
### Table 4.3

**Temperature-dependence of line-widths.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta H_{ms}$ (hyperfine quartet) (gauss)</th>
<th>$\Delta H_{ms}$ (singlet) (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-37</td>
<td>0.305</td>
<td>0.197</td>
</tr>
<tr>
<td>-17</td>
<td>0.302</td>
<td>0.255</td>
</tr>
<tr>
<td>+23</td>
<td>0.320</td>
<td>0.410</td>
</tr>
</tbody>
</table>

### Table 4.4

**Effect of microwave power upon line-width.**

<table>
<thead>
<tr>
<th>Power (milliwatts)</th>
<th>$\Delta H_{ms}$ (hyperfine quartet) (gauss)</th>
<th>$\Delta H_{ms}$ (singlet) (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.102</td>
<td>0.129</td>
</tr>
<tr>
<td>2</td>
<td>0.117</td>
<td>0.137</td>
</tr>
<tr>
<td>10</td>
<td>0.132</td>
<td>0.150</td>
</tr>
<tr>
<td>25</td>
<td>0.187</td>
<td>0.203</td>
</tr>
</tbody>
</table>

### Table 4.5

**Spin-concentrations.**

<table>
<thead>
<tr>
<th></th>
<th>$10^9 c$</th>
<th>$10^9 [K]$</th>
<th>$10^9 [c^-]$</th>
<th>$10^9 [K]+[c^-]$</th>
<th>$10^9 \frac{[c^-]^2}{[K]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>satd.</td>
<td>43,000</td>
<td>1410</td>
<td>68</td>
<td>1478</td>
<td>0.034</td>
</tr>
<tr>
<td>dilx10</td>
<td>4,300</td>
<td>195</td>
<td>61</td>
<td>256</td>
<td>0.060</td>
</tr>
<tr>
<td>dilx100</td>
<td>430</td>
<td>31</td>
<td>39</td>
<td>70</td>
<td>0.16</td>
</tr>
<tr>
<td>quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>satd.</td>
<td>32,000</td>
<td>1091</td>
<td>54</td>
<td>1145</td>
<td>0.036</td>
</tr>
<tr>
<td>dilx6</td>
<td>5,300</td>
<td>178</td>
<td>55</td>
<td>233</td>
<td>0.044</td>
</tr>
<tr>
<td>dilx10</td>
<td>3,200</td>
<td>154</td>
<td>25</td>
<td>179</td>
<td>0.056</td>
</tr>
<tr>
<td>dilx17</td>
<td>1,890</td>
<td>-</td>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*All concentrations are in moles l$^{-1}$.
where \( N_1 \) and \( N_2 \) represent the fraction of electrons in the lower and upper spin-states respectively (\( N_1 + N_2 = 1 \)), the two spin-states being separated by energy \( \Delta E \).

Increasing the microwave power incident upon the resonance cavity causes an increase in the rate of induced transitions between the lower and upper spin-states. If this rate becomes comparable to the rate of relaxation back to thermal equilibrium, then there is a net decrease in the population difference between the two spin-states, \( N_1 - N_2 \), with a resultant decrease in the net rate at which absorption transitions occur. This is detected as a decrease in area under the ESR absorption. In the case of homogeneously-broadened systems \(^{114,115}\) (i.e. those in which the line-width is determined by rapidly-fluctuating electron-lattice interactions), the decrease in area is accompanied by an increase in line-width, corresponding to the shorter mean life-time of a given spin-state. The increase in line-width leads ultimately to a decrease in amplitude \( A \) (equation 4.2), which is readily observed.

At low microwave power (\( P \leq 1 \) milliwatt) both hyperfine quartet and singlet line-widths were independent of power. At higher microwave powers, both sets of lines broadened (Table 4.4) as predicted above for homogeneous broadening.

The decrease in amplitude \( A \), at high microwave powers, has been observed for both singlet and hyperfine lines, as shown in Figures 4.4(a) and (b) respectively. At all metal concentrations studied, the amplitudes of both the singlet and hyperfine components were proportional to \( P^{1/2} \) for \( P \leq 1 \) milliwatt, but deviations from linearity were observed at higher microwave
Saturation plots for the singlet in potassium-ethylamine solutions.

In pyrex:  • (c = 4.3 × 10⁻⁵ moles l⁻¹),  x (c = 4.3 × 10⁻⁶ moles l⁻¹)

□ (c = 4.3 × 10⁻⁷ moles l⁻¹).

In quartz:  △ (c = 2.5 × 10⁻⁵ moles l⁻¹).
Saturation plots for the monomer in potassium-ethylamine solutions.

In pyrex: o (c = 4.3 x 10^{-5} moles l^{-1}), □ (c = 1.4 x 10^{-5} moles l^{-1}),

x (c = 4.3 x 10^{-6} moles l^{-1})
powers. The onset of these saturation effects occurred at higher powers for the broader lines from the more concentrated solutions. The curves in Figures 4a, 4(a) and (b) are in accord with the predicted behaviour for homogeneously-broadened systems 114, 115

(v) effect of decomposition. As reported previously, 65, 74 the line-widths of the components of the hyperfine quartet increased as the concentration of potassium cations increased during repeated cycles of decay and regeneration. This contribution to the line-width of the hyperfine quartet was significant only after many decomposition cycles. The singlet line-width, at all metal concentrations, was virtually unaffected by the presence of concentrations of decomposition products sufficient to broaden the hyperfine lines to approximately 2 gauss.

(c) ESR line-shapes. Line-shapes of both hyperfine and singlet lines, for freshly-prepared and decomposed solutions in both pyrex and quartz vessels, were compared with theoretical Lorentzian and Gaussian line-shapes 116.

For under-modulated signals i.e., a natural line-width ratio $\geq 8$, both hyperfine and singlet modulation lines, in freshly-prepared solutions, were very close to Lorentzian in shape. Over-modulation resulted in deviations from Lorentzian towards Gaussian line-shapes. The very broad hyperfine quartet lines characteristic of decomposed solutions were found to have shape intermediate between those of Lorentzian and Gaussian lines.

A Lorentzian line-shape is characteristic of a
Line-shapes for selected singlet lines in K-EtNH₂ solutions.

--- Theoretical Lorentzian line-shape

--- Theoretical Gaussian line-shape

In pyrex: x (0.12), + (0.13), □ (0.14), ◻ (0.19), ▽ (0.20), Δ (0.27).

In quartz: ⊕ (0.10), ☐ (0.20).

The figures in parentheses are ΔH_{ms} values, in gauss.

All line-shapes were measured at modulation 0.025 gauss.
Line-shapes for selected monomer lines in K-EtNH$_2$ solutions.

- - - Theoretical Lorentzian line-shape
--- - Theoretical Gaussian line-shape

In pyrex: $m_T = \frac{1}{2}$; +(0.14), x(0.15), @ (0.17), □ (0.17)

The figures in parentheses are $\Delta H_{ms}$ values, in gauss.

All line-shapes were measured at modulation 0.025
homogeneously-broadened system i.e., is indicative of a rapidly-fluctuating interaction such that,

\[(\omega \tau_c)^2 \ll 1\]  (see page 9)

and the ESR signal is a time-average of all these interactions.

If the ESR signal arises from a very long-lived interaction, as in the solid-state, such that,

\[(\omega \tau_c)^2 \gg 1\]

an envelope of unresolved lines is observed and tends to be Gaussian in shape if the electron interacts with a sufficiently large number of equivalent magnetic nuclei e.g., interaction with 6 equivalent \( ^1 \text{H} \) nuclei \((I = \frac{1}{2})\) leads to a line-shape very close to Gaussian.

For the interaction modulated at intermediate rate, such that,

\[(\omega \tau_c)^2 \sim 1\]

the line-shape function is extremely complex but tends towards Gaussian. This, as discussed previously (page 37) is the situation when excess potassium cations are present. The tendency towards Gaussian line-shape observed in this case is thus explained.

(d) \( g \)-factors.

Although no absolute measurements of \( g \)-factors were performed, the quantity \( \Delta g \) (the \( g \)-factor of the singlet minus that of the centre of the \(^{39}\text{K} \) hyperfine quartet) was measured accurately, to second order, for saturated solutions prepared in both pyrex and quartz vessels. In agreement with results reported for rubidium- and caesium-ethylamine solutions \(^{80,81}\) but in conflict with previous published results for the present system \(^{65,80}\), \( \Delta g \) was found to be temperature-dependent. In Figure 4.6, the present data is compared with that of Catterall \(^{117}\) for the same system, \( \Delta g \) being plotted against the \(^{39}\text{K} \) hyperfine splitting constant in order to
Correlation between $A_{iso}^{(39K)}$ and $\Delta g$ for saturated solutions of potassium in ethylamine.

In pyrex: $\times$ (present work), $\circ$ (reference 117)

In quartz: $\triangle$ (present work)

The straight line has been drawn through present data points only.
eliminate the errors of temperature-measurement believed to have been present in the latter work.

(e) **Concentrations of unpaired spins.**

Concentrations of both solvated electron, \( e^- \) and monomer (or ion-pair) species, \( K^+ e^- \), were determined by applying the procedure outlined in the experimental section to the singlet and hyperfine signals respectively, for saturated and diluted solutions in both pyrex and quartz vessels. The results are given in Table 4.5, along with corresponding values of \( C \), the total concentration of species in solution, estimated using equation 4.1.

\[
\alpha, \text{ the fraction of unpaired spin, given by }
\]

\[
\alpha = \frac{\text{concentration of paramagnetic species in solution}}{\text{total concentration of species in solution}} = \frac{[e^-]}{C + [K]}
\]

was thus calculated and values are included in Table 4.5. Values of \( \alpha \) for saturated solutions (\( \sim 10^{-5} \) M in potassium) indicated that only 3-4% of the electron spins were unpaired. For metal-ammonia solutions at comparable concentrations, spin-unpairing was essentially complete i.e., \( \alpha = 1.0 \). This contrast between metal-amine and metal-ammonia solutions is discussed in detail later.

**DISCUSSION.**

1. **Optical spectra.**

A detailed discussion of band positions and assignments is reserved for a later section.

In Figure 4.7, several bands, both in the infrared and visible regions of the optical spectra of metal
\[ \frac{\nu - \nu_{\text{max}}}{\nu_{\frac{1}{2}^+} - \nu_{\frac{1}{2}^-}} \]

**Fig 4.7**

Optical-band shapes for the V-band \(66\) in sodium-ethylenediamine (ED)(0), the R-band \(66\) in rubidium -ED(+), the infrared bands for caesium-ED \(66\)(x), sodium-ammonia (\(\Delta\)) and the aquated electron \(125\) (\(\Box\))
solutions, have been normalised to the same band maximum position, $\lambda_{\text{max}}$ and band-width, $\Delta\lambda/2$, and can be seen to have identical shapes.

2. Electron spin resonance spectra.

(1) The presence of a central singlet.

The presence and origin of the central singlet have been the subject of some controversy. Some workers $72,118,119$ have failed to observe it all, some $73$ observed the singlet only in decomposing solutions and therefore concluded that it was due to a product of decomposition, whilst others $65,74$ observed the central singlet in freshly-prepared solutions and attributed it to $e^{-}\text{solv}$.

In the present study, the central singlet was always observed, in freshly-prepared, diluted or partially-decomposed solutions. Dilution or decomposition led to similar growths in singlet amplitude, which were associated with decrease in singlet line-width (Figure 4.3), not to an increase in singlet intensity as Dalton et al $73$ assumed in assigning the singlet to a decomposition product.

(11) Variation of hyperfine splitting constant with temperature.

The present measurements, in both pyrex and quartz vessels, confirm the temperature-dependence of the $^{39}$K hyperfine splitting constant reported by Bar-Eli et al $72$ and Catterall et al $65$. It has not been found possible, under any conditions, to reproduce the "plateau" observed by Dalton et al $73$ (see page 41).

The models proposed to explain the sensitivity of hyperfine splitting constants to temperature have been outlined in Chapter 2. The present measurements are not sufficiently precise to distinguish between these models.
3. EQUILIBRIA IN POTASSIUM-ETHYLAMINE SOLUTIONS.

Using the data contained in Table 4.5, the equilibria established in potassium-ethylamine solutions can be investigated.

One - equilibrium scheme.

One of the first attempts to describe the equilibria established in metal-amine solutions was that of Catterall et al. As mentioned in Chapter 2 (page 38) they reported that the ratio \( \frac{[\text{singlet}]}{[\text{quartet}]} \) was independent of metal concentration which implies, by analogy with ammonia, a single ion-pairing equilibrium scheme, viz,

\[
K^+ + e^- \rightleftharpoons K \quad K_1 = \frac{[K]}{[e^-]}^{2} \quad \text{since} \quad [K^+] = [e^-]
\]

Values of \( \frac{[e^-]}{[K]}^{2} \) obtained from the spin-concentration measurements in the present work, are contained in Table 4.5 and clearly do not show the constancy reported by Catterall et al. i.e. the present data cannot be interpreted in terms of a single ion-pairing equilibrium. This observation is not really surprising since measurements of \( \alpha \) reported previously show that approximately 96% of the species present in saturated potassium-ethylamine solutions are diamagnetic i.e. spin-pairing, which is totally ignored by the above treatment, is of great importance in potassium-ethylamine solutions.

Two - equilibrium scheme.

A second equilibrium, to account for spin-pairing, was proposed by Becker, Lindquist and Alder for metal-ammonia solutions. For the two- equilibrium scheme proposed viz.

\[
M^+ + e^- \rightleftharpoons M \quad K_2
\]

\[
M + M \rightleftharpoons M_2
\]
The equation,
\[
\frac{[e^-] + [M]}{[M_2]^\frac{1}{2}} = \frac{1}{K_1^{\frac{1}{2}} K_2^{\frac{1}{2}}} + \frac{[M_2]^{\frac{1}{2}}}{K_2^{\frac{1}{2}}}
\] (equation 4.5)
was derived.

In the present work, for samples prepared in either pyrex or quartz vessels, \( [e^-] \) and \( [M] \) are identified as the concentrations of paramagnetic species associated with the singlet and potassium hyperfine ESR signals respectively.

Since a single band only was observed in the optical spectra of potassium-ethylamine solutions, whether prepared in pyrex or quartz vessels, it is assumed that the factor \( C \), derived from equation 4.1, is the sum of the concentrations of all the species present in solution, paramagnetic and diamagnetic. Thus, for the two-equilibrium scheme above,
\[
c = 2 \frac{[M_2]}{diamagnetic} + \left[ M \right] + \left[ e^- \right] \quad (equation 4.6)
\] (\( K^+ \) is not expected to absorb in this region of the spectrum).

From equation 4.6, \( [M_2] \) can be evaluated.

There is some evidence \(^{32}\), principally by analogy with metal-ammonia solutions, that the paramagnetic species, \( e^- \) and \( K^+ e^- \), absorb in the near infrared (\( \sim 7,000 \text{ cm}^{-1} \)) though no infrared absorption has yet been definitely detected for solutions in ethylamine, due, presumably to the very low concentrations of paramagnetic species in these solutions. If this is so, then \( M_2 \) alone is responsible for the optical band and
\[
c = 2 [M_2] \quad (equation 4.7)
\]

Since, however, the concentrations of the paramagnetic species are so much less than those of the diamagnetic species, equations...
4.6 and 4.7 are virtually equivalent.

For solutions prepared in quartz vessels, $M_2$ can be unequivocally identified as $K_2$. For solutions prepared in pyrex vessels, however, the possibility of sodium contamination discussed earlier prevents absolute identification of $M_2$ i.e. $K_2$, Na$_2$, KNa, NaK or any mixture of some, or all, of these are possible.

For present purposes, equation 4.5 therefore becomes,

$$\frac{[e^-] + [K]}{[M_2]^{1/4}} = \frac{1}{K_1^{1/2} K_2^{1/2}} + \frac{[M_2]^{1/4}}{K_2^{1/2}} \quad \text{(equation 4.8)}$$

For solutions prepared in either pyrex or quartz vessels, $[e^-]$ and $[K]$ are known from spin-concentration measurements, $[M_2]$ can be calculated using equation 4.6.

As shown in Figure 4.8, the plot of $\frac{[e^-] + [K]}{[M_2]^{1/4}}$ against $[M_2]^{1/4}$ was not linear for solutions prepared in either pyrex or quartz vessels. A two-equilibrium scheme is therefore inadequate to describe the behaviour of potassium-ethylamine solutions.

**Three-equilibrium scheme.**

A third equilibrium, introducing a second diamagnetic species, variously written as $M^+$ $e^-$, $M^- e^-$, $e^- M^+ e^-$ or $M^+ e^- e^-$, has been widely proposed for metal-ammonia solutions. The present data on potassium-ethylamine solutions has been analysed in terms of the three-equilibrium scheme,

$$M^+ + e^- \rightleftharpoons K_A M^+ e^-$$

$$M^+ e^- + e^- \rightleftharpoons K_B M^-$$

and $$M^+ + e^- \rightleftharpoons K_C M^+e^-$$

though it has been pointed out that all three-equilibrium
Fig 4.8

2 - equilibrium plots for potassium-ethylamine solutions prepared in pyrex (o) and quartz (+) vessels.

(see equation 4.8)

All concentrations are in moles l$^{-1}$. 
Schemes involving species of the same overall stoichiometry are formally equivalent and have equilibria constants related in simple algebraic manner.

The application of an equilibrium scheme serves only to indicate whether species of the stoichiometry proposed in the scheme are reasonable constituents of solution. The writing of formulae such as \( M^+e^- \), \( M^- \) and \( M^+M^- \) is for convenience only and no structural implications are intended.

For solutions prepared in quartz vessels, \( M^+e^- \), \( M^- \) and \( M^+M^- \) are identified as \( K^+e^- \), \( K^- \) and \( K^+K^- \). For solutions prepared in pyrex vessels, \( M^+e^- \) is unequivocally identified as \( K^+e^- \) since, as shown quantitatively by the \(^{41}\text{K}\) hyperfine splitting intensities (Table 4.1), only potassium hyperfine splittings are observed. Because of sodium contamination from the pyrex, however, \( M^- \) can be identified as either \( \text{Na}^- \) or \( K^- \) or a mixture of the two and \( M^+M^- \) as \( K^+K^- \), \( \text{Na}^+\text{Na}^-\text{Na}^+K^-\text{K}^+\text{Na}^- \) or a mixture of some or all of these possibilities.

For the above three-equilibrium scheme, with the identification of \( M^+e^- \) as \( K^+e^- \) for solutions prepared in either pyrex or quartz vessels, the equation

\[
\frac{[M^+M^-]}{[K^+e^-]^2} + \frac{[M^-]}{[K^+e^-]}^2 = K_B \frac{[e^-]}{[K^+e^-]} + K_B \frac{K_C}{K_A} \tag{equation 4.9}
\]

can be derived.

The sum \([M^+M^-] + [M^-] \) was determined using,

\[
c = 2 \ [M^+M^-] + [M^-] + [K^+e^-] + [e^-] \tag{equation 4.10}
\]

which is analogous to equation 4.6.

Thus \([e^-]\) and \([K^+e^-]\) are determined from spin-counts, the sum \([M^+M^-] + [M^-]\) from optical spectra.

Equation 4.9 predicts that, if the proposed three-equilibrium scheme satisfactorily describes the system, then a
plot of \( \frac{[M^+M^-] + [M^-]}{[K^+e^-]^2} \) against \( \frac{[e^-]}{[K^+e^-]} \) ought to be linear, with slope \( K_B \) and intercept \( \frac{K_C}{K_A} \).

For solutions prepared in pyrex vessels, the linearity was excellent for a hundred-fold change in the total concentration of species in solution, \( C \). (Figure 4.9).

For solutions prepared in quartz vessels, however, the lower stability referred to earlier was a serious complication. For relatively-concentrated solutions (\( \sim 6 \times 10^{-6}M - 3 \times 10^{-7}M \)), for which decomposition was sufficiently slow to enable accurate spin-count measurements to be made, the observed behaviour was identical to that of the solutions prepared in pyrex vessels. For more dilute solutions, however, rapid decomposition resulted in systematic deviations from linearity, in the sense expected, as shown in Figure 4.9.

The plot on Figure 4.9 enabled \( K_B \) and the ratio \( \frac{K_C}{K_A} \) to be determined. The assumption of electrical neutrality, viz.

\[
[M^+] = [M^-] + [e^-] \quad (\text{equation 4.11})
\]

enabled \( K_A \) and \( K_C \) to be determined separately. Values of \( K_A, K_B \) and \( K_C \) and of equilibrium concentrations of \( K^+e^- \), \( M^- \), \( M^+M^- \) and \( e^- \), at several different total concentrations of species in solution, are shown in Table 4.6. The present data is compared with that for ammonia in a later section of this chapter.

4. WIDTHS OF ESR LINES.

The variation of line-widths, of both singlet and hyperfine quartet, with total concentration of species in solution has been noted previously (Table 4.2).

In order to determine the factor governing these line-
Fig 4.9

3 - equilibrium plots for potassium-ethylamine solutions prepared in pyrex (o) and quartz (x) vessels. (see equation 4.9)

All concentrations are in moles l⁻¹
### Table 4.6

<table>
<thead>
<tr>
<th></th>
<th>PYREX</th>
<th>QUARTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SATD.</td>
<td>DILX10</td>
</tr>
<tr>
<td>$10^9$ C</td>
<td>43,000</td>
<td>4,300</td>
</tr>
<tr>
<td>$10^9$ [K]</td>
<td>1,410</td>
<td>195</td>
</tr>
<tr>
<td>$10^9$ [e$^-$]</td>
<td>68</td>
<td>61</td>
</tr>
<tr>
<td>$10^9$ [K$^-$]</td>
<td>31,000</td>
<td>3,840</td>
</tr>
<tr>
<td>$10^9$ [K$_2$]</td>
<td>10,600</td>
<td>265</td>
</tr>
<tr>
<td>$10^{-5}$[K$_A$]</td>
<td>6.70</td>
<td>8.20</td>
</tr>
<tr>
<td>$10^{-8}$[K$_B$]</td>
<td>3.23</td>
<td>3.23</td>
</tr>
<tr>
<td>$10^{-4}$[K$_C$]</td>
<td>1.11</td>
<td>1.78</td>
</tr>
</tbody>
</table>

(All concentrations in moles $1^{-1}$)
(All equilibria constants in l.mole$^{-1}$).

### Table 4.7

<table>
<thead>
<tr>
<th></th>
<th>Saturated potassium-ethylamine at $-27^\circ$C</th>
<th>potassium-ethylamine diluted $\times$ 10 at $23^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^9$ C</td>
<td>43,000</td>
<td>4,300</td>
</tr>
<tr>
<td>$10^9$ [K]</td>
<td>259</td>
<td>195</td>
</tr>
<tr>
<td>$10^9$ [e$^-$]</td>
<td>54</td>
<td>61</td>
</tr>
<tr>
<td>$10^9$ ([K] + [e$^-$])</td>
<td>313</td>
<td>256</td>
</tr>
<tr>
<td>$10^9$ [D]</td>
<td>42,700</td>
<td>4,044</td>
</tr>
<tr>
<td>$\Delta$$H_{ms}$ (hyperfine) quartet (gauss)</td>
<td>0.32</td>
<td>0.14</td>
</tr>
<tr>
<td>$\Delta$$H_{ms}$ (singlet) (gauss)</td>
<td>0.75</td>
<td>0.12</td>
</tr>
</tbody>
</table>

(all concentrations in moles $1^{-1}$).
widths, an experiment was performed in which singlet and hyperfine quartet line-widths were compared at similar total concentrations of paramagnetic species but widely-differing concentrations of diamagnetic species. The results are contained in Table 4.7 and confirm the qualitative observation of Catterall et al. that the line-widths are governed by the concentration of diamagnetic species in solution, not of the paramagnetic species.

In theory, several exchange processes could contribute to the line-widths. None of the possible spin-exchange processes between the paramagnetic species themselves could account for the above dependence. Furthermore, since concentrations of paramagnetic species in potassium-ethylamine solutions are so small (\( \leq 1 \times 10^{-6} \)M) it can easily be shown that, assuming diffusion control, such spin-exchange processes could contribute 0.10 gauss at most to the line-widths.

The concentration-dependence of the line-widths was attributed by Catterall et al. to the equilibrium,

\[ e^- + D \rightleftharpoons M + D' \]

where \( D \) and \( D' \) represent two distinct diamagnetic species.

On the basis of the three-equilibrium scheme employed in the present work, \( D \) is identified with \( M^+M^- \) and \( D' \) with \( M^- \) viz

\[ e^- + M^+M^- \rightleftharpoons K_D \rightleftharpoons M^+e^- + M^- \]

This equilibrium is merely a combination of the two ion-pairing equilibria used in the three-equilibrium scheme, such that,

\[ K_D = \frac{K_A}{K_C} \quad \text{(equation 4.12)} \]

The widths of the singlet and hyperfine lines are related to the mean life-times of the solvated electron and monomer (or ion-pair) species respectively. For diffusion control, these
life-times, $\tau_{e^-}$ and $\tau_{M^+e^-}$ are given by,

$$\tau_{e^-} \text{ (secs.)} = \frac{1}{D_{e^-}} \left( \frac{125 \pi^{\frac{1}{6}}}{10^3 [M^+M^-]} \right)$$

(equation 4.13)

and

$$\tau_{M^+e^-} \text{ (secs.)} = \frac{1}{D_{M^+e^-}} \left( \frac{125 \pi^{\frac{1}{6}}}{10^3 [M^-]} \right)$$

(equation 4.14)

where $D_{e^-}$ and $D_{M^+e^-}$ represent the diffusion coefficients of solvated electron and monomer (or ion-pair).

Since

$$\tau = \frac{2 \hbar}{\sqrt{3} g_e \mu_e \Delta H_{\text{ms}}} \text{ i.e. } \Delta H_{\text{ms}} \text{ (milligauss)} = \frac{65.58}{\tau (\mu\text{secs.})}$$

(equation 4.15)

the line-widths corresponding to equations 4.13 and 4.14 are given by

$$\Delta H_{\text{ms}} \text{ (singlet) (milligauss)} = 65.58 \times 10^{-6} \frac{D_{e^-}}{125 \pi^{\frac{1}{6}}} \left( \frac{10^3 [M^+M^-]}{[M^-]} \right)$$

(equation 4.16)

and

$$\Delta H_{\text{ms}} \text{ (hyperfine) (milligauss)} = 65.58 \times 10^{-6} \frac{D_{M^+e^-}}{125 \pi^{\frac{1}{6}}} \left( \frac{10^3 [M^-]}{[M^+M^-]} \right)$$

(equation 4.17).

(1) the line-width of the singlet.

Values of $[M^+M^-]$, at several different values of the total concentration of species in solution, have been listed in Table 4.6. If the diffusion coefficient of the solvated electron is ethylamine at 23°C is assumed to be equal to that of the solvated electron in ammonia at -33°C (D$_{e^-} = 2.7 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$)50,113, under which conditions the two solvents have almost identical viscosities, then the experimental variation of singlet line-width with total concentration, $C$, is quite well-reproduced (Figure 4.10). A "best fit" is obtained for $D_{e^-} = 3.8 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$, which suggests that the solvated electron is slightly
Dependence of line-widths upon total concentration, C, for solutions of potassium in ethylamine.

(1) singlet: observed (Δ); calculated using \( D_e^- = 3.8 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \). (-----)

(II) hyperfine quartet: observed (O); calculated using
\[ D_{M^+e}^- = 0.4 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \) (-----).

(see text, page 89; for details of calculations).
more mobile in ethylamine than in ammonia, possibly due to looser solvation in the former solvent.

(11) the line-widths of the components of the hyperfine quartet. Values of $[m^-]$, at several different values of the total concentration of species in solution, have been listed in Table 4.6. The diffusion coefficient of the monomer in ethylamine at 23°C, $D_{M^+ e^-}$, is equated with that for the cation in ammonia at -33°C ($D_{M^+} = 0.3 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$) since the combination of a fast species ($e^-$) and slow species ($M^+$) will have diffusion rate controlled by the slower. This value of $D_{M^+ e^-}$ leads to a fair reproduction of concentration-dependence of the line-widths of the hyperfine quartet (Figure 4.10) but a "best fit" was obtained using $D_{M^+ e^-} = 0.44 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ indicating, as above, that the monomer, or ion-pair, species is about 50% more mobile in ethylamine than in ammonia.

5. ORIGINS OF THE SO-CALLED V- AND R- BANDS.

Optical spectra of potassium-ethylamine solutions consisted of a 14,000 cm$^{-1}$ band in pyrex, an 11,000 cm$^{-1}$ band in quartz, the former being assigned by Hurley et al. to sodium species, the latter to potassium species. In either case, however, the ESR hyperfine spectrum observed was characteristic of K$_{solv}$ and no contribution from Na$_{solv}$ has been detected in metal-pure ethylamine solutions. It has been one of the aims of the present work to resolve this apparent contradiction.

On the basis of the three-equilibrium model, the 11,000 cm$^{-1}$ band in quartz was assigned to $K^+ K^-$ and $K^-$, ESR line-broadening being attributed to the equilibrium

$$e^- + K^+ K^- \rightleftharpoons K^+ e^- + K^-$$

If the 14,000 cm$^{-1}$ band in pyrex were due to sodium species alone i.e. to Na$^+ Na^-$ and Na$^-$, ESR line-broadening would be
attributed to
\[ e^- + Na^+Na^- \rightleftharpoons Na^+e^- + Na^- . \]

This equilibrium, however, cannot be established in these solutions since the hyperfine splitting observed is still from \( K_{solv} \) not \( Na_{solv}^- \). If ESR line-broadening for solutions prepared in pyrex vessels were due to an equilibrium involving potassium species, just as for those prepared in quartz vessels then, since the intensity of the 11,000 cm\(^{-1}\) band in pyrex vessels \( \leq \) one-tenth the intensity of the same band in quartz vessels, i.e.,
\[
\left( \left[ K^+K^- \right] + \left[ K^- \right] \right)_{pyrex} \leq \frac{1}{10} \left( \left[ K^+K^- \right] + \left[ K^- \right] \right)_{quartz}
\]

line-broadening of the same magnitude in the two types of vessels would require an increase in the diffusion coefficients of the solvated electron and monomer by an order of magnitude in the pyrex vessels, which is clearly not reasonable.

The only alternative is to assign the 14,000 cm\(^{-1}\) band in pyrex to a mixture of sodium and potassium species i.e., to

\[ K^- + Na^+K^- \] \hspace{1cm} (1)

or \[ Na^- + K^+Na^- \] \hspace{1cm} (2).

For (1) and (2) ESR line-broadening would be attributed to equilibria,
\[ e^- + Na^+K^- \rightleftharpoons Na^+e^- + K^- \]
and \[ e^- + K^+Na^- \rightleftharpoons K^+e^- + Na^- . \]

The observation of potassium hyperfine splitting but no sodium hyperfine splitting eliminates (1). The 14,000 cm\(^{-1}\) band in pyrex is therefore assigned to \( Na^- \) and \( K^+Na^- \).

For solutions prepared in quartz vessels, the three-equilibrium scheme involving potassium species only is established, with 11,000 cm\(^{-1}\) band due to \( K^- \) and \( K^+K^- \) and overall reaction,
\[ 2K^+ + 2e^- \rightleftharpoons K^+ \ K^- \]
For solutions prepared in pyrex vessels, however, the same equilibria are established in a freshly-prepared solution, so that initially a band at 11,000 cm\(^{-1}\) is observed. Sodium cations, however, are then extracted from the pyrex by the metal solution and, since no sodium hyperfine splitting is observed, must be removed quickly before aggregates such as Na\(^+\)e\(^-\) form. There are two likely mechanisms for their removal, viz.

\[
K^+K^- + Na^+ \rightarrow K^+Na^- + K^+
\]

and

\[
K^- + Na^+ \rightarrow Na^- + K^+
\]

For excess potassium present, the equilibrium scheme becomes

\[
K^+ + e^- \xrightarrow{K_A} K
\]

\[
Na^+ + K + e^- \xrightarrow{K_B} Na^- + K^+
\]

\[
K^+ + Na^- \xrightarrow{K_C} K^+Na^-
\]

with overall reaction

\[
Na^+ + K^+ + 2e^- \rightarrow K^+Na^-
\]

to be compared with the overall reaction for solutions prepared in quartz, viz

\[
K^+ + K^+ + 2e^- \rightarrow K^+K^-
\]

For experiments performed with an excess of potassium, as in the present study, all the sodium cations extracted from the pyrex are reduced by the species K\(^+\)K\(^-\) and K\(^-\), as above, so that after a few hours only the band at 14,000 cm\(^{-1}\) (due to Na\(^+\) + K\(^+\)Na\(^-\)) is observed, that at 11,000 cm\(^{-1}\) (due to K\(^-\) + K\(^+\)K\(^-\)) disappears. No sodium hyperfine splitting is observed since their rapid removal means that the concentration of sodium cations, and therefore of sodium monomers, is negligible.

It has been observed that if such a solution as the above undergoes many cycles of decomposition and regeneration, the
band at 11,000 cm\(^{-1}\) is re-formed. On the basis of the assignment of the two bands proposed in the present work, this hitherto-inexplicable observation is explained as being due to an excess of potassium cations, constraining the equilibria,

\[
\begin{align*}
K^+K^- + Na^+ &\rightleftharpoons K^+Na^- + K^+ \\
\text{and} & \\
K^- + Na^+ &\rightleftharpoons Na^- + K^+
\end{align*}
\]

in the directions shown, causing an increase in \([K^-] + [K^+K^-]\) and therefore a growth of the 11,000 cm\(^{-1}\) band. In the ESR spectra, the presence of an excess of potassium cations under these conditions is indicated by the broadening of the components of the hyperfine quartet \(^{65,74}\) as discussed earlier in this chapter and in Chapter 2. (page 37)

In experiments performed with excess sodium present, all the sodium cations produced are not reduced by potassium species. The species present are,

\[
K^+, Na^+, e^-, K^+e^-, Na^+e^-, K^+K^-, K^-, K^+Na^-, Na^-
\]

so that, in the optical spectrum, both 11,000 and 14,000 cm\(^{-1}\) bands are observed and, in an ESR experiment, hyperfine splitting characteristic of both Na\(_{\text{solv}}\) and K\(_{\text{solv}}\) is present.

The only observation, to date, of both resolved sodium and potassium hyperfine splittings together, in a metal solution, is that of Catterall et al \(^{83}\) who dissolved sodium, with traces of potassium impurity, in a 40% ammonia-ethylamine solvent mixture i.e. under conditions of excess sodium, as above.

CONCLUSION TO SECTIONS 2. - 5.

In conclusion, the assignment of the 11,000 cm\(^{-1}\) band in quartz vessels to K\(^-\) and K\(^+K^-\) and of the 14,000 cm\(^{-1}\) band in pyrex vessels to Na\(^-\) and K\(^+Na^-\), with the hyperfine splitting observed attributed to K\(^+e^-\) in either case, satisfactorily explains the qualitative and quantitative observations on potassium-ethylamine solutions. The species Na\(^+Na^-\) has been
shown not to be a major component of potassium-ethylamine solutions. Further evidence for this conclusion is provided by the fact that sodium alone, in the absence of potassium, will not dissolve in pure ethylamine $^{65,72,73}$.

Although it is easily explained that a three-equilibrium scheme describes the behaviour of potassium-ethylamine solutions prepared in quartz vessels, the observation that similar behaviour is observed for solutions prepared in pyrex vessels is not, since more than three equilibria must be established in this case. It has been demonstrated that the complex equilibrium scheme in this case readily reduces to a three-equilibrium scheme involving species of stoichiometry $M, M^{+}, M_{2}$ etc. with an overall reaction very similar to that in quartz, so that the linearity observed in Figure 4.9 is not too surprising. It is surprising, however, that the straight line defined by the solutions prepared in pyrex vessels is identical with that defined by the solutions prepared in quartz vessels. According to equation 1.17, this must imply that ion-pairs such as $(K^{+}Na^{-})_{solv}$ and $(K^{+}K^{-})_{solv}$ have very similar sizes so that very nearly equal equilibrium constants govern their formation.

6. COMPARISONS WITH AMMONIA.

(1) The nature of the monomeric species.

Ion-pairing constants for the reaction,

$$\text{Cs}^{+} + e^{-} \rightleftharpoons \text{Cs}^{+}e^{-}$$

in ammonia, have been determined at three temperatures by Dewald and Roberts$^{3}$ and ion-size parameters, $a$, have been calculated, at these three temperatures, using equation 1.17. The value of $a$, at room temperature, was 6.9 Å.

For the ion-pairing equilibria proposed in the present work, viz,
application of equation 1.17 to the values of the ion-pairing constants contained in Table 4.6 leads to ion-sizes of $4.4\,\text{Å}$ for $\text{K}^+\text{e}^-$ and $6.6\,\text{Å}$ for $\text{K}^+\text{K}^-$ and $\text{K}^+\text{Na}^-$. Since the ion-sizes of $\text{Cs}^+_{\text{solv}}$ and $\text{K}^+_{\text{solv}}$ in ammonia are very similar (1.88Å and 1.96Å respectively), this decrease in ion-size from ammonia to ethylamine is due to the solvent alone. These ion-size changes are in accord with the increase in $^{39}\text{K}$ hyperfine splitting constant from ammonia (calculated as 0.46 gauss) to ethylamine ($\sim 9.3$ gauss at 23°C). In ethylamine, the monomeric species is a considerably more compact unit than in ammonia, which appears to be further evidence for writing the monomeric species, in amine solvents, as $(\text{K}^+\text{e}^-)_{\text{solv}}$, rather than $\text{K}^+_{\text{solv}}\text{e}^-_{\text{solv}}$.

(11) spin-pairing.

With regard to spin-pairing, there is a marked contrast between the behaviour of potassium-ethylamine and potassium-ammonia solutions.

At concentrations $\sim 10^{-5}\text{M}$, potassium-ethylamine solutions have 96 - 97% of spins paired whilst, at all concentrations $< 10^{-3}\text{M}$, there is no significant pairing of spins at all for potassium-ammonia solutions. This abrupt change in behaviour is shown in Figure 4.11, where the concentrations of the major species, expressed as a fraction of the total concentration of species in solution, have been plotted against $\log_{10} R$ ($R = \frac{\text{no. of moles of solvent}}{\text{no. of moles of potassium}}$), for both potassium-ammonia and potassium-ethylamine solutions. The spin-pairing behaviour of a $10^{-5}\text{M}$ potassium-ethylamine solution appears to compare with that of a $\text{M}$ potassium-ammonia solution, e.g. $[\text{e}^-]_e$ is small ($< 0.1$), but rising, in each case.
Concentration-dependence of composition of (1) sodium-ammonia (ref. 117) and (11) potassium-ethylamine (Table 4.6) solutions.

(1) $\frac{[M]}{C}$ (---), $\frac{[e^-]}{C}$ (---), $\frac{[M^-]}{C}$ (-----), $2 \frac{[M_2]}{C}$ (--x-x--).

(11) $\frac{[M]}{C}$ (+), $\frac{[e^-]}{C}$ (o), $\frac{[M^-]}{C}$ (Δ), $2 \frac{[M_2]}{C}$ (□).

where C is the sum concentration of all absorbing species in solution.
For the gas-phase alkali metal, a distribution between \( M \) and \( M_2 \) exists. In a polar solvent, such as ethylamine, the tendency to solvate ionic species leads to dissociation and appreciable concentrations of \( M^+, e^- \) and \( M^- \) in solution but non-polar species \( M \) and \( M_2 \) are still present (Table 4.6) and the fraction of unpaired spins is similar to that for the gas-phase alkali metal (\( \alpha \sim 0.05 \)). In potassium-ethylamine solutions, the gas-phase-like structure is modified, but not totally destroyed.

In metal-ammonia solutions, however, only polar species, \( M^+ \) and \( e^- \), appear to be important \(^{50} \) (Figure 4.11). Since the increase in dielectric constant from ethylamine to ammonia is only by a factor of two, solvation of \( M^+ \) would not be expected to change dramatically. It appears most likely that the difference in the observed behaviour of metal-ethylamine and metal-ammonia solutions is due to a difference in solvation of the electron species. In ammonia, the electron must presumably be strongly solvated by the ammonia molecules i.e. the electron is localised and pairing of electron spins is therefore only observed in concentrated solutions, when the concentration of electrons is very high and overlap of the unpaired electron wave functions occurs. In metal-ethylamine solutions, however, the aliphatic portion of the amine prevents complete solvent orientation around the electron i.e. the amine solution is analogous to that of a mixture of ammonia and a hydrocarbon. The electron is therefore less tightly-solvated i.e. is more mobile and can undergo spin-pairing interactions at lower concentrations.

\(^{111} \) magnetic properties.

In metal-ammonia solutions, electron relaxation proceeds predominantly by a rapid modulation of the
scalar electron-nitrogen hyperfine interactions (see pages 8-10).

There is considerable evidence that the correlation time, $\tau_c$, for this process varies with temperature and solvent in the manner predicted by the Debye theory of molecular rotation in liquids i.e. $\tau_c \propto \tau_D$, where $\tau_D$, the Debye correlation time, is given by,

$$\tau_D = \frac{3\pi \eta}{L_0 k \rho T}$$  \hspace{1cm} (equation 4.18).

(see Forward for definitions of symbols).

Assuming interaction of the unpaired electron with 7 equivalent nitrogen nuclei, the observed ESR line-width (0.02 gauss) led to a value of $\frac{\tau_D}{\tau_c}$ of 10.

Assuming the same value of $\frac{\tau_D}{\tau_c}$ in ethylamine and interaction of the unpaired electron with 5 equivalent nitrogen nuclei, $\tau_c$ was evaluated for metal-ethylamine solutions and related to the observed relaxation rate, $T_{2e}^{-1}$, by equation 1.14., $T_{2e}^{-1}$ being obtained from the line-width at infinite dilution (0.06 gauss). Hence, using equation 1.15,

$$\chi_N n |\psi(0)|^2_N$$ was calculated for the solvated electron in ethylamine and in Table 4.8 is compared with corresponding values obtained for ammonia $^{23}$ and hexamethylphosphoramide (HMPA) $^{62}$ by Knight-shift measurements.

If the unpaired electron were contained solely in an $N(2s)$ orbital then,

$$10^{-24} \chi_N n |\psi(0)|^2_N = 3.4 \times 10^{-22}$$ for a $N(2s)$ orbital.

The unpaired electron, however, must be contained in $N(3s)$ or $N(3s)$ and $N(3p)$ orbitals. Unfortunately, no values of
<table>
<thead>
<tr>
<th>Property</th>
<th>Ammonia</th>
<th>Ethylamine</th>
<th>HMPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{ms}(\infty)$ (gauss)</td>
<td>0.02</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>$10^{-5} \tau_{2e}^{-1}$ (secs)</td>
<td>3.10</td>
<td>9.14</td>
<td>5.35</td>
</tr>
<tr>
<td>$10^{14} \frac{\tau_{c}}{n}$ (secs)</td>
<td>6.9</td>
<td>4.1</td>
<td>830</td>
</tr>
<tr>
<td>$n$</td>
<td>7</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>$10^{12} \tau_{c}$ (secs)</td>
<td>0.483</td>
<td>2.04</td>
<td>16.6</td>
</tr>
<tr>
<td>$10^{12} \tau_{D}$ (secs)</td>
<td>4.80</td>
<td>20.4</td>
<td>750</td>
</tr>
<tr>
<td>$\frac{\tau_{D}}{\tau_{c}}$</td>
<td>10</td>
<td>10†</td>
<td>45</td>
</tr>
<tr>
<td>$10^{-2}/x_{N}n</td>
<td>\psi(0)</td>
<td>^{2}$ (ccs)</td>
<td>6.44</td>
</tr>
<tr>
<td>$x_{N}n_{a}N$</td>
<td>110</td>
<td>73.4</td>
<td>21.4</td>
</tr>
</tbody>
</table>

(Total coupling to nitrogen, in gauss)

† assumed, by analogy with ammonia (see text)
where available for $N(3s)$ but it has been suggested that the value in this case is approximately one-seventh of that for the $N(2s)$ orbital i.e.

$$10^{-24} x_N n |\psi(0)|^2_N \sim 5$$ for a $N(3s)$ orbital.

This value, compared with the corresponding values in Table 4.8, suggests that, in ammonia and ethylamine solutions but not in HMPA solutions, almost all the unpaired electron spin-density is on the nitrogen nucleus. (In metal-HMPA solutions, there is presumably appreciable unpaired electron spin-density on the oxygen nuclei).
CHAPTER 5.

SOLUTIONS OF POTASSIUM IN ETHERS.
INTRODUCTION.

As shown in Chapter 2, metal-ether solutions have been considerably less extensively studied than metal-amine or metal-ammonia solutions. There have been several reports of the optical spectra of such solutions but only one report of a well-resolved ESR signal - a single line for solutions of potassium in tetraglyme.

In the present work, well-resolved ESR signals, displaying hyperfine splitting to the metal nucleus, have been detected for solutions of potassium in tetrahydrofuran, diglyme and triglyme. The resemblance of metal-ether solutions to metal-amine solutions has been established.

EXPERIMENTAL.

Purification of solvents.

Tetrahydrofuran and 1-methyltetrahydrofuran were purified by distillation from calcium hydride and stored either over potassium-benzophenone or over sodium-potassium alloy (1 part sodium: 3 parts potassium, by volume).

Diglyme (diethylene glycol dimethyl ether, \( \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3 \)) was purified by a single distillation from calcium hydride, de-oxygenated with argon and transferred to a vessel containing sodium-potassium alloy. When evolution of hydrogen had ceased and a deep-blue colour formed, the diglyme solution was rapidly transferred to the vacuum line and thoroughly out-gassed prior to solution preparation. In earlier experiments involving diglyme, both alone and in solvent mixtures, the diglyme was used without prior de-oxygenation and contamination by organic radicals frequently resulted, principally by the benzene and biphenyl radical anions.
Preparation of solutions.

Solution preparation was by standard high-vacuum technique, the solvent being condensed on to a thin film of freshly-distilled potassium metal at -78°C. Because of its high boiling-point (161°C at 760 mm) diglyme was distilled from a side-arm directly attached to the vessel in which the solution was to be prepared. A little heat was used, if necessary, to facilitate the distillation.

It was not found possible to use this technique in the preparation of metal-triglyme solutions since triglyme (triethyleneglycol dimethyl ether, \( \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2 \text{OCH}_2\text{CH}_2\text{OCH}_3 \)) has a very high boiling-point (244°C) and could not be conveniently distilled. In this case, samples were prepared in air by pouring the triglyme, purified in the same way as diglyme, on to freshly-prepared sodium-potassium alloy contained in a tube suitable for direct insertion into the microwave cavity of an ESR spectrometer. The tube was then rapidly sealed and a deep-blue colour formed upon brief agitation of the mixture.

In earlier experiments, the same technique was used for the preparation of metal-diglyme solutions but all the results reported in the present work for these solutions were obtained from samples prepared by the standard high-vacuum technique outlined previously. The properties of samples prepared by the two techniques were very similar, though ESR lines were somewhat broader for samples prepared in air, probably due to the presence of excess cations, as has been discussed previously.

Electron spin resonance (ESR)

Details of the ESR equipment have been given in Chapter 4. In the present work, g-factors were
measured by recording the ESR spectrum of the metal solution in a quartz variable-temperature Dewar which displayed a narrow line ( $\Delta H_m = 0.10$ gauss) at $g = 2.0001 \pm 0.0001$, the $g$-factor of this line having been determined using charred dextrose ($g = 2.0023$) as standard.

**Nuclear magnetic resonance (NMR)**

Proton magnetic resonance spectra were recorded, at temperatures from $15^\circ$C to $45^\circ$C, on a Varian Associates A60 spectrometer.

**RESULTS.**

1. **Stability.**

The stability of the pale-blue saturated solutions of potassium in tetrahydrofuran and of the deep-blue saturated solutions of potassium or sodium-potassium alloy in diglyme or triglyme was very good at room-temperature, the solutions decaying with half-lives $\sim 4-6$ hours. For solutions of potassium in methyltetrahydrofuran, however, transient pale-blue colours only were observed.

2. **Optical spectra.**

Optical spectra of potassium-tetrahydrofuran solutions, prepared in pyrex vessels, have generally consisted $^{105,107,110,111}$ of a band at $14,000$ cm$^{-1}$, with varying amounts of a second band at $11,000$ cm$^{-1}$.

In the present work, potassium-tetrahydrofuran samples prepared entirely in quartz vessels exhibited a single broad band ($\gamma_{max} = 11,000$ cm$^{-1}$; $\Delta \gamma \frac{\nu}{\Delta} = 3,500$ cm$^{-1}$) asymmetrically broadened on the high-energy side. No change in the spectrum was observed after several cycles of decay and regeneration. For solutions freshly-prepared in pyrex vessels, overlapping bands at $11,000$ cm$^{-1}$ and $13,800$ cm$^{-1}$ were observed. The
11,000 cm\(^{-1}\) band disappeared after a few hours, leaving only the high-energy band. No band was observed in the near infrared (\(\sim 7,000 - 10,000\) cm\(^{-1}\)) for samples prepared in either pyrex or quartz vessels.

For samples prepared in pyrex and quartz vessels, \(C\), the total concentration of absorbing species in solution, was estimated, as described on page 72, to be \(6 \times 10^{-6}\) and \(4.7 \times 10^{-6}\) moles l\(^{-1}\) respectively.

3. Electron spin resonance spectra.

(1) Tetrahydrofuran.

ESR spectra of solutions of potassium in tetrahydrofuran were markedly dependent upon both temperature (Figure 5.1) and total concentration of absorbing species in solution, \(C\) (Figure 5.2) and showed a close similarity to those reported for potassium-ethylamine solutions in the previous chapter. ESR spectra were identical for solutions prepared in both pyrex and quartz vessels. Freshly-prepared, saturated solutions had ESR spectra consisting of two quartets (\(\Delta H_{ms} = 0.12\) gauss) and a central singlet (\(g = 2.0019 \pm 0.0001, \Delta H_{ms} = 0.12\) gauss).

The relative intensities and the ratio of the splittings for the two quartets conformed closely to those expected for the two naturally-occurring potassium isotopes (Table 5.1). The outer \(m_I = \pm \frac{3}{2}\) lines of the more intense quartet were slightly broader than the inner \(m_I = \pm \frac{1}{2}\) lines, as gauged by their amplitudes. The factor \(\Delta g\), i.e. \(g_{\text{singlet species}} - g_{\text{hyperfine species}}\), was \(0.0010 \pm 0.0001\).

Dilution with pure solvent resulted in a change in the relative intensities of the ESR signals (Figure 5.2) the central singlet becoming narrower (\(\Delta H_{ms} \leq 0.06\) gauss in ~
**Fig 5.1**

ESR spectra of saturated potassium-tetrahydrofuran solutions at (a) 8°C, (b) 25°C, (c) 55°C.

(central portion of ESR spectra only).
Fig 5.2

ESR spectra of solutions of potassium in tetrahydrofuran at room temperature.

(a) saturated solution ($6 \times 10^{-6}$ moles $l^{-1}$)
(b) dilute ($4 \times 10^{-6}$ moles $l^{-1}$); (c) very dilute ($6 \times 10^{-8}$ moles $l^{-1}$).
10^{-8}M solution) and therefore more prominent relative to the hyperfine quartet. No significant changes in g-factors or hyperfine coupling constants were detected, though there was a slight decrease in hyperfine line-widths (Table 5.1).

The spectra showed marked saturation effects, the lines broadening and decreasing in amplitude at high microwave power. The saturation curves (Figures 5.3 and 5.4) were characteristic of homogeneous broadening.

The temperature-dependence of the ESR spectrum was studied from -10°C to +55°C. The $^{39}$K hyperfine splitting constant increased with increasing temperature (Figure 5.5) ($\frac{d\Delta_{iso}}{dT} = 0.123$ gauss / C deg.). The central singlet was less prominent at higher temperatures (Figure 5.1).

Spin-concentrations were measured as described previously (page 70) and are shown in Table 5.1, along with corresponding values of $C$. $\alpha$, the fraction of paramagnetic species, increased from about 0.015 to 0.25 at room temperature, after hundred-fold dilution and also increased with increase in temperature, from approximately 0.006 at 0°C to 0.03 at 65°C.

The ESR and optical properties of potassium-tetrahydrofuran solutions are summarised in Table 5.1, along with those of the corresponding saturated solutions of potassium in ethylamine.

(11) Diglyme.

The spectra obtained were markedly dependent upon total concentration, $C$ (Figure 5.6) and temperature (Figure 5.7). The hyperfine lines were considerably broader than in potassium-tetrahydrofuran solutions ($\Delta H_{ms} \sim 2-3$ gauss) and the $m_I = \pm 3/2$ lines were substantially broader than the $m_I = \pm 1/2$ lines.

Solution decomposition (Figure 5.6)
Saturation plots for the singlet in potassium-tetrahydrofuran solutions.

- o saturated \((6 \times 10^{-6} \text{ moles l}^{-1})\)
- x dilute \((1 \times 10^{-6} \text{ moles l}^{-1})\)
- △ very dilute \((6 \times 10^{-8} \text{ moles l}^{-1})\)
Saturation plots for the monomer in potassium - tetrahydrofuran solutions.

- o saturated ($6 \times 10^{-6}$ moles $l^{-1}$)
- x dilute ($4 \times 10^{-6}$ moles $l^{-1}$)
Temperature-dependence of $A_{\text{iso}}(^{39}\text{K})$ for a solution of potassium in tetrahydrofuran.
Concentration-dependence of ESR spectra of potassium-diglyme solutions. (a) - (e) represents progressive decomposition of the solution i.e. progressive decrease in total metal concentration, C.
ESR spectra of saturated potassium-diglyme solutions at
(a) 10°C  (b) 15°C  (c) 20°C  (d) 30°C
led to a rapid narrowing of the singlet from several gauss in a saturated solution \((C \sim 10^{-3} \text{M})\) to 0.15 gauss in an almost completely-decayed solution \((C \sim 10^{-6} - 10^{-7} \text{M})\). As observed for potassium-ethylamine solutions (page 75), there was an initial increase in the singlet amplitude before ultimate decay. The outer \(m_I = \pm 3/2\) hyperfine lines, however, narrowed by only about 0.5 gauss upon decay.

A large excess of cations, e.g., for samples prepared in air, resulted in a broadening of the hyperfine lines with apparent preferential broadening of those on the high-field side of the centre of the spectrum (Figure 5.8).

The hyperfine splitting constant for potassium-diglyme solutions was considerably lower than that for potassium-tetrahydrofuran solutions, (\(\sim 3.7\) gauss and 29.7 gauss respectively, at room temperature) but was affected by temperature in much the same way (Figure 5.5).

(III) Triglyme.

ESR spectra of potassium-triglyme solutions were rather similar to those of potassium-diglyme solutions but the hyperfine splitting constant in the former case was somewhat lower (\(\sim 3\) gauss). Both singlet and hyperfine lines were even broader in potassium-triglyme solutions than in potassium-diglyme solutions and there was more marked broadening of the high-field lines relative to the low-field lines.

Decay of potassium-triglyme solutions led to a narrowing of the singlet, from several gauss in a saturated solution to 0.3 gauss in almost fully-decayed solutions, with only a slight narrowing of the hyperfine lines.

(IV) 1-methyltetrahydrofuran.

No ESR spectra were detected from solutions of potassium in methyltetrahydrofuran.
Effect of excess potassium cations on ESR spectra.
(a)–(e) represents progressive decomposition of a solution of sodium-potassium alloy in diglyme, (d) a saturated solution of NaK in triglyme.
4. Nuclear magnetic resonance spectra.

(1) diglyme.

The proton magnetic resonance spectra were recorded for saturated solutions of potassium and sodium-potassium alloy in diglyme. No proton Knight shift, \( K(H) \), was detected, presumably due to the low concentration of unpaired electrons in solution.

DISCUSSION.

1. Optical spectra.

The dependence of the optical spectrum upon the material of the vessel in which the metal solution was prepared is very similar to that for potassium-ethylamine solutions and no significant solvent-induced shifts of band positions were detected.

The metal solubility was an order of magnitude less than in ethylamine and, as observed for solutions of potassium in ethylamine, was greater for samples prepared in pyrex vessels than for those prepared in quartz vessels, as expected (see Chapter 4, pages 90-93).

2. ESR spectra.

For potassium-tetrahydrofuran solutions, the presence of \( ^{41}\text{K} \) hyperfine structure demonstrates unequivocally that the hyperfine interaction is always with potassium nuclei and no traces of any sodium splittings were observed in pyrex vessels even when the optical spectra were characteristic of sodium-containing species. This behaviour is similar to that observed for ethylamine solutions, for which hyperfine coupling characteristic of a mixture of both sodium and potassium species was observed only after the addition of 1 to 5 mole percent of ammonia.
Table 5.1

Summary of results obtained for potassium-tetrahydrofuran solutions in pyrex and quartz apparatus (data on the potassium-ethylenamine system are included for comparison.)

<table>
<thead>
<tr>
<th>Item</th>
<th>K-THF(pyrex)</th>
<th>K-EtNH₂(pyrex)</th>
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</thead>
<tbody>
<tr>
<td>( \nu_{\text{max}} ) (cm(^{-1}))</td>
<td>13,800.</td>
<td>14,000</td>
</tr>
<tr>
<td>10(^6) C</td>
<td>6. 6 1 0.06</td>
<td>43</td>
</tr>
<tr>
<td>A((^{39})K)(g)</td>
<td>29.7 29.7 29.7 29.5</td>
<td>9.3</td>
</tr>
<tr>
<td>g(_K)</td>
<td>2.0009 2.0009</td>
<td>2.0014</td>
</tr>
<tr>
<td>g(_e)'</td>
<td>2.0019 2.0019</td>
<td>2.0019</td>
</tr>
<tr>
<td>( \Delta H_K ) (G)</td>
<td>0.125 0.125</td>
<td>0.100 0.37</td>
</tr>
<tr>
<td>( \Delta H_e ) (G)</td>
<td>0.120 0.120</td>
<td>≤ 0.060 0.84</td>
</tr>
<tr>
<td>10(^8) [K]</td>
<td>7.4 8.7 6.1 &lt; 0.5</td>
<td>140</td>
</tr>
<tr>
<td>10(^8) [e(^-)]</td>
<td>1.3 2.0 1.6 1.3</td>
<td>7</td>
</tr>
<tr>
<td>10(^8) ([K] + [e(^-)])</td>
<td>8.7 10.7 7.7 1.3→1.8</td>
<td>147</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.015 0.018 0.08 0.21→0.30</td>
<td>0.034</td>
</tr>
<tr>
<td>(</td>
<td>10(^8) \frac{[e^-]^2}{[K]})</td>
<td>0.22 0.48 0.44 &gt; 2.7</td>
</tr>
<tr>
<td>( \Delta g )</td>
<td>0.0010 0.0010 0.0010</td>
<td>0.0005</td>
</tr>
<tr>
<td>dA/dT</td>
<td>0.123</td>
<td>0.116(C25°C)</td>
</tr>
<tr>
<td>A((^{41})K)(g)</td>
<td>16.2</td>
<td>5.5</td>
</tr>
<tr>
<td>A((^{39})K)/A((^{41})K)</td>
<td>1.83 (1.82)</td>
<td></td>
</tr>
<tr>
<td>100 I((^{41})K)</td>
<td>7.7</td>
<td>7.8</td>
</tr>
<tr>
<td>( \frac{\text{I}((^{41})K)}{\text{I}((^{41})K)+\text{I}((^{39})K)} ) (6.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10(^6)a ( \Delta g/dT )</td>
<td>2.58/Cdeg</td>
<td></td>
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(continued on page 109)
<table>
<thead>
<tr>
<th>Item</th>
<th>( K\text{-THF (quartz)} )</th>
<th>( K\text{-EtNH}_2\text{(quartz)} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>11,000</td>
<td>11,000</td>
</tr>
<tr>
<td>( 10^6 )C</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>( A(39\text{K})(G) )</td>
<td>29.2</td>
<td>29.2</td>
</tr>
<tr>
<td>( e\text{K} )</td>
<td>2.0009</td>
<td>2.0009</td>
</tr>
<tr>
<td>( e\text{e} )</td>
<td>2.0019</td>
<td>2.0019</td>
</tr>
<tr>
<td>( \Delta H_{\text{K}}(0) )</td>
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<td>0.110</td>
</tr>
<tr>
<td>( \Delta H_{\text{e}}(0) )</td>
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<td>0.10</td>
</tr>
<tr>
<td>( 10^8 [\text{K}] )</td>
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<td>7.0</td>
</tr>
<tr>
<td>( 10^8 [\text{e}^-] )</td>
<td>4.14</td>
<td>4.17</td>
</tr>
<tr>
<td>( 10^8 ([\text{K}] + [\text{e}^-]) )</td>
<td>12.9</td>
<td>11.7</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.027</td>
<td>0.025</td>
</tr>
<tr>
<td>( {10^8 \frac{[\text{e}^-]^2}{[\text{K}]}} )</td>
<td>2.29</td>
<td>3.20</td>
</tr>
<tr>
<td>( \Delta g )</td>
<td>0.0010</td>
<td>0.0010</td>
</tr>
<tr>
<td>( \frac{dA}{dT} )</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>( A(41\text{K})(G) )</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>( A(39\text{K})/A(41\text{K}) )</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>( {100 \frac{I(41\text{K})}{I(41\text{K})+I(39\text{K})}} )</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>( 10^6 \frac{d\Delta g}{dT} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All concentrations are in moles l\(^{-1}\).

Theoretical values, where applicable, are given in parentheses.
For potassium-diglyme and potassium-triglyme solutions, the ESR spectra were not such as to render detection of $^{41}$K hyperfine structure possible. Consequently, unequivocal assignment of the hyperfine interaction to potassium nuclei is not possible though it appears likely, by analogy with results for other systems, that this is the origin of the hyperfine splitting observed.


For potassium-tetrahydrofuran solutions, $\alpha$, the fraction of unpaired spins (Table 5.1) is much lower than in ammonia $^{11}(\alpha = 1.0$ for $c < 10^{-3}M)$ or hexamethylphosphoric triamide $^{62}(\alpha = 0.13$ for $c = 7 \times 10^{-2}M)$ but is similar to the values observed for lithium-ethylamine $^{85}(\alpha = 0.01$ for $c = 0.1M)$ and potassium-ethylamine ($\alpha = 0.034$ for $c = 4 \times 10^{-5}M$).

For potassium-diglyme solutions, the value of $c$, the total concentration of species in solution, must be at least an order of magnitude greater than that in tetrahydrofuran, as indicated by the deep-blue colour of the glyme solutions and the solubility data of Cafasso and Sundheim $^{109}$ for monoglyme and tetraglyme which suggests a value of $c$, for potassium-diglyme, of $\sim 4 \times 10^{-3}M$. Since the total concentration of paramagnetic species is only a factor of three or four higher in potassium-diglyme solutions than in potassium-tetrahydrofuran solutions, the values of $\alpha$ must be considerably lower in the former case.

4. Equilibria and line-widths in metal-ether solutions.

Measurements of unpaired electron spin-concentrations in potassium-tetrahydrofuran solutions were considerably more difficult than those in potassium-ethylamine solutions, because the ESR signals were an order of magnitude weaker in the former case, so that measurements were performed
very nearly at the sensitivity limit of the E-3 ESR spectrometer. For this reason, although the trends displayed in Table 5.1 were reproducible, the absolute magnitudes were subject to some error (± 20-25%).

For the application of equations 4.8 and 4.9, however, very precise spin-concentration data is required and consequently poor agreement has been obtained using the present set of data for potassium-tetrahydrofuran solutions and it is not possible to distinguish between two- and three-equilibria schemes for this system.

No rigid quantitative treatment of line-widths is therefore possible but, for both potassium-tetrahydrofuran and potassium-diglyme solutions, it has been found possible accurately to predict the observed concentration broadening of both singlet and hyperfine lines by assuming broadening by the same mechanism as for potassium-ethylamine solutions (page 86) and behaviour analogous to that of potassium-ethylamine solutions at corresponding values of C, with diffusion coefficients related to those in ammonia, adjusted to reflect changes in solvent viscosities.

Thus, for potassium-tetrahydrofuran solutions, \([K^-] = 5.4 \times 10^{-6} \text{M}\) and \(2 [K_2] = 0.45 \times 10^{-6} \text{M}\) so that, at \(c = 6 \times 10^{-6} \text{M}\)

\[
\left( \frac{[K^-]}{[K_2]} \right)_{\text{THF}} = \left( \frac{[K^-]}{[K_2]} \right)_{\text{ethylamine}}
\]

(equation 5.1)

Using diffusion coefficients \(D_e^-\) and \(D_{M+}e^-\) where,

\(D_{e^-}\) \(_{\text{THF}} = \left( D_{e^-}\right)_{\text{NH}_3} = 2.7 \times 10^{-4} \text{cm}^2\text{sec}^{-1}\) (equation 5.2)

and \(D_{M+}e^-\) \(_{\text{THF}} = \left( D_{M+}e^-\right)_{\text{NH}_3} = 0.32 \times 10^{-4} \text{cm}^2\text{sec}^{-1}\) (equation 5.3)

(see pages 89, 90) leads to predicted singlet and hyperfine quartet line-broadening, from very dilute to saturated...
solutions, of 0.065 gauss and 0.031 gauss, to be compared with the experimental values of 0.060 gauss and 0.025 gauss respectively.

For potassium-diglyme solutions, \([K^-] = 2 \left[ K_2 \right] = 2 \times 10^{-3} M\) so that, at \(c = 4 \times 10^{-3} M\),

\[
\left( \frac{[K^-]}{[K_2]} \right)_{\text{diglyme}} = \left( \frac{[K^-]}{[K_2]} \right)_{\text{ethylamine}}
\]  
(equation 5.4).

Using diffusion coefficients \(D_e^-\) and \(D_{M^+e^-}\) where,

\[(D_e^-)_{\text{diglyme}} = 0.5 \ (D_e^-)_{\text{NH}_3} = 1.35 \times 10^{-4} \text{cm}^2 \text{sec}^{-1} \] (equation 5.5)

and

\[(D_{M^+e^-})_{\text{diglyme}} = 0.5 (D_{M^+e^-})_{\text{NH}_3} = 0.16 \times 10^{-4} \text{cm}^2 \text{sec}^{-1} \] (equation 5.6)

leads to predicted singlet and hyperfine line broadening, from very dilute to saturated solutions, of 4.2 gauss and 0.45 gauss, to be compared with the experimental values of 4.5 gauss and 0.5 gauss respectively.

5. The nature of the monomer unit.

There are some important differences between the properties of the monomeric species in ammonia and those of the monomeric species in the solvents studied in the present work e.g.

(1) Hyperfine splitting constants.

The room-temperature value of \(A_{iso}^{(39K)}\) is considerably lower for solutions of potassium in ammonia (0.46 gauss) than for solutions of potassium in triglyme (∼3 gauss), diglyme (3.7 gauss), ethylamine (9.3 gauss) and tetrahydrofuran (29.7 gauss).

(11) \(g\)-shifts.

The factor \(\Delta g\) i.e. \(g_{\text{singlet species}} - g_{\text{monomeric species}}\) is considerably lower for potassium-ammonia solutions
than for potassium-ethylamine (0.0005) and potassium-tetrahydrofuran (0.0010).

(111) **Life-times.**

The life-time of the monomeric unit in metal-ammonia solutions is \( \sim 10^{-12} \) secs., determined \(^2^3\) by measurements of the metal nucleus relaxation rate, \( T_{2M}^{-1} \), compared with the values, obtained from the inverse of the hyperfine coupling constant, of \( 1 \times 10^{-6} \) secs, \( 3 \times 10^{-7} \) secs and \( 1 \times 10^{-7} \) secs, for solutions of potassium in diglyme, ethylamine and tetrahydrofuran respectively.

(1V) **Ion-sizes.**

The ion-size parameter, \( a \), given by equation 1.17, is approximately 50% greater for the \( \text{M}^+\text{e}^- \) unit in ammonia than for the corresponding unit in ethylamine (see page 94).

(V) **Temperature-dependence of the hyperfine splitting constant.**

Recently Catterall \(^{12}\) has shown that the sodium hyperfine splitting constant in sodium-ammonia solutions is temperature-insensitive, in contrast to the behaviour observed for the systems studied in the present work (Figure 5.5).

These observations suggest that the monomeric unit in ammonia has an appreciably different structure from that in the solvents studied in the present work.

In this section, the structure of the monomeric species in ammonia, amine and ether solvents is discussed in terms of different types of ion-pairs \(^{12}\) viz solvent-separated ion-pairs,

\[
\text{S} \quad \text{M}^+ \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{e}^- \quad \text{S} \quad \text{S} \quad \text{S} \\
(\text{1})
\]

solvent-shared ion-pairs,

\[
\text{S} \quad \text{M}^+ \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{e}^- \quad \text{S} \quad \text{S} \\
(\text{11})
\]
and contact ion-pairs,

\[
\begin{array}{ccc}
\text{S} & \text{S} & \text{M}^+ \\
\text{S} & \text{S} & \\
\end{array}
\]

where S represents a solvent molecule.

It is proposed that the monomeric unit in metal-ammonia solutions is best represented as a solvent-separated ion-pair, (I) that in ethylamine, tetrahydrofuran and probably diglyme solutions as a combination of the solvent-shared and contact ion-pairs (II) and (III), the latter being favoured at high temperatures. On this basis, several properties of the monomeric unit in amine and ether solvents can be understood.

A. Hyperfine splitting constants.

The $^{39}$K isotropic hyperfine splitting constant, $A_{iso}^{(39)K}$, is a measure of the unpaired electron spin-density in the K(4s) atomic orbital or of the K(4s)-like character of the molecular orbital containing the unpaired electron, as described in section B. In either case equation 1.10 becomes,

\[
A_{iso}^{(39)K} = \frac{8}{3} e_s e_n \mu_B \mu_n |\psi(0)|^2 \text{K(4s)}
\]

i.e. $A_{iso}^{(39)K} \propto |\psi(0)|^2 \text{K(4s)}$

Since $A_{iso}^{(39)K}$ has been found to be very solvent-dependent, the solvent must modify the cation-electron interaction, presumably by solvation of both species, as indicated in II and III though the stable, concentrated solutions formed in solvents such as ethylenediamine and diglyme, which are known to form chelate complexes with metal ions, suggest that solvation of the cation is the dominant factor, at least in amine and ether solvents.
The solvent can interact with the cation either by acting as a bulk dielectric medium, characterised by dielectric constants $D_S$ and $D_{OP}$, or by involving specific, relatively long-lived interactions between cation and solvent molecules.

In Table 5.2 are contained room-temperature values of $A_{iso}(^{39}_K)$, $D_S$ and $D_{OP}$ (obtained from the square of the refractive index) for several amine and ether solvents.

Table 5.2

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$A_{iso}(^{39}_K)$</th>
<th>$D_S$</th>
<th>$D_{OP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>0.46</td>
<td>16.9</td>
<td></td>
</tr>
<tr>
<td>ethylenediamine</td>
<td>&lt; 1</td>
<td>16.0</td>
<td>2.10</td>
</tr>
<tr>
<td>diglyme</td>
<td>3.7</td>
<td>5.8</td>
<td>1.96</td>
</tr>
<tr>
<td>ethylamine</td>
<td>9.3</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>iso-propylamine</td>
<td>18.4</td>
<td>5.5</td>
<td>1.89</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>29.7</td>
<td>7.3</td>
<td>1.98</td>
</tr>
<tr>
<td>1,4 dioxan</td>
<td>&gt; 30</td>
<td>2.2</td>
<td>2.02</td>
</tr>
</tbody>
</table>

It has not been found possible to obtain satisfactory correlations between $A_{iso}(^{39}_K)$ and any of the factors $\frac{1}{D_S}$, $\frac{1}{D_{OP}}$, $1 - \frac{1}{D_S}$, or $1 - \frac{1}{D_{OP}}$, which suggests that the specific interaction postulate is more realistic, as was tacitly assumed when structures I, II and III were written.

For a good solvator, the cation-solvent interaction is strong and the unpaired electron is forced away from the region of the metal nucleus and $A_{iso}(^{39}_K)$ is low. Thus, comparing solutions of potassium in ethylamine with those in tetrahydrofuran, the basicity of the nitrogen atom is greater than that of the oxygen atom, so that lone-pair donation from the ethylamine into the $K(4s)$ orbital is greater and the unpaired electron spin-density in the $K(4s)$ orbital, $|\psi(0)|^2_{K(4s)}$, is
lower i.e. $A_{\text{iso}}^{39\text{K}}$ is lower. The comparison between the
cation-nitrogen interaction in ethylamine solutions and the
cation-oxygen interactions in a chelating solvent such as
diglyme, is less clear-cut but, from a consideration of the
relevant $A_{\text{iso}}^{39\text{K}}$ values, it is concluded that the effect of
less unfavourable entropy change associated with chelation out-
weighs that of the difference in basicities of the nitrogen
and oxygen. This conclusion is borne out by results obtained
for solutions of potassium in ethylamine-diglyme solvent
mixtures, reported in Chapter 8.

**B. $g$- shifts (a) the solvated electron.**

The $g$- factors for the solvated electron in both potassium-
ethylamine and potassium-tetrahydrofuran solutions ($g_e' = 2.0019
\pm 0.0001$) are shifted from the free-spin position ($g = 2.0023$).
This shift is presumably due to interaction of the unpaired
electron with solvent nuclei. In the case of potassium-
ethylamine solutions, it has previously been demonstrated
(page 99) that the unpaired electron spin-density is predom-
inantly on the nitrogen. For present purposes, therefore, it
is necessary to consider both contact interactions arising from
partial occupancy of the $N(3s)$ orbital and spin-orbit coupling
arising from partial occupancy of the $N(3p)$ orbital set.

1. **Contact interactions: the Overhauser shift of the electron
   resonance position.**

   Whereas the Knight shift, $K(N)$, is the shift in position
   of the magnetic resonance of the nitrogen nucleus, caused by
   unequal population of the two spin-states of the electron, the
   Overhauser shift, $O(N)$, is the corresponding shift in the
   magnetic resonance position of the electron, caused by unequal
   population of the nuclear magnetic states of the nitrogen
   nucleus with which the electron interacts.
From equations 1.5 and 1.10,

$$K(N) = \frac{8\pi}{3} L_0 \frac{S(S+1)}{3kT} (g_e \mu_B)^2 n \left| \psi(0) \right|^2 \frac{2}{N} (\frac{g}{R})$$  \hspace{1cm} \text{(equation 5.8)}

where $K(N)$ represents the Knight shift per mole of nitrogen nuclei.

$O(N)$ is given by,

$$O(N) = \frac{8\pi}{3} L_0 \frac{I(I+1)}{3kT} (g_N \mu_n)^2 n \left| \psi(0) \right|^2 \frac{2}{N}$$  \hspace{1cm} \text{(equation 5.9)}

Thus, since $S = \frac{1}{2}$ and, for $^1\text{H}_N, I = 1$,

$$\frac{K(N)}{O(N)} = -\frac{3}{8} \left( \frac{g_e \mu_B}{g_N \mu_n} \right)^2 \alpha \frac{1}{N}$$  \hspace{1cm} \text{(equation 5.10)}

In the absence of reliable $^1\text{H}_N$ Knight shift data for solutions of potassium in ethylamine, $K(N)$ was calculated from equation 5.8, using the value of $n \left| \psi(0) \right|^2 \frac{2}{N}$ in Table 4.8, and values of $\alpha$ and $R$ appropriate to a saturated solution. Substitution into equation 5.10 led to the conclusion that the shift in $g_{\text{singlet}}$ attributable to electron-nitrogen contact interactions was negligible ($\ll 0.00001$) and, furthermore, was in the wrong sense viz a shift to higher $g$, to explain the observed effect.

(11) \textbf{spin-orbit coupling via solvent nuclei.}

In ammonia or ethylamine solutions, the solvated electron must be contained in a molecular orbital composed of the $N(3S), N(3p)$ and $H(2s)$ atomic orbitals, the $N(2s), N(2p)$ and $H(1s)$ orbitals being involved in the $\sigma^*$ bonding.

The normalised molecular orbital $\psi_e$ can thus be written,

$$\psi_e = C_1 \psi_{N(3S)} + C_2 \psi_{N(3p)} + C_3 \psi_{H(2s)}$$  \hspace{1cm} \text{(equation 5.11)}

If overlap is neglected, the amount of $N(3s)$ involved is $C_1^2$ and the amount of $N(3p)$ involved is $C_2^2$ etc.

From the magnetic properties data on page 98 it was shown
that the unpaired electron spin density was predominantly in the \( N(3s) \) orbital i.e. \( C_4^2 \) is large and a high total hyperfine coupling to nitrogen is averaged by the rapid modulation of the electron-nitrogen scalar interactions.

Since the \( g \)-factor of the singlet is shifted from the free-spin value, \( C_2^2 \) is presumably non-zero. i.e. the unpaired electron in molecular orbital \( \psi_e \) has appreciable \( p \)-character. i.e. the molecular orbital, \( \psi_e \), has behaviour characteristic of that of the \( N(3p) \) atomic orbital set.

Interaction with the unpaired electron induces an asymmetry into the magnetic environment of the nitrogen atom and removes the degeneracy of the \( p \)-orbital set, stabilising the \( p(x) \) and \( p(y) \) orbitals, destabilising the \( p(z) \) orbital, where the \( z \)-axis represents the axis of the electron-nitrogen interaction. The unpaired electron therefore occupies the \( p(x) \) and \( p(y) \) orbitals equally. Application of an external magnetic field leads to a coupling of the \( p(x) \) and \( p(y) \) levels with the higher \( p(z) \) level i.e. a resultant orbital angular momentum which enhances the applied field \( ^{126} \) and causes a negative \( g \)-shift, small because of the low \( N(3p) \)-type character of \( \psi_e \).

(b) the monomer species.

The \( g \)-factors of the monomer species for solutions of potassium in ethylamine and tetrahydrofuran are 2.0014 and 2.0009 respectively i.e. in addition to the negative \( g \)-shift caused by interaction of the unpaired electron with solvent nuclei, there is a further negative \( g \)-shift, \( \Delta g \).

The molecular orbital containing the unpaired electron in the monomer unit, \( \psi_k \), can be written

\[
\psi_k = C_4 \psi_{K(4s)} + C_5 \psi_{K(4p)} + C_6 \psi_{K(3d)} + C_7 \psi_{N(3s)} + C_8 \psi_{N(3p)} \quad (equation ~5.12)
\]
The shift of the $g$-factor of the monomer from free-spin is therefore attributed to appreciable $N(3p)$ and $K(4p)$ character in $\psi_K$. If the former is assumed to produce a shift approximately equal to that for the solvated electron ($0.0004$), then the latter is responsible for the remainder of the shift, $\Delta g$ ($0.0005$ and $0.0010$ for solutions of potassium in ethylamine and tetrahydrofuran respectively). Thus the factor $\Delta g$, which was introduced in previous sections for reasons of experimental ease of measurement, can now be seen to have theoretical importance since it is a measure of the $K(4p)$-like character of the molecular orbital containing the unpaired electron in the monomer unit.

Hyperfine splitting to the metal nucleus is a measure of the $K(4s)$ character of $\psi_K$ which enables an estimate of $C_4^2$ using

$$C_4^2 = \frac{A_{\text{iso}}(39\text{K})}{A_{\text{iso}}(39\text{K})} \text{(free atom)} \times \frac{\text{observed}}{\text{expected}} \text{(equation 5.13)}.\$$

Since $A_{\text{iso}}(39\text{K}) = 82 \pm 38$ gauss, values of $C_4^2$ are $0.11$ and $0.60$ for solutions of potassium in ethylamine and tetrahydrofuran, respectively.

For a given system at different temperatures (Fig 4.6) or different systems at given temperatures, a linear correlation has been observed between $\Delta g$ and $A_{\text{iso}}(39\text{K})$. Since $A_{\text{iso}}(39\text{K})$ and $\Delta g$ are effectively measures of $C_4^2$ and $C_5^2$ (or $C_5^2 + C_6^2$) respectively, it appears that, as the extent of the interaction between the cation and electron changes, there are sympathetic changes in $C_4^2$ and $C_5^2$ i.e. in the $K(4s)$- and $K(4p)$-like behaviour of $\psi_K$.

For changes in solvent, high $A_{\text{iso}}(39\text{K})$ and $\Delta g$ values indicate a strong cation-electron interaction, as for a poor cation-solvator e.g. tetrahydrofuran, whereas low $A_{\text{iso}}(39\text{K})$ and
Δg values indicate a weak cation-electron interaction, as for a good cation-solvator e.g. ammonia, solutions in amine solvents being intermediate in behaviour.

The effect of changes in temperature on cation-electron interactions can be discussed in terms of a continuum or multi-state model for the monomer.

On the basis of a continuum model, for the solvent-shared ion-pair (II), increase in temperature leads to progressive increase in solvent motion so that the solvent molecule S' librates in directions perpendicular to the cation-electron axis i.e. the shielding effect of S' is reduced and the electron-cation interaction increases, so that $λ_{iso}^{(39K)}$ and Δg both increase.

On the basis of a two-state model, a solvent-shared ion-pair (II) is considered to be in rapid equilibrium with a contact ion-pair (III), III having the characteristics of the solvated metal atom (see page 57), and being favoured at high temperatures.

These approaches are clearly related since they both postulate some degree of interchange of e' and S'. Both indicate that the monomeric unit should be smaller at higher temperatures, in contrast with the results for ammonia solutions. This prediction appears to be confirmed by the observation that the singlet is less prominent at higher temperatures, relative to the hyperfine quartet, so that ion-pairing appears to be more important at high temperatures i.e. the ion-size parameter $\mathbf{a}$, in equation 1.17(page 17) is smaller at higher temperatures, changes in $\mathbf{b}$ with temperature being insufficient to explain the observed effect.

Attempts to distinguish experimentally between the continuum-type monomer and the multi-state-type monomer have
not been successful.

One of the obvious methods to observe separate, distinct multi-states, if present, would be to study the solutions at very low temperatures, when interconversion rates are slow. This, however, is not practicable because the concentration of monomeric species falls drastically at low temperatures. A room-temperature ESR experiment, at sufficiently high frequency, would require a magnetic field of about a million gauss. For present purposes, optical spectroscopy is not informative, for reasons discussed previously (page 57).

In principle, the experimental form of the distribution of $\lambda$-values could be elucidated by accurate line-shape analysis. In practice, however, line-shapes cannot be measured sufficiently precisely to enable any distinction to be made.

It is possible that the monomer, $M^+e^-$, could be generated by pulse radiolysis, optical spectra being recorded before further diamagnetic aggregates e.g. $e^-M^+e^-$, $e^-M^+e^-M^+$ formed and dominated the optical spectrum. Baxendale and Rogers pulsed a solution of potassium cations in tetrahydrofuran and observed a strong band at $11,000 \text{ cm}^{-1}$ in $10^{-6} \text{ secs}$. This band, on the basis of the present work, is probably due to diamagnetic species. In a faster experiment ($\sim 10^{-12} \text{ secs}$) it may be possible to observe an initial infrared band, due to $e^-$ solv, followed by a decay of this band and a growth in the band due to $(M^+e^-)_{\text{solv}}$, wherever it occurs, with a final growth in the band(s) due to $M^-_{\text{solv}}$ and $M^+M^-_{\text{solv}}$.

In the present work, the structure of the monomer has been probed by using solvent mixtures in which one of the components of the mixture would preferentially solvate the cation. The results obtained are presented in the following chapters.
CHAPTER 6.

SOLUTIONS OF POTASSIUM IN ETHYLAMINE-

TETRAHYDROFURAN SOLVENT MIXTURES.
There have been several studies, both by optical and ESR spectroscopy, of solutions of potassium in mixed solvents, principally in ammonia - amine \(15,73,83\) or amine-amine \(65,72\) solvent mixtures.

Although the ESR spectra of solutions of potassium in ethylamine-dioxan solvent mixtures have been studied \(117\), the metal was found to be soluble only if less than 40 mole percent of dioxan were present in the solvent mixture. The present study is the first amine-ether solvent mixture accessible to study at all solvent compositions and provides an important contrast to the solutions of potassium in solvent mixtures containing a chelating solvent, results for which are reported in Chapters 7, 8 and 9.

EXPERIMENTAL.

Purification of the tetrahydrofuran and ethylamine has been described in chapters 4 and 5 respectively.

Solution preparation was by standard high-vacuum technique, in pyrex vessels, the solvents being successively condensed on to a thin film of potassium metal at \(-78^\circ C\), all volumes being measured at \(0^\circ C\).

All ESR spectra were recorded on an E-3 spectrometer (see page 70), \(g\)-factors being measured as described in Chapter 5.

RESULTS.

1. Hyperfine splitting constants \(a\) dependence upon solvent composition.

The \(39K\) and \(41K\) isotropic hyperfine splitting constants increased in similar manner as the mole fraction of tetrahydrofuran in the solvent mixture increased (Fig. 6.1). A
hyperfine splitting constant (gauss).

Variation of $A_{1\text{so}} ({}^{39}\text{K})(x)$ and $A_{1\text{so}} ({}^{41}\text{K})(o)$ with solvent composition for solutions of potassium in ethylamine-tetrahydrofuran mixed solvents.

Fig 6.1
124.

relatively slow initial increase, up to approximately 0.6 mole fraction of tetrahydrofuran, was followed by a rapid increase towards the values in pure tetrahydrofuran.

(b) temperature-dependence.

The variation with temperature of the $^{39}\text{K}$ hyperfine splitting constant, $A_{\text{iso}}(^{39}\text{K})$, is shown for solutions of potassium in a series of ethylamine-tetrahydrofuran solvent mixtures. Solutions of potassium in the pure solvents, tetrahydrofuran and ethylamine, had approximately equal temperature coefficients for $A_{\text{iso}}(^{39}\text{K})$ (0.123 and 0.116 gauss/C deg., respectively, at 25°C). In solvent mixtures, however, temperature coefficients were greater than those in either pure solvent, being a maximum (0.199 gauss/C deg. at 25°C) for the solvent mixture containing 0.2 mole fraction of ethylamine. This maximum is clearly shown in Figure 6.3 where the temperature coefficient at 25°C, \( \left(\frac{dA_{\text{iso}}}{dT}\right)_{25^\circ C} \), is plotted as a function of the mole fraction of ethylamine in the solvent mixture.

2. g-factors (a) dependence upon solvent composition.

The dependence of $g_e'$ and $g_M$, the g-factors of the singlet and monomer species respectively, upon solvent composition is shown in Figure 6.4. Within experimental error, $g_e'$ was independent of solvent composition ($g_e' = 2.0019 \pm 0.0002$) whereas $g_M$, corrected to second order, fell as the mole fraction of tetrahydrofuran increased, though there appeared to be a region of insensitivity to changes in solvent composition, for solutions containing 0.3 to 0.8 mole fraction of tetrahydrofuran.

In Figure 6.5, the factor $g_e' - g_M$ i.e. $\Delta g$, has been plotted
Figure 6.2.

Temperature-dependence of the $^{39}\text{K}$ hyperfine splitting constant for solutions of potassium in ethylamine-tetrahydrofuran (THF) mixed solvents containing 1.0 (o), 0.8 (x), 0.56 (+), 0.31 (□) and 0.0 (Δ) mole fraction of THF.
Variation of the temperature coefficient of $A_{iso}^{(39K)}$, at $25^\circ C$, with change in solvent composition for solutions of potassium in ethylamine-tetrahydrofuran mixed solvents.
Dependence of $g^o(0)$ and $g^M(x)$ upon solvent composition for solutions of potassium in ethylamine-tetrahydrofuran solvent mixtures.
Fig. 6.5

Plot of $\Delta g$ (i.e. $g_e^f - g_M$) against $A_{iso}(^{39}K)$ for solutions of potassium in pure ethylamine ($x$ - present work; □ - reference 117), ethylamine - THF mixtures (⊕), THF - diglyme mixtures (o) and ethylamine-ethylenediamine mixtures (△).
against $A_{iso}(^{39}K)$ for the present system. Corresponding data for solutions of potassium in ethylamine (Figure 4.6), tetrahydrofuran - diglyme solvent mixtures (Chapter 7) and ethylamine-ethylenediamine solvent mixtures (Chapter 9) have been included for comparison.

(b) temperature-dependence.

Results for the temperature-dependence of $g'_e$ and $g'_M$ are summarised in Table 6.1, for several ethylamine-tetrahydrofuran solvent mixtures. Over the relatively-narrow range of temperatures which could be studied without seriously affecting the solvent composition, both $g'_e$ and $g'_M$ were insensitive to changes in temperature.

3. line-widths (a) dependence upon solvent composition.

(1) the $^{39}K$ hyperfine quartet.

The line-widths of the $m_I = -\frac{3}{2}$ and $m_I = -\frac{1}{2}$ lines of the hyperfine quartet were equal at any given solvent composition. There was a decrease as the mole fraction of tetrahydrofuran increased, from 0.35 gauss in pure ethylamine to 0.12 gauss in pure tetrahydrofuran (Figure 6.6).

(11) the singlet.

In saturated solutions, the singlet line-width was markedly dependent upon solvent composition, decreasing from 0.84 gauss in pure ethylamine to 0.12 gauss in pure tetrahydrofuran, with a resulting increase in relative singlet intensity. In almost completely-decayed solutions, however, the singlet line-width was independent of solvent composition. These effects are shown in Figure 6.6.

(b) dependence upon metal concentration.

In ethylamine-rich solvent mixtures, a marked narrowing of the singlet
Dependence upon solvent composition of singlet (+) and monomer (o) line-widths in saturated solutions and of singlet (Δ) line-widths in decayed solutions, for solutions of potassium in ethylamine-THF solvent mixtures.
Table 6.1
$\varepsilon'_0$, $\varepsilon_M$ and $\Delta \varepsilon$ values for solutions of potassium in ethylamine-tetrahydrofuran solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of ethylamine</th>
<th>temp. ($^\circ$C)</th>
<th>$A_{iso}^{(39)K}$ ( gaussa)</th>
<th>$\varepsilon'_0$</th>
<th>$\varepsilon_M$</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>29.7</td>
<td>2.0019</td>
<td>2.0009</td>
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<td>2.00112</td>
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<td>8.6</td>
<td>2.00192</td>
<td>2.00122</td>
<td>0.00070</td>
</tr>
<tr>
<td></td>
<td>13</td>
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<td>2.00180</td>
<td>2.00115</td>
<td>0.00065</td>
</tr>
<tr>
<td></td>
<td>29</td>
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<td>2.00177</td>
<td>2.00104</td>
<td>0.00073</td>
</tr>
<tr>
<td>1.0</td>
<td>-7</td>
<td>6.5</td>
<td>-</td>
<td>-</td>
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<td>35</td>
<td>11.3</td>
<td>-</td>
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</tbody>
</table>

Table 6.2. mole fraction of ethylamine, $10^6$ $10^8[K]$ $10^8[e^-]$ $10^8([K]+[e^-])$ $\alpha$

<table>
<thead>
<tr>
<th>mole fraction of ethylamine</th>
<th>$10^6$</th>
<th>$10^8[K]$</th>
<th>$10^8[e^-]$</th>
<th>$10^8([K]+[e^-])$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6</td>
<td>7.4</td>
<td>1.3</td>
<td>8.7</td>
<td>0.014</td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
<td>61.0</td>
<td>4.8</td>
<td>65.8</td>
<td>-</td>
</tr>
<tr>
<td>0.44</td>
<td>-</td>
<td>105.3</td>
<td>4.6</td>
<td>109.9</td>
<td>-</td>
</tr>
<tr>
<td>0.69</td>
<td>-</td>
<td>123.0</td>
<td>7.0</td>
<td>130.0</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>43</td>
<td>141</td>
<td>6.8</td>
<td>147.8</td>
<td>0.034</td>
</tr>
</tbody>
</table>

(all concentrations are in moles 1$^{-1}$)
and a slight narrowing of the lines of the hyperfine quartet were observed as solutions decayed, i.e., as the overall concentration of species in solution decreased. (see Figure 6.6).

4. Spin-concentrations.

Values of \([K], [e^-], \) and \([K] + [e^-]\), where \([K]\) and \([e^-]\) represent the unpaired spin-concentrations associated with monomer (hyperfine) and solvated electron (singlet) species respectively, are contained in Table 6.2 and show a trend in properties between those of the pure solvents.

DISCUSSION.

1. Effect of solvent composition.

Solutions of potassium in the solvent mixtures show steady trends in hyperfine splitting constants, unpaired electron spin-concentrations and line-widths, for both saturated and partially-decayed solutions, between the values for solutions of potassium in the pure solvents. There was marked preferential solvation by the ethylamine, as will be discussed in Chapter 10.

It has been observed (Figure 6.5) that the plot of \(\Delta g\) against \(A_{iso}(^{39}K)\) led to two separate and distinct lines, an "ether" line and an "amine" line such that, at any given \(A_{iso}(^{39}K)\) value, \(\Delta g\) was less for the ether than for the amine. The results for the present system are therefore of interest in that, as the mole fraction of tetrahydrofuran increases, they show a transition in behaviour from that characteristic of a metal-amine solution (0.0 - 0.3 mole fraction of tetrahydrofuran) to that characteristic of a metal-ether solution (0.8 - 1.0 mole fraction of tetrahydrofuran). This explains the observed insensitivity of both \(g_M\) and \(\Delta g\) to changes in solvent composition for solvent mixtures containing
0·3 to 0·8 mole fraction of tetrahydrofuran.

Since the temperature-dependence of $g_M$ and $\Delta g$ was studied for such mixtures (Table 6.1), the observed insensitivity of these factors to changes in temperature is also thus rationalized.

In conclusion, with the exception of $\frac{dA_{iso}(^{39}\text{K})}{dT}$ (which will be discussed in Chapter 10), the observed properties of $K_{solv}$ for solutions of potassium in ethylamine-tetrahydrofuran solvent mixtures are such as would be expected from the corresponding properties of solutions of potassium in the pure solvents. This is not surprising since it has been suggested, in Chapter 5, that the nature of $K_{solv}$ is not greatly changed between the two solvents, there being a change in $A_{iso}(^{39}\text{K})$ due to differing basicities of the nitrogen and oxygen atoms but no dramatic change in the life-time of the cation-solvent interaction, so that replacement of a tetrahydrofuran solvating molecule by an ethylamine molecule, or vice versa, causes a slight modification of the structure of $K_{solv}$, rather than any fundamental change.
CHAPTER 7.

SOLUTIONS OF POTASSIUM IN TETRAHYDROFURAN-

DIGLYME SOLVENT MIXTURES.
INTRODUCTION.

The present study, of solutions of potassium in tetrahydrofuran-diglyme mixed solvents, is the first study, either by ESR or optical spectroscopy, of solutions of an alkali metal in an ether-ether mixed solvent and is of particular interest in view of the marked difference between the two pure solvents as regards solvation of the cation, a difference which has been discussed in Chapter 5.

EXPERIMENTAL.

All sample preparation was by standard high-vacuum technique, the solvents, purified as described in Chapter 5, being successively condensed on to a thin film of potassium at \(-78^\circ\text{C}\).

RESULTS.

1. Hyperfine splitting constants (a) dependence upon solvent composition.

The ESR spectra obtained were markedly dependent upon solvent composition (Figure 7.1). At room temperature, there was an initial rapid decrease in the $^{39}K$ hyperfine splitting constant, $A_{\text{iso}}(^{39}K)$, as the proportion of diglyme in the solvent mixture increased, from 29.7 gauss in pure tetrahydrofuran to 13.9 gauss in the solvent mixture containing 0.2 mole fraction of diglyme (Figure 7.2). Thereafter, the decrease in $A_{\text{iso}}(^{39}K)$ with added diglyme was slower, with the value approaching that for potassium in pure diglyme ($\sim 3.7$ gauss).

(b) temperature-dependence.

$A_{\text{iso}}(^{39}K)$ was very temperature-dependent, as shown in Figure 7.3 where its variation with temperature is shown for several tetrahydrofuran-
Room-temperature ESR spectra of solutions of potassium in THF-diglyme solvent mixtures containing (a) 0.01 (b) 0.10 and (c) 0.50 mole fraction of diglyme, (corresponding spectra for solutions of potassium in pure THF and diglyme are shown in Figs. 5.2 (a) and 5.6 (a) respectively).
$A_{iso}(^{39}K)$ (gauss).

Fig. 7.2

Variation of $A_{iso}(^{39}K)$ with solvent composition for solutions of potassium in THF - diglyme solvent mixtures, at 5°C (□), 25°C (o) and 40°C (x).
Variation of $A_{\text{iso}}^{39K}$ with temperature for solutions of potassium in THF-diglyme solvent mixtures containing 0.0 (o), 0.01 (□), 0.05 (+), 0.10 (Δ), 0.15 (x), 0.25 (▽), 0.50 (⊗), 0.75 (<), and 1.0 (◇) mole fraction of diglyme.
diglyme solutions. Solutions of potassium in the pure solvents, tetrahydrofuran and diglyme, had similar temperature coefficients for $A_{iso}^{(39K)}(0.123$ and 0.160 gauss/C deg, respectively, at $25^\circ C$). In solvent mixtures, however, the temperature coefficients were greater than those in either pure solvent, being a maximum ($0.304$ gauss/C deg at $25^\circ C$) for the solution containing 0.2 mole fraction of diglyme. This maximum is clearly shown in Figure 7.4, where the temperature coefficient, $\frac{dA_{iso}}{dT}$, at $25^\circ C$, has been plotted against diglyme concentration.

2. g-factors (a) dependence upon solvent composition.

The variation of the g-factors of the singlet ($g'_e$) and hyperfine quartet ($g_M$) with diglyme concentration is shown in Figure 7.5. Within experimental error, there was no apparent change in $g'_e(2.0020 \pm 0.0002)$ but, as the proportion of diglyme in the solvent mixture increased, there was an initial rapid increase, followed by a slower increase, in $g_M$, from $2.0009 \pm 0.0002$ in pure tetrahydrofuran to $2.0018 \pm 0.0002$ in a mixture containing 0.5 mole fraction of diglyme. In Figure 6.5, $\Delta g (g'_e-g_M)$ was plotted against $A_{iso}^{(39K)}$ together with data for other systems studied. The contrast between the behaviour of amine and ether solvents on such a plot was noted in the previous chapter.

(b) temperature-dependence.

Results for the variation of g-factors with temperature, for several tetrahydrofuran-diglyme mixtures, are summarised in Table 7.1. For a given solvent mixture, $\Delta g$ appeared to increase with increasing temperature i.e. with increase in $A_{iso}^{(39K)}$, which is similar behaviour to that observed for change in solvent composition at a given temperature.
Variation of the temperature coefficient of $A_{180}^{(39)K}$, at 25°C, with change in solvent composition for solutions of potassium in THF-diglyme solvent mixtures.

Fig. 7.4
Variation of $g_e(x)$ and $g_M(o)$ with change in solvent composition for solutions of potassium in THF - diglyme solvent mixtures.
### TABLE 7.1

$g'_e$, $g_m$ and $\Delta g$ values for solutions of potassium in tetrahydrofuran-diglyme solvent mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of diglyme (mole fraction)</th>
<th>Temp (°C)</th>
<th>$A_{iso}^{(39K)}$ (gauss)</th>
<th>$g'_e$</th>
<th>$g_m$</th>
<th>$\Delta g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23</td>
<td>29.7</td>
<td>2.0019</td>
<td>2.0009</td>
<td>0.00100</td>
</tr>
<tr>
<td>0.01</td>
<td>23</td>
<td>27.1</td>
<td>2.00224</td>
<td>2.00152</td>
<td>0.00072</td>
</tr>
<tr>
<td>0.05</td>
<td>17</td>
<td>20.6</td>
<td>2.00214</td>
<td>2.00146</td>
<td>0.00068</td>
</tr>
<tr>
<td>0.10</td>
<td>22</td>
<td>21.7</td>
<td>2.00220</td>
<td>2.00152</td>
<td>0.00068</td>
</tr>
<tr>
<td>0.15</td>
<td>27</td>
<td>23.1</td>
<td>2.00204</td>
<td>2.00135</td>
<td>0.00069</td>
</tr>
<tr>
<td>0.20</td>
<td>32</td>
<td>23.0</td>
<td>2.00224</td>
<td>2.00151</td>
<td>0.00073</td>
</tr>
<tr>
<td>0.25</td>
<td>3.5</td>
<td>13.1</td>
<td>2.00220</td>
<td>2.00170</td>
<td>0.00050</td>
</tr>
<tr>
<td>0.30</td>
<td>10</td>
<td>10.8</td>
<td>2.00210</td>
<td>2.00165</td>
<td>0.00045</td>
</tr>
<tr>
<td>0.35</td>
<td>15</td>
<td>12.1</td>
<td>2.00220</td>
<td>2.00170</td>
<td>0.00050</td>
</tr>
<tr>
<td>0.40</td>
<td>20</td>
<td>13.8</td>
<td>2.00220</td>
<td>2.00170</td>
<td>0.00050</td>
</tr>
<tr>
<td>0.45</td>
<td>25</td>
<td>15.6</td>
<td>2.00200</td>
<td>2.00165</td>
<td>0.00055</td>
</tr>
<tr>
<td>0.50</td>
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<td>2.00216</td>
<td>2.00157</td>
<td>0.00059</td>
</tr>
<tr>
<td>0.55</td>
<td>35</td>
<td>18.4</td>
<td>2.00205</td>
<td>2.00147</td>
<td>0.00058</td>
</tr>
<tr>
<td>0.60</td>
<td>40</td>
<td>19.4</td>
<td>2.00225</td>
<td>2.00161</td>
<td>0.00064</td>
</tr>
<tr>
<td>0.65</td>
<td>17.5</td>
<td>10.2</td>
<td>2.00222</td>
<td>2.00178</td>
<td>0.00044</td>
</tr>
<tr>
<td>0.70</td>
<td>22.5</td>
<td>11.9</td>
<td>2.00205</td>
<td>2.00159</td>
<td>0.00046</td>
</tr>
<tr>
<td>0.75</td>
<td>13.5</td>
<td>5.2</td>
<td>2.00220</td>
<td>2.00196</td>
<td>0.00024</td>
</tr>
<tr>
<td>0.80</td>
<td>18.5</td>
<td>6.5</td>
<td>2.00224</td>
<td>2.00203</td>
<td>0.00021</td>
</tr>
</tbody>
</table>
3. Line-widths (a) dependence upon solvent composition.

(1) the $^{39}\text{K}$ hyperfine quartet.

The natural line-widths of the $^{39}\text{K}$ hyperfine quartet, measured at low power and modulation, initially increased rapidly as the concentration of diglyme in the solution increased (Figure 7.6). The line-width of the $m_I = -\frac{3}{2}$ line passed through a maximum, of approximately 4 gauss, at 0.2 mole fraction of diglyme. For solutions containing more than 0.9 mole fraction of diglyme, the $A_{\text{iso}}(^{39}\text{K})$ value was so low ($\sim 4$ gauss) that severe overlapping of lines occurred and line-widths could not be measured with any certainty. The marked selective broadening of the outer ($m_I = \pm \frac{3}{2}$) lines of the $^{39}\text{K}$ hyperfine quartet resulted in marked differences in amplitudes of the corresponding ESR derivative traces and, in Figure 7.7, the ratio amplitude of $m_I = -\frac{1}{2}$ line (narrow), hereafter referred amplitude of $m_I = -\frac{3}{2}$ line (broad)

to as $\frac{A_N}{A_B}$, is shown to vary dramatically with solvent composition, being a maximum ($\sim 10$) for the solution containing 0.2 mole fraction of diglyme. As shown in Figure 7.7, the values of $\frac{A_N}{A_B}$ observed directly were in fair agreement with those calculated from the natural line-widths plotted in Figure 7.6.

(11) the $^{41}\text{K}$ hyperfine quartet.

Owing to the decrease in intensity, natural line-widths of the $^{41}\text{K}$ hyperfine quartet were considerably more difficult to measure than those of the $^{39}\text{K}$ hyperfine quartet. Measurements were performed only on solutions containing 0.01 mole fraction of diglyme, for which broadening of the $^{41}\text{K}$ hyperfine quartet was not so drastic as to render detection impossible. The results
Solvent-dependence of $\Delta H_{ms} (-\frac{3}{2})_{obs, o}$ and $\Delta H(-\frac{1}{2})_{obs, x}$ for lines of the $^{39}$X hyperfine quartet in potassium/THF-diglyme solutions.
Solvent-dependence, for solutions of potassium in THF-diglyme solvent mixtures, of $\frac{A_N}{A_B}$, both measured directly (□) and calculated from the line-widths in Fig 7.6 (+)
are summarised in Table 7.2 in which are also included results for the $^{39}\text{K}$ hyperfine quartet for comparative purposes. It can be seen that the broadening of the $m_I = -\frac{3}{2}$ line, relative to the $m_I = -\frac{1}{2}$ line, was considerably less marked for the lines of the $^{41}\text{K}$ hyperfine quartet than for those of the $^{39}\text{K}$ hyperfine quartet and the factor $\frac{A_N}{A_B}$ was consequently appreciably lower in the former case. This is to be compared with the behaviour of the $^{41}\text{K}$ hyperfine splitting constant, whose solvent- and temperature-dependence closely paralleled those of the $^{39}\text{K}$ hyperfine splitting constant up to 0.09 mole fraction of diglyme, beyond which $^{41}\text{K}$ lines were not detected.

(111) the singlet - saturated solutions.

The effect of increasing diglyme concentration was to cause a rapid initial increase in the singlet line-width, from 0.12 gauss in pure tetrahydrofuran to approximately 1.6 gauss in a solution containing 0.2 mole fraction of diglyme (Figure 7.8). Further increase in diglyme concentration led to a slower increase in the singlet line-width, though the behaviour was complicated by overlap of the singlet with the $+\frac{1}{2}$ lines of the $^{39}\text{K}$ hyperfine quartet. At concentrations of diglyme greater than 0.5 mole fraction, the singlet in saturated solutions was no longer resolved as a separate line. (see Figure 7.1)

- decayed solutions.

Decay of saturated solutions of potassium in tetrahydrofuran-diglyme mixed solvents led to rapid narrowing of the singlet (Figure 7.9) with initial increase in singlet amplitude prior to final decay. As shown in Figure 7.8, the singlet narrowed ultimately to a
Dependence of singlet line-width upon solvent composition for saturated (o) and decayed (x) solutions of potassium in THF-diglyme solvent mixtures. The dashed line represents the change in viscosity with change in solvent composition.
Fig 7.9

Changes in singlet line-width with decay of saturated solutions of potassium in diglyme - THF solvent mixtures containing 0.1 (o), 0.7 (x) and 1.0 (Δ) mole fraction of diglyme.
Table 7.2
Comparison of the $^{39}_K$ and $^{41}_K$ hyperfine quartets for a solution of potassium in a 0.01 mole fraction diglyme-tetrahydrofuran solvent mixture.

<table>
<thead>
<tr>
<th>$^{39}_K$ hyperfine quartet.</th>
<th>$^{41}_K$ hyperfine quartet.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{iso}$ (gauss)</td>
<td>28.1</td>
</tr>
<tr>
<td>$\Delta H\left(-\frac{3}{2}\right)_{obs}$ (gauss)</td>
<td>0.70</td>
</tr>
<tr>
<td>$\Delta H\left(-\frac{1}{2}\right)_{obs}$ (gauss)</td>
<td>0.37</td>
</tr>
<tr>
<td>$\frac{A_N}{A_B}$</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 7.3
Spin-count data for solutions of potassium in tetrahydrofuran-diglyme solvent mixtures.

<table>
<thead>
<tr>
<th>Mole fraction of diglyme</th>
<th>$10^7$s (s=total spin-concentration, in moles l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.92</td>
</tr>
<tr>
<td>0.15</td>
<td>1.01</td>
</tr>
<tr>
<td>0.25</td>
<td>1.10</td>
</tr>
<tr>
<td>0.50</td>
<td>1.36</td>
</tr>
<tr>
<td>0.75</td>
<td>1.26</td>
</tr>
<tr>
<td>1.00</td>
<td>1.61</td>
</tr>
</tbody>
</table>
limit determined by the viscosity of the solvent mixture, so that the change in singlet line-width, in decayed solutions, between pure tetrahydrofuran and diglyme, closely followed the viscosity change between the two pure solvents.

(b) microwave power saturation.

Monomer and singlet lines, in solutions containing 0.01 and 0.09 mole fraction of diglyme, were tested for microwave power saturation up to 50 milli-watts. Lines were much broader than in pure tetrahydrofuran and in no case was departure from linearity observed in the plot of amplitude of the ESR derivative line against (microwave power)².

(c) temperature-dependence.

Although no absolute measurements of variation of line-widths with temperature were made, the variation of \( \frac{A_N}{A_B} \) with temperature was studied for two solutions, viz those containing 0.01 and 0.25 mole fraction of diglyme. The results are shown in Figures 7.10(a) and (b) from which it can be seen that, for the solution containing 0.01 mole fraction of diglyme, \( \frac{A_N}{A_B} \) fell steadily as the temperature increased, whilst for the solution containing 0.25 mole fraction of diglyme, there was a maximum in the plot at 20°C. Below this temperature, \( \frac{A_N}{A_B} \) increased with increasing temperature; above 20°C, it fell steadily with increasing temperature, as for the solution containing 0.01 mole fraction of diglyme.

4. Spin concentrations.

As shown in Table 7.3, spin-concentrations increased very little as the mole fraction of diglyme in the
Temperature-dependence of $\frac{A_N}{A_B}$ for a solution of potassium in a THF - 0.01 mole fraction of diglyme solvent mixture, at 3 different modulation ratios viz $2 (o)$, $1 (x)$ and $\frac{1}{2} (\Delta)$.

$\Delta H_{ms}(-\frac{1}{2})_{obs}$
Temperature-dependence of $\frac{A_N}{A_B}$ for a solution of potassium in a THF - 0.25 mole fraction of diglyme solvent mixture, at 3 different modulation ratios viz. 2 (o), 1 (x) and $\frac{1}{2}$ (△).
solvent mixture increased. No quantitative data on the variation of spin-concentrations with temperature was obtained, but presumably the fraction of paramagnetic species in solution, $\alpha$, increased with increasing temperature, since a marked improvement in the signal-to-noise ratio was observed at higher temperatures.

**DISCUSSION.**

1. Application of a two-state model to the dependence upon solvent composition of the nature of $K_{solv}$.

The concept of the multi-state model was introduced in Chapter 2 (page 53). For the present system, it is convenient to employ a two-state model, with a "tetrahydrofuran-like" species (A) rapidly interchanging with a "diglyme-like" species (B). On this basis, any observed property of the monomer, $X_{\text{obs}}$, can be written as,

$$X_{\text{obs}} = P_A X_A + P_B X_B$$  \hspace{1cm} (equation 7.1).

where $P_A$ and $P_B$ represent the fractions of A and B; $X_A$ and $X_B$ represent the values of $X$ for A and B.

Since $P_A + P_B = 1$,

$$P_A = \frac{X_{\text{obs}} - X_B}{X_A - X_B}$$  \hspace{1cm} (equation 7.2).

and hence both $P_A$ and $P_B$ can be determined for any given value of $X_{\text{obs}}$, if $X_A$ and $X_B$ are known.

(a) **Hyperfine splitting constants.**

The values of $P_A$ and $P_B$ calculated using $A_A = 29.7$ gauss, $A_B = 3.7$ gauss are shown in Table 7.4 and plotted in Figure 7.11 as a function of diglyme concentration.
Values of $P_A$ and $P_B$ calculated using $\Delta g_A = 0.0010$ and $\Delta g_B = 0$ are plotted in Figure 7.11 and can be seen to be in good agreement with those calculated in (a), which suggests that the assumption $\Delta g_B = 0$ is good, the singlet and hyperfine quartet not being observed separately for solutions of potassium in pure diglyme.

(c) line-widths of the hyperfine quartet.

The observed line-width of a particular component of the hyperfine quartet, $\Delta H(m_I)_\text{obs}$, can be split into two terms; an $m_I$-dependent exchange contribution, $\Delta H(m_I)$, arising from the $A \leftrightarrow B$ exchange (see pages 53-55) and a residual, $m_I$-independent line-width, $\Delta H(0)$.

\[ \Delta H(m_I)_{\text{obs}} = \Delta H(0) + \Delta H(m_I) \]  

(equation 7.3).

Simple two-state theory leads to the equation

\[ [T_2(m_I)]^{-1} = p_A^2 p_B^2 m_I^2 (A_A - A_B)^2 (T_A + T_B) \]  

(equation 7.4).

(see page 54 for definitions of symbols)

or

\[ [T_2(m_I)]^{-1} = p_A^2 (p_A^2 + p_B^2) m_I^2 (A_A - A_B)^2 T_B \]  

(equation 7.5).

So that, for a given solvent composition,

\[ \Delta H(m_I) \propto [T_2(m_I)]^{-1} \propto m_I^2 \]

i.e.

\[ \frac{\Delta H(-\frac{3}{2})}{\Delta H(-\frac{1}{2})} = (\frac{3}{2})^2 = 9 \]  

(equation 7.6).

Using the values of $\Delta H(-\frac{3}{2})_{\text{obs}}$ and $\Delta H(-\frac{3}{2})_{\text{obs}}$ in Figure 7.6, with values of $\Delta H(0)$ obtained at different solvent compositions by extrapolation to $m_I^2 = 0$ of the $\Delta H(m_I)_{\text{obs}}$ vs.
Fig. 7.11
Variation of $P_A$ and $P_B$ with change in solvent composition for solutions of potassium in THF - diglyme solvent mixtures.

(a) $P_A$ calculated from $^{39}\text{K}$ hyperfine splitting constants (o), residual line-widths (□) and $\Delta g$ values (△).

(b) $P_B$ calculated from $^{39}\text{K}$ hyperfine splitting constants (x), residual line-widths (+) and $\Delta g$ values (▽).
Table 7.4

$P_A$ and $P_B$ values calculated by the application of a two-state model to the $A$-values, $\Delta g$ and residual line-widths, for solutions of potassium in tetrahydrofuran-diglyme solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of diglyme</th>
<th>$A$-values</th>
<th>$\Delta g$</th>
<th>$\Delta H(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_A$</td>
<td>$P_B$</td>
<td>$P_A$</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.01</td>
<td>0.913</td>
<td>0.087</td>
<td>0.821</td>
</tr>
<tr>
<td>0.05</td>
<td>0.728</td>
<td>0.272</td>
<td>0.684</td>
</tr>
<tr>
<td>0.10</td>
<td>0.575</td>
<td>0.425</td>
<td>0.560</td>
</tr>
<tr>
<td>0.15</td>
<td>0.512</td>
<td>0.488</td>
<td>0.513</td>
</tr>
<tr>
<td>0.20</td>
<td></td>
<td>0.411</td>
<td>0.589</td>
</tr>
<tr>
<td>0.25</td>
<td>0.335</td>
<td>0.665</td>
<td>0.360</td>
</tr>
<tr>
<td>0.30</td>
<td></td>
<td>0.322</td>
<td>0.678</td>
</tr>
<tr>
<td>0.35</td>
<td>0.232</td>
<td>0.768</td>
<td>0.288</td>
</tr>
<tr>
<td>0.40</td>
<td></td>
<td>0.260</td>
<td>0.740</td>
</tr>
<tr>
<td>0.50</td>
<td>0.182</td>
<td>0.818</td>
<td>0.214</td>
</tr>
<tr>
<td>0.70</td>
<td>0.117</td>
<td>0.883</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
</tr>
</tbody>
</table>
\( m_I^2 \) plot, \( \Delta H(m_I) \) was evaluated as a function of diglyme concentration. The results are summarised in Table 7.5 and the validity of equation 7.6 is established. Values of \( \Delta H(-\frac{1}{2})_{\text{obs}} \), \( \Delta H(-\frac{3}{2})_{\text{obs}} \), \( \Delta H(-\frac{1}{2}) \), \( \Delta H(-\frac{3}{2}) \) and \( \Delta H(0) \) are plotted against diglyme concentration in Figure 7.12. Also included in Table 7.5 are values of \( \tau_B \), the lifetime of the "diglyme-like" species, calculated independently from \( \Delta H(-\frac{1}{2}) \) and \( \Delta H(-\frac{3}{2}) \), using equation 7.5 with values of \( P_A \) and \( P_B \) from Table 7.4. Values of \( \tau_B \) derived from the two sources are in good agreement and change in the sense expected i.e. a rapid increase in \( \tau_B \) as the mole fraction of diglyme in the solvent mixture increased.

residual line-widths.

Values of \( P_A \) and \( P_B \) calculated using equation 7.2, with \( \Delta H(0)_A = 0.12 \) gauss and \( \Delta H(0)_B = 1.18 \) gauss (see Figure 7.12) are plotted in Figure 7.11 and can be seen to be in good agreement with those calculated from \( A_{iso}^{39K} \) and \( \Delta g \) values.

(a) \( \frac{dA_{iso}^{39K}}{dT} \)

The dependence of \( \frac{dA_{iso}^{39K}}{dT} \) upon solvent composition is shown in Figure 7.4. Since the values of \( \frac{dA_{iso}}{dT} \) for solvent mixtures are greater than those of either pure solvent, application of equation 7.2 would require either one or both of \( P_A \) and \( P_B \) to have values greater than unity. The breakdown in the two-state model treatment in this case is associated with the fact that change in temperature effectively changes the solvent composition in the monomeric unit.

(e) Isotopic dependence of \( \frac{A_N}{A_B} \)

It has been noted previously that selective broadening of the \( m_I = \pm \frac{3}{2} \) lines relative to the
Fig 7.12
Variation of $^{39}$K hyperfine quartet line-widths with change in solvent composition for saturated solutions of potassium in THF - diglyme solvent mixtures.

$$
\Delta H (o) (\Delta) \quad \Delta H (o) (\Delta) \\
\Delta H(-\frac{3}{2})_{\text{exchange}} (x) \quad m_I = -\frac{3}{2} \quad \Delta H(-\frac{3}{2})_{\text{exchange}} (+) \quad m_I = -\frac{1}{2} \\
\Delta H(-\frac{3}{2})_{\text{obs.}} (o) \quad \text{line} \quad \Delta H(-\frac{1}{2})_{\text{obs}} (\square) \quad \text{line}
$$
Table 7.5

Application of a two-state model to the $^{39}$K hyperfine quartet line-width data for solutions of potassium in tetrahydrofuran-diglyme solvent mixtures.

(see text)

<table>
<thead>
<tr>
<th>Mole Fraction of Diglyme</th>
<th>$\Delta H(0)$</th>
<th>$\Delta H(-\frac{1}{2})$ (secs)</th>
<th>$\Delta H(-\frac{3}{2})$ (secs)</th>
<th>$\Delta H(-\frac{3}{2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.12</td>
<td>~0</td>
<td>~0.01</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.31</td>
<td>0.175</td>
<td>0.7</td>
<td>0.695</td>
</tr>
<tr>
<td>0.05</td>
<td>0.45</td>
<td>0.155</td>
<td>1.4</td>
<td>1.76</td>
</tr>
<tr>
<td>0.10</td>
<td>0.69</td>
<td>0.265</td>
<td>4.5</td>
<td>2.40</td>
</tr>
<tr>
<td>0.20</td>
<td>0.88</td>
<td>0.320</td>
<td>11.7</td>
<td>2.87</td>
</tr>
<tr>
<td>0.30</td>
<td>0.94</td>
<td>0.330</td>
<td>18.6</td>
<td>2.91</td>
</tr>
<tr>
<td>0.40</td>
<td>0.98</td>
<td>0.320</td>
<td>23.6</td>
<td>2.87</td>
</tr>
<tr>
<td>0.50</td>
<td>1.02</td>
<td>0.285</td>
<td>33.4</td>
<td>2.54</td>
</tr>
<tr>
<td>0.60</td>
<td>1.05</td>
<td>0.250</td>
<td>41.0</td>
<td>2.25</td>
</tr>
<tr>
<td>0.70</td>
<td>1.08</td>
<td>0.220</td>
<td>57.5</td>
<td>2.00</td>
</tr>
<tr>
<td>0.80</td>
<td>1.12</td>
<td>0.185</td>
<td>107</td>
<td>1.65</td>
</tr>
<tr>
<td>0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

accurate measurements of line-widths not possible.

(see text).
in a solution containing 0.01 mole fraction of diglyme, was less marked for the $^{41}\text{K}$ hyperfine quartet than for the $^{39}\text{K}$ hyperfine quartet.

Using equation 7.4 with equation 7.3,

$$\Delta H\left(-\frac{3}{2}\right)_{\text{obs}} - \Delta H\left(-\frac{1}{2}\right)_{\text{obs}} = 2P_{A}^{2}P_{B}^{2}(A_{A} - A_{B})^{2}(\tau_{A} + \tau_{B}) \quad \text{(equation 7.7)}$$

Since, for all solutions studied, $A_{\text{iso}}(39\text{K}) = \mu A_{\text{iso}}(41\text{K})$

where $\mu = \text{magnetic moment of } 39\text{K nucleus} = 1.82$, then

$$\frac{\Delta H\left(-\frac{3}{2}\right)_{\text{obs}} - \Delta H\left(-\frac{1}{2}\right)_{\text{obs}}}{\Delta H\left(-\frac{3}{2}\right)_{\text{obs}} - \Delta H\left(-\frac{1}{2}\right)_{\text{obs}}} = \mu^2 = 3.3$$

agreement with the observed value of 4.7 (from the data in Table 7.2), considering the experimental difficulty of measuring natural line-widths of the components of the $^{41}\text{K}$ hyperfine quartet.

2. Application of a two-state model to the temperature-dependence of the nature of K$_{\text{sol}}$.

(a) Hyperfine splitting constants.

For a given solvent composition, the $^{39}\text{K}$ hyperfine splitting constant was found to increase with increase in temperature (Figure 7.3). These changes can be discussed in terms of a two-state model in which, instead of a "tetrahydrofuran-like" species and a "diglyme-like" species, there are a "high-temperature" species ($A'$) and a "low-temperature" species ($B'$).

Thus,

$$A_{\text{obs.}} = P_{A'} A_{A'} + P_{B'} A_{B'} \quad \text{(equation 7.8)}$$

where $P_{A'}$ is high at high temperature, $P_{B'}$ is high at low
temperatures.

In practice, however, although data from metal-amine and metal-ether solutions suggest a value of approximately 3 gauss for \( A_B' \), any value of between 40 gauss and 82 gauss (the \( ^{39} \mathrm{K} \) hyperfine splitting in the free atom) is possible for \( A_A' \) and, in the absence of any corroborative data, the evaluation of \( A_A' \)-dependent values of \( P_A' \) and \( P_B' \) would seem to serve little useful purpose.

(b) \( \frac{A_N}{A_B} \)

The temperature-dependence of \( \frac{A_N}{A_B} \) has been shown in Figures 7.10(a) and (b).

Application of the two-state model, with

\[
\frac{A_N}{A_B} = \left( \frac{\Delta H(\frac{3}{2})_{\text{obs}}}{\Delta H(\frac{1}{2})_{\text{obs}}} \right)^2 = \left[ \frac{\Delta H(0) + \Delta H(\frac{3}{2})}{\Delta H(0) + \Delta H(\frac{1}{2})} \right]^2 \tag{equation 7.9}
\]

yields,

\[
\frac{1}{2} \left( \frac{A_N}{A_B} \right)^{-\frac{1}{2}} \left[ \frac{d}{dT} \left( \frac{A_N}{A_B} \right) \right]_{T_1} = \frac{2}{\Delta H(0)} \frac{\Delta H(0)_{T_1} - 9 \Delta H(\frac{1}{2})_{T_1}}{\Delta H(0)_{T_1} \Delta H(\frac{1}{2})_{T_1}}
\]

\[
x \left\{ \Delta H(0)_{T_1} \left( \frac{d \Delta H(\frac{1}{2})}{dT} \right)_{T_1} - \Delta H(\frac{1}{2})_{T_1} \left( \frac{d \Delta H(0)}{dT} \right)_{T_1} \right\}
\]

\( (equation 7.10). \)

Application of equation 7.10 to the solutions containing 0.01 and 0.25 mole fraction of diglyme, using room-temperature values of parameters, leads to,

\[
\frac{d}{dT} \left( \frac{A_N}{A_B} \right)_{298^0 \text{K}} = -0.31/\text{C. deg.} = 7.7 \left\{ 8 \left( \frac{d \Delta H(\frac{1}{2})}{dT} \right)_{298} - \left( \frac{d \Delta H(0)}{dT} \right)_{298} \right\}
\]

\( (equation 7.11) \)

for the solution containing 0.01 mole fraction of diglyme and
\[
\frac{d}{dT} (\frac{A_N}{A_B})_{298^0K} = -0.93/C \text{ deg} = 4.1 \left\{ 3 \left( \frac{d\Delta H(\frac{\lambda}{2})}{dT} \right)_{298} - \left( \frac{d\Delta H(0)}{dT} \right)_{298} \right\}
\]  
(equation 7.12)

for the solution containing 0.25 mole fraction of diglyme.

Since it is expected that both \( \frac{d\Delta H(\frac{\lambda}{2})}{dT} \) and \( \frac{d\Delta H(0)}{dT} \) be negative, the observation that \( \frac{d}{dT} (\frac{A_N}{A_B})_{298^0K} \) is negative, for both solutions, implies that

\[
8 \left| \left( \frac{d\Delta H(\frac{\lambda}{2})}{dT} \right)_{298} \right| > \left| \left( \frac{d\Delta H(0)}{dT} \right)_{298} \right|
\]

for the solution containing 0.01 mole fraction of diglyme and

\[
3 \left| \left( \frac{d\Delta H(\frac{\lambda}{2})}{dT} \right)_{298} \right| > \left| \left( \frac{d\Delta H(0)}{dT} \right)_{298} \right|
\]

for the solution containing 0.25 mole fraction of diglyme.

Thus it is clear that the situation is rather more delicately-balanced for the latter solution, at least for temperatures fairly close to 298\(^0K\), as studied in the present work i.e., the reversal in sign of \( \frac{d}{dT} (\frac{A_N}{A_B}) \) for the solution containing 0.25 mole fraction of diglyme can be rationalized in a semi-empirical manner.

A more detailed discussion of the implications of the application of the two-state model, and of the preferential solvation observed, is reserved for Chapter 10 so that results for the further solvent mixtures studied can be incorporated into the discussion.
CHAPTER 8.

SOLUTIONS OF POTASSIUM IN ETHYLAMINE -

DIGLYME SOLVENT MIXTURES.
INTRODUCTION.

In Chapters 6 and 7, ESR results have been reported for solutions of potassium in solvent mixtures, the components of which differed markedly in their ability to solvate the potassium cation. For solutions of potassium in ethylamine-diglyme solvent mixtures, however, both components solvate positively-charged species well and, as will be discussed in Chapter 10, there was considerably less preferential solvation of the cation than encountered in any of the other mixed solvent systems studied.

EXPERIMENTAL.

Purification of the ethylamine and diglyme has been described in Chapters 4 and 5 respectively. Solutions were prepared in pyrex vessels, by standard high-vacuum technique and were studied by ESR spectroscopy (Chapter 4).

RESULTS.

1. Hyperfine splitting constants.

(a) dependence upon solvent composition.

For freshly-prepared, saturated solutions containing less than approximately 0.2 mole fraction of diglyme, ESR spectra consisted of two hyperfine quartets, attributed to $^{39}\text{K}_{\text{solv.}}$ and $^{41}\text{K}_{\text{solv.}}$ with a broad central singlet, attributed to $\text{e}^{-}_{\text{solv.}}$ (Figures 4.1(a) and 8.1(a)). For freshly-prepared, saturated solutions containing more than 0.2 mole fraction of diglyme, no central singlet was observed (Figures 8.1(b) and (c) and 5.6(a)).

Increase in the proportion of diglyme in the solvent mixture led to a decrease in $A_{\text{iso}}(^{39}\text{K})$ (Figure 8.2). The degree of preferential solvation by the diglyme was, however,
Room-temperature ESR spectra of solutions of potassium in ethylamine-diglyme solvent mixtures containing (a) 0.10, (b) 0.25, and (c) 0.75 mole fraction of diglyme (corresponding spectra of solutions of potassium in pure ethylamine and diglyme are shown in Figs. 4.1 (a) and 5.6 (a) respectively.)
Solvent-dependence of $A_{iso}(^{39}K)$ (at room temperature) for solutions of potassium in ethylamine-diglyme solvent mixtures.
considerably lower than for solutions of potassium in tetra-hydrofuran-diglyme solvent mixtures. Thus, at room temperature, for solutions containing 0.2 mole fraction of diglyme, values of \( \frac{A_{iso}(^{39}K) \text{ (observed)}}{A_{iso}(^{39}K) \text{ (ideal)}} \) were 0.90 and 0.57 respectively.

(b) temperature-dependence.

The temperature-dependence of \( A_{iso}(^{39}K) \), for solutions of potassium in ethylamine-diglyme solvent mixtures, is shown in Figure 8.3. In Figure 8.4, the variation of \( \frac{dA_{iso}(^{39}K)}{dT} \) with change in solvent composition is shown. Values of this factor were always intermediate between those for solutions of potassium in the pure solvents, in contrast with the behaviour of the solvent mixtures discussed in Chapters 6 and 7.

2. \( g \)-factors.

No absolute measurements of \( g \)-factors were performed. Furthermore, values of \( \Delta g \) could be measured only for ethylamine-rich solutions, since it was only for such solutions that the singlet was resolved as a separate signal. The limited data obtained are contained in Table 8.1.

3. Line-widths.

(1) Dependence of hyperfine quartet line-widths upon solvent composition.

Both \( m_I = -\frac{3}{2} \) and \( m_I = -\frac{1}{2} \) lines broadened as the proportion of diglyme in the solvent mixture increased (Figure 8.5). Although selective broadening of the \( m_I = -\frac{3}{2} \) line was observed, as for solutions of potassium in tetra-hydrofuran-diglyme solvent mixtures, there were no maxima in the plots of \( \Delta H_{ms}(^{3/2})_{obs} \) (Figure 8.5) or \( \frac{A_N}{A_B} \) (Figure 8.6) against solvent composition.
Temperature-dependence of $A_{180}^{^{39}K}$ for solutions of potassium in ethylamine-diglyme solvent mixtures containing 0.0 (O: pyrex, @: quartz), 0.25 (X), 0.40 (Δ), 0.75 (+) and 1.0 (□) mole fraction of diglyme.
Fig. 6.4
Solvent-dependence of $dA_{iso}^{(39K)}$ for solutions of potassium in ethylamine-diglyme solvent mixtures.
Fig. 8.5

Solvent-dependence of $\Delta H_{ms}(-\frac{1}{2})_{obs}$ (0) and $\Delta H_{ms}(-\frac{3}{2})_{obs}$ (X) for solutions of potassium in ethylamine-diglyme solvent mixtures.
Solvent-dependence of $\frac{A_N}{A_B}$, both observed directly (X) and calculated from the line-widths in Fig. 8.5 (O), for solutions of potassium in ethylamine-diglyme solvent mixtures.
Table 8.1

Values of $\Delta g$, at room temperature, for solutions of potassium in ethylamine-diglyme solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of diglyme</th>
<th>$A_{iso}^{(39K)}$ (gauss)</th>
<th>$\Delta g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.33</td>
<td>0.00062*</td>
</tr>
<tr>
<td>0.10</td>
<td>8.17</td>
<td>0.00040</td>
</tr>
<tr>
<td>1.0</td>
<td>~3.7</td>
<td>~0 †</td>
</tr>
</tbody>
</table>

* Figure 4.6.
† page 138.

Table 8.2

Concentrations of paramagnetic species for saturated solutions of potassium in ethylamine-diglyme solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of diglyme</th>
<th>$10^9[K]$</th>
<th>$10^9[e^{-}]$</th>
<th>$10^9([K]+[e^{-}])$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1410</td>
<td>68</td>
<td>1478*</td>
</tr>
<tr>
<td>0.10</td>
<td>1130</td>
<td>102</td>
<td>1232</td>
</tr>
<tr>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>380</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>161 †</td>
</tr>
</tbody>
</table>

* Table 4.6.
† Table 7.3.

(all concentrations are in moles l$^{-1}$)
(11) Dependence of singlet line-width upon solvent composition.

In freshly-prepared saturated solutions, the singlet line-width increased steadily with increase in the proportion of diglyme in the solvent mixture, up to approximately 1.4 gauss for a solution containing 0.2 mole fraction of diglyme (Figure 8.7). As the proportion of diglyme in the solvent mixture increased further, the singlet continued to broaden, the $\Delta_{iso}^{(39\text{K})}$ value decreased, with the result that the singlet was no longer resolved as a separate component of the ESR spectrum (Figure 8.1).

As was observed for solutions of potassium in the pure solvents themselves (Chapters 4 and 5), progressive solution-decomposition produced a marked narrowing of the singlet (Figure 8.8) to a value depending, to a first approximation, upon the viscosity of the solution (Figure 8.7).

4. Spin concentrations.

Values of spin-concentrations are contained in Table 8.2.

DISCUSSION.

Although solutions of potassium in ethylamine-diglyme solvent mixtures contain higher concentrations of paramagnetic species than those of potassium in tetrahydrofuran-diglyme solvent mixtures, the results obtained from an ESR study of the former are less informative than those obtained from a similar study of the latter (Chapter 7) since there is less contrast in the properties of $K_{solv}$ in the two pure solvents. Of particular importance is the relatively-small change in $39\text{K}$ hyperfine splitting constant between the pure solvents, which has the effect of compressing and therefore, to some extent, obscuring the trend in properties of $K_{solv}$ with change.
Solvent-dependence of singlet line-width in saturated (O) and almost completely-decomposed (X) solutions of potassium in ethylamine-diglyme solvent mixtures.
Fig 8.8
Change in singlet line-width with solution decomposition for solutions of potassium in ethylamine-diglyme solvent mixtures containing 0.10 (O) and 0.25 (X) mole fraction of diglyme.
in solvent composition.

The properties of solutions of potassium in ethylamine-diglyme solvent mixtures are similar to those of the corresponding tetrahydrofuran-diglyme solutions though, as mentioned earlier and discussed in Chapter 10, the preferential solvation of the cation by the diglyme, as measured by $A_{iso}(^{39}K)$- or $\Delta g$- or $dA_{iso}(^{39}K)/dT$-values, was considerably less marked in the former case. In either case, however (and in contrast to the results for solutions of potassium in ethylamine-tetrahydrofuran solvent mixtures), line-widths of the hyperfine quartet could be usefully divided into two parts; an $m_I$-dependent exchange contribution, $\Delta H(m_I)$, and an $m_I$-independent residual contribution, $\Delta H(0)$. (Figures 7.12 and 8.9).

The significance of these and other observations will be discussed more fully in Chapter 10.
Variation of $^{39}$K hyperfine quartet line-widths with change in solvent composition for saturated solutions of potassium in ethylamine-diglyme solvent mixtures.

$$\Delta H(0) \quad (\triangle)$$
$$\Delta H(-\frac{3}{2})_{\text{exchange}} \quad (\square)$$
$$\Delta H(-\frac{3}{2})_{\text{obs.}} \quad (\circ)$$

$$m_I = \frac{3}{2} \quad \Delta H(0) \quad (\triangle)$$
$$\Delta H(-\frac{1}{2})_{\text{exchange}} \quad (\times)$$
$$\Delta H(-\frac{1}{2})_{\text{obs.}} \quad (\triangle)$$

$$m_I = -\frac{1}{2}$$

**Fig. 8.9**

"Fig. 8.9"

Variation of $^{39}$K hyperfine quartet line-widths with change in solvent composition for saturated solutions of potassium in ethylamine-diglyme solvent mixtures.
CHAPTER 9.

SOLUTIONS OF POTASSIUM IN ETHYLAMINE - 

ETHYLENEDIAMINE SOLVENT MIXTURES.
INTRODUCTION.

The object of the present study was to probe the change in nature of $K_{\text{solv}}$, caused by replacing the tridentate ether chelating solvent, diglyme (Chapter 8) by a bidentate amine chelating solvent, ethylenediamine. In practice, as will be discussed later, the two systems were found to have very different ESR properties, because of critical differences in cation-electron correlation times i.e. in ion-pair lifetime.

EXPERIMENTAL.

Ethylenediamine ($\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, boiling point $117^\circ\text{C}$ at 757 mm) was purified by fractional distillation and stored over sodium-potassium alloy. Solution preparation was by standard high-vacuum technique, the solvents being successively distilled from storage vessels on to a thin film of potassium at $0^\circ\text{C}$. For a solution prepared thus, the solvent composition could be varied, over a small range, by cooling the ESR side-arm containing some of the solution and carefully distilling thereinto an ethylamine-rich solvent mixture from the solution contained in the main limb of the solution preparation vessel.

RESULTS.

1. Hyperfine splitting constant.

For freshly-prepared, saturated solutions containing less than 0.2 mole fraction of ethylenediamine, ESR spectra consisted of an intense hyperfine quartet, attributed to $3\mathbf{g}K_{\text{solv}}$, with a central singlet, attributed to $e_{\text{solv}}^-$ (Figures 4.1(a) and 9.1(a)). For freshly-prepared, saturated solutions containing more than 0.22 mole fraction of
Room-temperature ESR spectra of solutions of potassium in ethylamine-ethylenediamine solvent mixtures containing (a) 0.07, (b) 0.26 and (c) 1.0 mole fraction of ethylenediamine (the corresponding spectrum for solutions of potassium in pure ethylamine is shown in Fig. 4.1 (a)).
ethylene diamine, a single line only was observed (Figure 9.1 (b) and (c)).

In ethylamine-rich solutions for which hyperfine splitting was observed, $A_{iso}^{39K}$ decreased with increase in the proportion of ethylenediamine in the solvent mixture (Figure 9.2) and with decrease in temperature (Figure 9.3).

2. g-factors.

No absolute measurements of g-factors were performed. Furthermore, values of $\Delta g$ could be measured only for solutions containing less than 0.2 mole fraction of ethylene diamine, since it was only for such solutions that separate signals from $K_{solv.}$ and $e^-_{solv.}$ were observed. The limited data obtained are contained in Table 9.1 and plotted in Figure 6.5.

3. Line-widths.

(a) dependence upon solvent composition.

In saturated solutions, increase in the proportion of ethylenediamine in the solvent mixture resulted in an initial broadening of both singlet and hyperfine lines, up to approximately 1.5 gauss and 3.0 gauss respectively for the solution containing 0.15 mole fraction of ethylenediamine. At 0.22 mole fraction of ethylenediamine, a single broad line was observed ($\Delta H_{ms} \sim 5$ gauss). Further increase in the proportion of ethylenediamine in the solvent mixture led to an initial rapid narrowing, followed by a slower narrowing, of this single line, down to 0.11 gauss in pure ethylenediamine. These line-width effects are shown in Figure 9.4.

For solutions containing less than 0.22 mole fraction of ethylenediamine i.e. those whose ESR spectra show separate features characteristic of $K_{solv.}$ and $e^-_{solv.}$ solution
Variation of $A_{iso}(^{39}K)$ with change in solvent composition (at room temperature) for solutions of potassium in ethylamine-ethylenediamine solvent mixtures.

- O data from solutions prepared directly
- X data from solutions prepared by dilution (see text).
Temperature-dependence of $A_{iso}^{39K}$ for solutions of potassium in ethylamine-ethylenediamine solvent mixtures containing 0.0 (O:pyrex, X:quartz), 0.07(+) and 0.13(Δ) mole fraction of ethylenediamine.
Dependence of line-widths upon solvent composition for solutions of potassium in ethylamine-ethylenediamine solvent mixtures.

(1) in saturated solutions:
\[ m_1 = -\frac{1}{2} \text{ line at } 1^\circ C (\square), \ 3^\circ C (\vee) \text{ and } 23^\circ C (\text{o}) \]
\[ m_1 = +\frac{1}{2} \text{ line at } 23^\circ C (\text{x}) \]
"motionally-narrowed" single line at 23° C (+)

(1t) in almost completely-decayed solutions:
singlet or motionally-narrowed single line (see text) at 23° C (△)
Table 9.1.

Values of $\Delta g$, at room temperature, for solutions of potassium in ethylamine-ethylenediamine solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of ethylenediamine</th>
<th>$A_{iso}^{(39K)}$ (gauss)</th>
<th>$\Delta g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.33</td>
<td>0.00062</td>
</tr>
<tr>
<td>0.07</td>
<td>8.19</td>
<td>0.00052</td>
</tr>
<tr>
<td>0.13</td>
<td>7.15</td>
<td>0.00047</td>
</tr>
</tbody>
</table>

* Figure 4.6.

Table 9.2.

Temperature-dependence of line-widths for saturated solutions of potassium in ethylamine-ethylenediamine solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of ethylenediamine</th>
<th>temp (°C)</th>
<th>$\Delta H_{ms}(\frac{1}{2})$ (gauss)</th>
<th>$\Delta H_{ms}$ (single line) (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>1</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>23</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td>3</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>24</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
<td></td>
<td>0.16</td>
</tr>
<tr>
<td>&quot;</td>
<td>25</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>&quot;</td>
<td>45</td>
<td></td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Table 4.2.

Table 9.3.

Concentrations of paramagnetic species for saturated solutions of potassium in ethylamine-ethylenediamine solvent mixtures.

<table>
<thead>
<tr>
<th>mole fraction of ethylenediamine</th>
<th>$10^9 [K]$</th>
<th>$10^9 [e^-]$</th>
<th>$10^9 ([K] + [e^-])$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1410</td>
<td>68</td>
<td>1478</td>
</tr>
<tr>
<td>0.07</td>
<td>1538</td>
<td>112</td>
<td>1650</td>
</tr>
<tr>
<td>0.13</td>
<td>1580</td>
<td>156</td>
<td>1736</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Table 4.6.

(all concentrations are in moles l$^{-1}$).
decomposition resulted in a marked narrowing of the singlet, as observed in previous studies (Chapters 4, 5, 7 and 8). For solutions containing more than 0.22 mole fraction of ethylenediamine, solution decomposition resulted in only very slight narrowing of the single line observed in such solutions (Figure 9.5).

(b) temperature-dependence.

As shown in Table 9.2, increase in temperature led to line-broadening for saturated solutions containing less than 0.22 mole fraction of ethylenediamine, line-narrowing for saturated solutions containing more than 0.22 mole fraction of ethylenediamine.

4. Spin-concentrations.

Concentrations of paramagnetic species in solution are given in Table 9.3.

DISCUSSION.

1. Origin and magnitude of the ESR line-widths.

Whereas for solutions of potassium in ethylamine, the cation-electron correlation time, \( \tau_{M^+e^-} \) is long compared with the inverse of the hyperfine separation (see page 50), for solutions of potassium in ethylenediamine the situation appears to be very similar to that for metal-ammonia solutions (Chapter 1) viz \( \tau_{M^+e^-} \) is very short compared with the inverse of the hyperfine separation and a single narrow line, the weighted average of signals from \( e^- \) and \( M^+e^- \), is observed under all conditions.

As the proportion of ethylenediamine in the solvent mixture increases, \( \tau_{M^+e^-} \) decreases and line-broadening occurs, as for solutions of potassium in diglyme or propylenediamines
Fig 9.5
Change in singlet line-width with decay for solutions of potassium in ethylamine-ethylenediamine solvent mixtures containing 0.07(X), 0.13(0) and 0.50(□) mole fraction of ethylenediamine.
This region, for which lines are broadened, but not coalesced, is the "slow"-exchange region and both singlet and hyperfine quartet line-widths are essentially dominated by the ion-pairing reactions discussed in Chapters 4 and 5, viz.

\[
M^+ + e^- \rightleftharpoons M^+ e^- \quad (1)
\]

and

\[
M^+ M^- + e^- \rightleftharpoons M^+ e^- + M^- \quad (2)
\]

Solution decomposition leads to a rapid decrease in \([M^+ M^-]\) and \([M^-]\), but \([e^-]\) decreases significantly only when the decomposition is well-advanced (Figure 4.3). Thus, in the "slow"-exchange region, where line-widths are dominated by both (1) and (2), solution decomposition leads to pronounced narrowing of the singlet due to a decrease in \([M^+ M^-]\), the residual line-width being attributed to (1). (Figure 9.5).

As the proportion of ethylenediamine in the solvent mixture increases still further, \(\tau_{M^+ e^-}\) becomes equal to and then shorter than the inverse of the hyperfine separation.

In the "fast"-exchange region, where \(\tau_{M^+ e^-}\) is very much less than the inverse of the hyperfine separation, the line-width of the single line observed is dominated by (1), (2) being too slow to make appreciable contributions to line-widths. Thus the line-width is little affected by decay (Figure 9.5) but decreases rapidly as the concentration of ethylenediamine in the solvent mixture increases i.e. as the rates of both forward and reverse reactions for (1) increase.

The effect of increase in temperature is to cause an increase in the rates of both (1) and (2) i.e. a decrease in \(\tau_{M^+ e^-}\). In the "slow"-exchange region, this would be expected to lead to line-broadening, in the "fast"-exchange region to line-narrowing. These effects have been observed (Table 9.2). Thus the effect of increase in temperature is
to cause a shift of the coalescence point to lower ethylenediamine concentration (Figure 9.4).

2. Preferential solvation.

The change in $A_{iso}^{39K}$ values (Figure 9.2) is indicative of a strong preferential solvation of the cation by the ethylenediamine, as discussed in the following chapter.
CHAPTER 10.

THE STRUCTURE OF THE MONOMER IN

AMINE AND ETHER SOLVENTS.
INTRODUCTION.

There have been several previous studies, both by optical \(^{15,73}\) and ESR \(^{65,72,73,83,89}\) spectroscopy, of solutions of alkali metals in amine-ammonia \(^{15,73,83,89}\), amine-amine \(^{65,72}\) and, in one case, \(^{117}\) amine-ether solvent mixtures. Previous studies of such systems by ESR spectroscopy have been mainly concerned with the dependence of the metal hyperfine splitting constant, \(A_{iso}(M)\), upon solvent composition and reports of changes in e.g. hyperfine line-widths have generally been of a qualitative nature. The present studies, reported in Chapters 6-9, are the first in which the variation with solvent composition has been studied for all the principal ESR properties of the monomer viz. \(A_{iso}(M)\) and \(\frac{dA_{iso}(M)}{dT}\) values, g-factors and line-widths. In the present chapter, the effects observed are discussed in terms of both multi-state and continuum models for the monomer, with particular reference to the model proposed in Chapter 5.

1. The detection of the monomer by ESR spectroscopy.

In the present and previous works, the term "monomer" has been used for the species, of stoichiometry \(M\), formed by the aggregation of a cation, \(M^+\) and electron, \(e^-\). In the present work, the monomer has been written either as \((K^+e^-)_{Solv.}\) or \(K_{Solv.}\) without any structural implications. In Chapter 2 (page 49), the conditions under which the monomer could be unequivocally identified by ESR spectroscopy i.e. under which hyperfine splitting characteristic of nucleus \(M\) could be resolved, were discussed in terms of the equilibrium,

\[
M^+ + e^- \xrightarrow{k_1} M^+e^- (or M); \frac{k_1}{k_2} = K_{ass.}
\]
the correlation time for the cation-electron interaction, $\tau_{M^+e^-}$, determining the nature of the ESR spectrum observed from the $M^+e^-$ unit.

In this section, quantitative estimates of $\tau_{K^+e^-}$ are made for solutions of potassium in ammonia, amine and ether solvents, using data reported in Chapters 4 and 5 and data from previous studies. Values of $\tau_{K^+e^-}$ were calculated using

$$\frac{1}{\tau_{K^+e^-}} = k_1([K^+] + [e^-]) + \frac{k_1}{k_{ass}} \quad \text{(equation 10.1)}.$$

assuming that $k_1$ was diffusion-controlled \textsuperscript{132} viz.

$$k_1 = \frac{4\pi L_a Z_a Z_b e^2}{D_b kT} \frac{(D_e^- + D_{K^+})}{\exp \left( \frac{Z_a Z_b e^2}{D_S kT} \right) - 1}$$

\text{(equation 10.2)}.

where $Z_a = +1$, $Z_b = -1$, $D_e^-$ and $D_{K^+}$ are the diffusion coefficients of the solvated species and $a$ is an ion-size parameter (page 95). Values of $\tau_{K^+e^-}$ thus obtained are given in Table 10.1(b), together with corresponding values of the "infinite-dilution" correlation time, $\tau_{K^+e^-}$ (limit), obtained by neglecting the first term in equation 10.4, and of the inverse of the $^{39}_K$ hyperfine splitting constant ($A_{\text{iso}}(^{39}_K)$ in sec$^{-1}$) observed, or estimated, for the system in question. In order that resolved hyperfine splitting to the $^{39}_K$ nucleus be observed, the cation-electron correlation time, $\tau_{K^+e^-}$, i.e. the effective life-time of the monomer, must be greater than the inverse of the relevant $A_{\text{iso}}(^{39}_K)$ value (see page 49). The data contained in Table 10.1(b) are consistent with the experimental observations that hyperfine splitting to the $^{39}_K$
Tables 10.1(a) and (b)
The duration of the cation-electron interaction for solutions of potassium in ammonia, amine and ether solvents.

Table 10.1(a)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$a \times 10^8$</th>
<th>$b_3$</th>
<th>$10^{-11}k_4$</th>
<th>$K_{ass}$ (l.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>6.9</td>
<td>16.9</td>
<td>8.50</td>
<td>1.1x10$^2$(ref. 3)</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>6.9</td>
<td>16.0</td>
<td>4.25</td>
<td>6.5x10$^3$(ref. 133)</td>
</tr>
<tr>
<td>Diglyme</td>
<td>6.0</td>
<td>5.8</td>
<td>7.4</td>
<td>~1x10$^5$ a</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>4.4</td>
<td>8.7</td>
<td>7.74</td>
<td>6.7x10$^5$ b</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>4.0</td>
<td>7.3</td>
<td>9.18</td>
<td>4.3x10$^8$ c</td>
</tr>
</tbody>
</table>

Table 10.1(b)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_{K^+e}^-$ (secs x 10$^7$)</th>
<th>$\tau_{K^+e}^-$ (limit) (secs x 10$^7$)</th>
<th>$A_{iso}$($^{39}$K) (secs x 10$^7$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>0.00036</td>
<td>0.0017</td>
<td>66</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>0.108</td>
<td>0.154</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Diglyme</td>
<td>6.8</td>
<td>8.6</td>
<td>10</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>7.9</td>
<td>9.1</td>
<td>3</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>4.7</td>
<td>32.0</td>
<td>1</td>
</tr>
</tbody>
</table>

* Chapter 4 (pages 94, 95).

† Estimated from $A_{iso}$($^{39}$K) values, by comparison with ammonia and ethylamine values.

a Estimated from $K_{ass}$ vs. $A_{iso}$($^{39}$K) calibration plot.

b $K_A$, Table 4.6 (page 87).

c $\left[\frac{K}{e}\right]_2$ in Table 5.1 (page 108).
nucleus is observed for saturated and dilute solutions of potassium in ethylamine (Fig 4.1) and tetrahydrofuran (Fig 5.2), but for neither saturated nor dilute solutions of potassium in ammonia or ethylenediamine (Fig 9.1). For these systems a single line only, the weighted average of signals from e\(^{-}\) and M\(^{+}\)e\(^{-}\), is observed. For solutions of potassium in diglyme, the situation is intermediate between these extremes and partially-resolved \(^{39}\)K hyperfine structure is observed for saturated and dilute solutions (Fig 5.6).

2. The interpretation of the mixed-solvent results in terms of previous models for the monomer.

The rapid change in properties of the monomer, caused by the addition of 0.01 mole fraction of diglyme to solutions of potassium in pure tetrahydrofuran or ethylamine, suggests that, for statistical reasons, a confined model for the monomer i.e. a model in which the monomer unit contains a single layer of solvent molecules, is more intuitively attractive than a diffuse model, such as that of Bar-Eli and Tuttle \(^{72}\) (page 51), in which the monomer unit contains several layers of solvent molecules. If, on the basis of a diffuse model, it were assumed that the diglyme was preferentially added into the first solvation shell, the strong cation-diglyme interaction required to explain the observed effects would presumably considerably weaken the binding of subsequent solvation shells i.e. in the particular case of a very strong cation-solvator (diglyme) added, in small quantities, to a considerably-less effective cation-solvator, (e.g. tetrahydrofuran) the diffuse model for the monomer appears likely to assume the characteristics of a confined model.

Of the principal confined models for the monomer, that of
O'Reilly and Tsang (page 52) requires that the spin-density at $M^+$ be dependent upon the height of the potential barrier i.e. $A_{133}^{\text{iso}}(M)$ ought to correlate with $\frac{1}{D_{\text{OP}}} - \frac{1}{D_{S}}$. This type of correlation has been found (page 115) to hold approximately only in the absence of the possibility of chelation.

The ion-pair solvated atom model for the monomer (see page 56) is not inconsistent with the present data for solvent mixtures. In particular, diglyme would presumably stabilise the ion-pair by solvation of the cation, leading to a decrease in $A_{133}^{\text{iso}}(M)$, as observed. The main facts weighing against this type of model are the low $g$-factor of the "solvated-atom" species, which has been rationalized by analogy with the corresponding silver species (page 56) and the failure of a two-state model to describe the behaviour of $A_{133}^{\text{iso}}(133\text{Cs})$ and $g_{\text{Cs}}$ for solutions of caesium in ethylamine (page 56, Figure 2.4).

3. The multi-state and continuum models for the monomer.

A two-state model.

As mentioned in the previous section, any model for the monomer must account for its variation in properties with both change in solvent composition and change in temperature. On the basis of a simple two-state model, an equilibrium of the form,

$$m^- \text{diglyme} + K^+ (\text{THF})_n e^- \rightleftharpoons n^- \text{THF} + K^+ (\text{diglyme})_m e^-$$

would require a consideration of states A and B at temperatures $T_1$ and $T_2$, where $T_1$ is lower than the lowest temperature at which measurements are performed and $T_2$ is higher than the highest temperature at which measurements are performed. The complete scheme is,
where $A_1$ represents the state $A$ at temperature $T_1$ etc. On this basis, $[T_2(m_I)]^{-1}_{\text{total}}$, which is proportional to the observed $m_I$-dependent contribution to the hyperfine quartet line-widths, is given by

$$[T_2(m_I)]^{-1}_{\text{total}} = [T_2(m_I)]^{-1}_{A_1 \rightleftharpoons B_1} + [T_2(m_I)]^{-1}_{A_2 \rightleftharpoons B_2} + [T_2(m_I)]^{-1}_{A_1 \rightleftharpoons A_2} + [T_2(m_I)]^{-1}_{B_1 \rightleftharpoons B_2} + [T_2(m_I)]^{-1}_{A_1 \rightleftharpoons B_2} + [T_2(m_I)]^{-1}_{B_1 \rightleftharpoons A_2}$$

(equation 10.3).

where $[T_2(m_I)]^{-1}_{A_1 \rightleftharpoons B_1}$ is the contribution to $[T_2(m_I)]^{-1}_{\text{total}}$ arising from the $A_1 \rightleftharpoons B_1$ interchange, etc.

It is clear that the application of such a scheme would serve little purpose in the present case, the number of variable parameters vastly out-numbering the number of experimental observables. The application of a two-state model to the present type of system therefore reduces to a consideration of what, if any, useful approximations can be introduced into equation 10.3.

In Chapter 7, for solutions of potassium in tetrahydrofuran-diglyme solvent mixtures, the properties of the monomer were interpreted in terms of a two-state model, with a "tetrahydrofuran-like" species (A) and a "diglyme-like" species (B) at temperature $T_3$ ($T_1 < T_3 < T_2$). In effect, $[T_2(m_I)]^{-1}_{\text{total}}$ was
set equal to some complex function of the first two terms in equation 10.3 and all subsequent terms were ignored i.e.

\[
\left[ T_2(m_1) \right]^{-1}_{\text{total}} = \left[ T_2(m_1) \right]^{-1}_{A_3 \leftrightarrow B_3}
\]

\[= \frac{P_{A_3}^2 P_{B_3}^2 m_1^2 (A_{A_3} - A_{B_3})^2 (T_{A_3} + T_{B_3})}{(T_{A_3} + T_{B_3})} \quad \text{(equation 10.4).}
\]

This simple two-state model, though admittedly crude, was very successful in explaining the dependence of the properties of the monomer upon solvent composition. Values of \(P_{A_3}\) and \(P_{B_3}\) required to fit the \(A_{iso}(39K), A_g\) and \(\Delta H_{ms}(0)\) data were in very good agreement (Fig. 7.11). This simplified model, however, was quite unable to explain the finite, but small, \(m_1\)-dependent line-width, \(\Delta H(m_1)\), observed for solutions of potassium in pure tetrahydrofuran (Fig. 7.12) and the finite (and large) \(\Delta H(m_1)\) observed for solutions of potassium in pure diglyme (Figs 7.12 and 8.9). In the former case, \(P_{B_3} = 0\) and, in the latter, \(P_{A_3} = 0\). In either case, \(\left[ T_2(m_1) \right]^{-1}_{\text{total}}\), given by equation 10.4, and therefore \(\Delta H(m_1)\), must be zero. This failure occurs because of the terms ignored in equation 10.3.

For solutions of potassium in tetrahydrofuran at temperature \(T_3\), \(P_{A_3}\) and \(P_{A_2}\) are non-zero i.e. \(\left[ T_2(m_1) \right]^{-1}_{A_1 \leftrightarrow A_2}\) is finite; for solutions of potassium in diglyme at temperature \(T_3\), \(P_{B_1}\) and \(P_{B_2}\) are non-zero i.e. \(\left[ T_2(m_1) \right]^{-1}_{B_1 \leftrightarrow B_2}\) is finite. The magnitudes of these terms are given by application of equation 7.4, viz by

\[
\left[ T_2(m_1) \right]^{-1}_{A_1 \leftrightarrow A_2} = \frac{2^2 2^2 m_1^2 (A_{A_1} - A_{A_2})^2 (T_{A_1} + T_{A_2})}{(T_{A_1} + T_{A_2})} \quad \text{(equation 10.5)},
\]

and

\[
\left[ T_2(m_1) \right]^{-1}_{B_1 \leftrightarrow B_2} = \frac{2^2 2^2 m_1^2 (A_{B_2} - A_{B_1})^2 (T_{B_1} + T_{B_2})}{(T_{B_1} + T_{B_2})} \quad \text{(equation 10.6)}.
\]
where $P_{A_1}$ etc. are governed by $T_3$. The observation that $\Delta H(\beta/2)$ is much higher for solutions of potassium in pure diglyme ($\sim 1$ gauss) than for solutions of potassium in pure tetrahydrofuran ($\sim 0.005$ gauss) probably implies that

$$\tau_{A_1} + \tau_{A_2} \ll \tau_{B_1} + \tau_{B_2}$$

Since the $A_1 \rightleftharpoons A_2$ and $B_1 \rightleftharpoons B_2$ interconversions must presumably involve some re-arrangement of the solvent attached to the cation (see section 5), the above observation is quite consistent with the conclusion of Chapter 5, that the cation-diglyme interaction is considerably stronger than the cation-tetrahydrofuran interaction (pages 115, 116).

As the mole fraction of diglyme in the solvent mixture increases, $[T_2(m_I)]_{B_1 \rightleftharpoons B_2}$ increases and the deviation of $[T_2(m_I)]_{\text{obs}}$ i.e. of $\Delta H(m_I)$, from the values given by equation 10.4 increases, as observed (Figs. 7.12 and 8.9).

Any attempt to describe the behaviour in diglyme-rich solutions therefore requires an interchange incorporating both change in solvent composition and change in temperature, subject to the conditions imposed upon $T_1$ and $T_2$ at the beginning of this section. The last term in equation 10.3 represents the only such interchange covering the entire range of the experimental observations viz.

interchange between a "low-temperature", "diglyme-like" species ($B_1$) and a "high-temperature", "tetrahydrofuran-like" species ($A_2$). Such a model has the advantage that it does not require $\Delta H(m_I)$ to be zero in the pure solvents, at temperature $T_3(T_1 < T_3 < T_2)$, since $P_{A_2}$ and $P_{B_1}$ do not themselves become zero under such conditions. In principle, therefore, the model is capable of describing the system throughout the entire
range of solvent composition. In practice, however, the same difficulty arises as for the application of a simple two-state model to caesium-ethylamine solutions (see the caption to Figure 2.3) i.e. the evaluation of $A_2$ requires data at a much higher temperature than that practically feasible, while the evaluation of $A_1$ requires data at a temperature lower than that at which hyperfine splitting is lost. In general, therefore, $X_{B_1}$ and $X_{A_2}$, where X represents $A_{iso}^{39K}$, $\Delta g$ or $\Delta H(0)$ can be neither directly observed nor can data at intermediate temperatures be satisfactorily extrapolated i.e. there is no meaningful way of comparing $P_{A_2}$ and $P_{B_1}$ values derived from these different sources and the model is of no practical use in the present case.

A multi-state model.

On the basis of a two-state model, the need to cover the whole solvent-composition range required that, for a conversion of the type

$$m S_2 + K^+(S_1)_n e^- \rightleftharpoons n S_1 + K^+(S_2)_m e^-,$$

only the species $K^+(S_1)_n e^-$ and $K^+(S_2)_m e^-$ be considered. In practice, of course, it is unrealistic to expect the solvent structure within the monomer unit to change thus completely in the time required ($\sim 10^{-10}$ - $10^{-11}$ secs). Intermediate structures, such as $K^+(S_1)_{n-1} S_2 e^-$ and $K^+(S_1)_{n-2} (S_2)_2 e^-$ (with "high" and "low" temperature forms of each) must be considered. The situation rapidly becomes extremely complex e.g. with $m = n = 6$, a total of 14 states are required, with over 50 potential contributions to $[T_2(m_1)]^{-1}$. The introduction of so many variable parameters clearly renders quantitative application of the model of little value. The success in replacing this complex $n$-state model by a simple
two-state model could not have been predicted, but very probably implies that the distribution of $P$ and $A$ values, among the $n$ states, is symmetrical in form.

**The Continuum model.**

On the basis of a continuum model, the effect of a change in environment e.g. solvent composition and/or temperature, is to cause a continuous change in the structure of the monomer, without the formation of discrete chemical species as postulated on the basis of a multi-state model. The chief theoretical difference between the two types of models is the form of the distribution of e.g. the $A^-$ values. In the case of a multi-state model, the distribution function consists of a series of discrete peaks, with maxima at $A_1^-, A_2^-, \ldots, A_n^-$ and the variables are $A_1^-, P_1^-, \ldots, A_n^-, P_n^-$. For a continuum model, the distribution function consists of a single, broad band with peak at $A^-$ related to the above by,

$$A_{av} = \frac{\sum_{i=1}^{n} P_i A_i}{\sum_{i=1}^{n} P_i} = \sum_{i=1}^{n} P_i A_i \quad \text{(equation 10.7)}.$$  

In this case, the band is characterized by its position, width and shape and these factors are, in principle, the variables to be used in fitting the experimental data, though there have been no attempts, as yet, to apply this kind of treatment.

At the present time, it is quite impossible to distinguish between the two types of models, either theoretically or practically (see page 121) and it seems that the controversy is not one which is likely to be resolved in the near future.
4. **Referential Solvation.**

For all the solvent mixtures studied in the present work, the change in any particular property of the monomer has deviated from that expected for an ideal mixture. Similar behaviour has been observed in previous studies, though only, in general, for the metal hyperfine splitting constant (Figs 10.1 and 10.2). It was suggested earlier (Chapter 5) that the monomeric unit must be defined to include solvent molecules; the above observation suggests that the solvent composition in the monomeric unit must differ from that in the bulk solvent. From the results obtained in solvent mixtures, an order of the affinity of the solvents for the unsolvated gas-phase unit, $M^+e^-$, can be deduced viz, $\text{NH}_3 > \text{ED} \sim \text{MeNH}_2 > \text{diglyme} > \text{EtNH}_2 > \text{Pr}^+\text{NH}_2 > \text{THF}$. 

The importance of basicity and/or chelation strongly suggests that solvation of $M^+$ rather than of $e^-$, dominates the properties of the monomer. The phenomenon of chelation, in this context, has been investigated by Chan and Smid, who, from a study of the temperature-dependence of the association constant of the $\text{F}^-\text{Na}^+$ ion-pair ($\text{F}^-$ represents the fluorenyllium radical anion) in tetrahydrofuran-tetraglyme solvent mixtures, concluded that the enthalpy change associated with solvation changed little from tetrahydrofuran to diglyme ($\Delta H_S \sim -7 \text{ kcal mole}^{-1}$) whereas the entropy change associated with solvation, $\Delta S_S$, changed significantly, from -40 e.u. in pure tetrahydrofuran to -12 e.u. in pure tetraglyme. Thus, from equation 10.8,

$$\Delta G_S = \Delta H_S - T\Delta S_S \quad (\text{equation } 10.8).$$
Dependence of $A_{180}(^{39}\text{K})$ upon solvent composition for solutions of potassium in solvent mixtures containing ethylamine.

- $\Delta$ : K-ethylamine /1,4 dioxan (25°C, ref. 117).
- $\times$ : K-ethylamine/n- butylamine (25°C, ref. 65).
- $+$ : K-ethylamine/i- propylamine (35°C).
- $0$ : K-ethylamine/methylamine (35°C).
- $\nabla$ : K-ethylamine/methylamine (27°C) (ref. 72).
- $\square$ : K-ethylamine/ammonia (25°C, ref. 73).
Dependence of $A_{iso}(^{85}\text{Rb})(0)$ and $A_{iso}(^{133}\text{Cs})(X)$ upon solvent composition for solutions of rubidium and caesium in ethylamine-ammonia solvent mixtures at room temperature (ref. 89).

Fig 10.2.
the free-energy change associated with solvation $\Delta G_s$, is more negative in the latter case i.e. the solvation process is more favourable.

The anomalous behaviour of ammonia in the above series is presumably due to the ability of this solvent to solvate effectively both the cation and electron (page 96).

For the mixed-solvent systems reported in Chapters 6-8, it has been possible to record the properties of the monomer at all intermediate solvent compositions and, in particular, in both pure solvents. Thus the change in relative deviations from ideality, with change in solvent composition or solvent system can be quantitatively expressed using the fraction,

$$\frac{|X_{obs} - X_{ideal}|}{X_{ideal}} = x'$$

where $X$ represents any particular property of the monomer.

For these systems, the variation of $x'$ with change in solvent composition has been computed for $X = A_{iso}^{(39K)}$ (Figure 10.3), $\frac{dA_{iso}^{(39K)}}{dT}$ (Figure 10.4), $\Delta H_{ms}(0)$ (Figure 10.5), $\Delta H_{ms}(m_1)$ (Figure 10.6) and $\Delta g$ (Figure 10.7). For a given property, $X$, the magnitude of the maximum value of $x'$ is a convenient measure of the degree of the preferential solvation, which can thus be seen to be most marked for the potassium-tetrahydrofuran/diglyme system, least so for the potassium-ethylamine/diglyme system. The position of the maximum in $x'$ depends upon $X$. For all the solvent systems studied, $A_{iso}^{(39K)}$' was symmetrical with respect to the solvent-composition axis (Figure 10.3) i.e. the maximum in $A_{iso}^{(39K)}$' occurred where the mole fractions of the "good" and "poor" solvators were equal viz. 0.5 (Figure 10.3). In general, however, the
Fig 10.3

Dependence of $A_{\text{iso}(^{39}\text{K})_{\text{ideal}}} - A_{\text{iso}(^{39}\text{K})_{\text{obs.}}}$ upon solvent composition, at 25°C, for the potassium-diglyme (†)/THF(0), potassium-ethylamine (†)/THF(X) and potassium-diglyme (†)/ethylamine (△) systems. (The more effective cation-solvator in the solvent mixture is indicated by (†)).
dependence of $(\frac{dA}{dT})_{\text{obs}} - (\frac{dA}{dT})_{\text{ideal}}$ upon solvent composition, at 25°C, for the potassium-diglyme (†)/THF(0), potassium-ethylamine (†)/THF(X) and potassium-diglyme (†)/ethylamine (△) systems (The more effective cation-solvator in the solvent mixture is indicated by (†)).
Dependence of \( \frac{\Delta H_{\text{obs}}(0) - \Delta H_{\text{ideal}}(0)}{\Delta H_{\text{ideal}}(0)} \) (where \( \Delta H_{\text{ms}}(0) \) represents the residual, \( m_s \) - independent contribution to hyperfine line-widths) upon solvent composition for the potassium-diglyme/THF(0) and potassium-diglyme/ethylamine(X) systems.
Dependence of $\frac{\Delta H_{\text{ms}}(\frac{3}{2})_\text{obs} - \Delta H_{\text{ms}}(\frac{3}{2})_{\text{ideal}}}{\Delta H_{\text{ms}}(\frac{3}{2})_{\text{ideal}}}$ (where $\Delta H_{\text{ms}}(\frac{3}{2})_{\text{ideal}}$ represents the $m_1$-dependent contribution to the $m_1=\frac{3}{2}$ line-width) upon solvent composition for the potassium-diglyme/THF(0) and potassium-diglyme/ethylamine(X) systems.
Dependence of $\frac{\Delta g_{\text{ideal}} - \Delta g_{\text{obs}}}{\Delta g_{\text{ideal}}}$ upon solvent composition, at $25^\circ\text{C}$, for the potassium-diglyme (†)/THF(0) and potassium-ethylamine (†)/THF(X) systems (the more effective cation-solvator in the solvent mixture is indicated by (†)).
maximum in \( x' \) occurred when the mole fraction of the "good" solvator was significantly less than 0.5, generally less than 0.2 (Figures 10.3-10.7). The significance of these observations is discussed in the following section.

5. The Equilibrating Ion-Pairs Model for the Monomer.

In Chapter 5 (pages 113-114) it was proposed that the change in properties of the monomer, in amine or ether solvents, with change in solvent or temperature, could be satisfactorily accommodated in terms of a solvent-shared ion-pair such as,

\[
\begin{align*}
S_1 & \quad M^+ \quad S_1' \\
\quad e^- & \quad S_1 \\
S_1 & \quad S_1
\end{align*}
\]

the unbroken line represents a strong interaction; the dashed line a weak interaction.

with progressively greater interchange of \( e^- \) and \( S_1' \) at higher temperatures. On the basis of a simple two-state model, the dependence of properties of this type of monomer upon solvent composition and temperature would require the scheme,

\[
\begin{align*}
S_1 & \quad M^+ \quad S_1' \quad \text{(b)} \\
\quad e^- & \quad S_1 \quad \text{(a)} \\
S_1 & \quad S_1
\end{align*}
\]

where change in temperature, in pure solvents \( S_1 \) and \( S_2 \), is
represented by the $a_1 \rightleftharpoons a_2$ and $b_1 \rightleftharpoons b_2$ interconversions respectively and change in solvent composition, at temperatures $T_1$ and $T_2$, is represented by the $a_1 \rightleftharpoons b_1$ and $a_2 \rightleftharpoons b_2$ interconversions respectively. This scheme is related to the general scheme discussed at the beginning of section 3 of the present chapter, with $a_1$ in the former corresponding to $A_1$ in the latter etc. The application of this type of model, with modifications, was discussed in some detail.

For solutions of potassium in pure solvent $S_1$ at temperature $T_3 (T_1 < T_3 < T_2)$.

$$X_{obs} = p_{a_1} X_{a_1} + p_{a_2} X_{a_2} \quad \text{(equation 10.9)}.$$ 

where $X$ represents $A_{iso}^{39K}$, $\Delta g$ or $\Delta H_{ms}(0)$. In this section, an attempt is made to analyse the effect of progressive replacement of $S_1$ by $S_2$, e.g., the addition of a single molecule of diglyme ($D$) to a solution of potassium in tetrahydrofuran ($T$) is represented by the equilibrium,

$$K^+ T_n e^- + D \rightleftharpoons K^+ T_{n-3} De^- + 3T \quad \text{(equilibrium A)}$$

assuming that the diglyme co-ordinates to the potassium cation using all three oxygen atoms. For $n = 6$, two possible schemes must be considered, viz.

(1) TT

(2) TD

(3) TT

(4) TT
Assuming that,

(i) cross-terms are negligible.

(ii) the strength of the $M^+-e^-$ interaction in the "atom-like" species (3, 4 and 6) weakens both the $M^+-T$ and $M^+-D$ interactions so that processes $3 \Rightarrow 4$ and $3 \Rightarrow 6$ are too rapid to contribute to $[T_2(m_1)]^{-1}_{\text{obs}}$ for equilibrium (A).

(iii) In the case of the "low-temperature" species, only reactions involving the breaking and re-forming of cation-diglyme bonds will be sufficiently slow to contribute to $[T_2(m_1)]^{-1}_{\text{obs}}$

for the first scheme,

$$[T_2(m_1)]^{-1}_{\text{obs}} = [T_2(m_1)]^{-1}_{1 \Rightarrow 2} + [T_2(m_1)]^{-1}_{2 \Rightarrow 4}$$ (equation 10.10)

for the second scheme,

$$[T_2(m_1)]^{-1}_{\text{obs}} = [T_2(m_1)]^{-1}_{1 \Rightarrow 5}$$ (equation 10.11)

i.e. if the diglyme molecule is inserted between the cation and electron, there are two possible sources of $m_1$-dependent line-width, from changes in the solvent composition in the monomeric unit and from changes in temperature. If the diglyme molecule is not inserted in this position, only the
former can contribute to $\Delta H(m_I)$.

A possible simplification, discussed in section 3 of the present chapter, assumes that, at all solvent compositions, a "low-temperature" species is in rapid equilibrium with a "high-temperature" species and that the properties of the monomer are governed by the respective fractions of the states. Change in solvent composition results in change in the fractions of the two states but has no effect upon their properties.

At any solvent composition, all the $m_I$-dependent line-width arises from the interconversion of the "high" and "low"-temperature species. This model is in direct contrast with that employed in Chapter 7, where it was assumed that all the $m_I$-dependent line-width arose from solvent exchange, but is not inconsistent with the data for e.g. $\Delta H(3/2)$ in Figures 7.12 and 8.9. From these Figures, it has been concluded that the $m_I$-dependent line-widths for solutions of potassium in pure diglyme and, to a lesser extent, in pure tetrahydrofuran, must be attributed to a rapid equilibration of temperature-dependent states. Since experiments cannot be performed at temperature $T_1$ or $T_2$, under no conditions can an $m_I$-dependent line-width be unequivocally assigned to solvent exchange between the monomeric unit and the bulk solvent.

On the basis of the notation introduced earlier, states 1, 2 and 5 are indistinguishable (i.e. $A_1 = A_2 = A_5$ etc), so that, from a consideration of equation 7.14, $[T_2(m_I)]^{\frac{1}{1+2}} = [T_2(m_I)]^{\frac{1}{1+5}} = 0$. Thus equation 10.10 reduces to

$[T_2(m_I)]^{\frac{1}{1+2}} = [T_2(m_I)]^{\frac{1}{2+4}}$  \hspace{1cm} (equation 10.12).

and equation 10.11 to

$[T_2(m_I)]^{\frac{1}{1+2}} = 0$
Since \([T_2(m_1)]^{\text{obs.}} \neq 0\), the above simplification requires that the first diglyme molecule be inserted between the cation and the electron.

The simplified scheme is therefore written thus,

\[
\text{(1)} \quad \text{(2)} \quad \text{(7)}
\]

\[
\text{(3)} \quad \text{(4)} \quad \text{(8)}
\]

where the \(1 \Rightarrow 3\), \(2 \Rightarrow 4\) and \(7 \Rightarrow 8\) interchanges lead to \(\Delta H(m_1)\). For an interchange of type \(i \Rightarrow j\), where \(j\) has the larger hyperfine splitting, equation 7.4 becomes,

\[
\Delta H(m_1) \propto \left[p_2(m_1)\right]^{\text{obs.}} = p_1^2 p_3^2 m_1^2 (A_j - A_1)^2 (T_1 + T_j).
\]

(equation 10.13)

For solutions of potassium in pure tetrahydrofuran, \(\Delta H(m_1)\) is small because the cation-tetrahydrofuran interaction is weak i.e. \((T_1 + T_3)\) is small. Since the cation-diglyme interaction is strong, however,

\[
(T_2 + T_4) \gg (T_1 + T_3)
\]

so that the effect of adding a single molecule of diglyme is to cause a sudden increase in \(\Delta H(m_1)\). For a second diglyme molecule, added in the positions remote from the cation-electron region, the effect upon the rate is expected to be negligible i.e.

\[
(T_7 + T_8) \ll (T_2 + T_4)
\]
In actual fact, $\Delta H(m^\uparrow)$ falls as the mole fraction of diglyme is increased past the maximum. (Fig 7.12). This is due to the fact that the factor $P_i^2 P_j^2$ in equation 10.13 increases while $(\tau_i + \tau_j)$ increases, but then decreases steadily at higher concentrations of diglyme, while $(\tau_i + \tau_j)$ is approximately constant. $P_i$ and $P_j$ were calculated, at any given solvent composition, using

$$A_{\text{obs}} = P_i A_i + P_j A_j$$

(equation 10.14)

a good fit to the form of the decrease in $\Delta H(m^\downarrow)$ at higher diglyme concentrations being obtained using $A_i = 1$ gauss and $A_j = 55$ gauss.

This behaviour explains the form of the

$$\frac{\Delta H(m^\downarrow)_{\text{obs}} - \Delta H(m^\downarrow)_{\text{ideal}}}{\Delta H(m^\downarrow)_{\text{ideal}}}$$

function plotted in Fig. 10.6.

The residual line-width, $\Delta H(0)$, is a measure of the rate of the interchange of solvent in the monomer unit with that in the bulk solvent i.e. of,

$$M^+ S_n e^- + S^* \rightarrow M^+ S_{n-1} S^* e^- + S.$$ 

For the cation-solvent correlation time, $\tau_{M^+ - S}$, short, $\Delta H(0)$ is low; As $\tau_{M^+ - S}$ increases, $\Delta H(0)$ increases. The observation that the addition of the first molecule of diglyme causes a rapid increase in $\Delta H(0)$, subsequent molecules being considerably less effective (Figs 7.12 and 8.9) must imply that the diglyme molecule is least easily displaced from the cation when occupying the position between the cation and electron. This must presumably be due to the spheres of solvent molecules, polarized around the cation and electron, shielding this particular diglyme molecule from the approach
of, and consequential exchange with, diglyme molecules from the bulk solvent.

The asymmetry of the $\Delta g$ function plotted in Figure 10.7 must imply that the effect of the first diglyme molecule upon the symmetry of the environment of the cation i.e. upon the degeneracy of the p-orbital set, is greater than that of subsequent diglyme molecules, whilst the symmetry of the corresponding $A_{iso}(39,K)$ function (Fig. 10.3) implies that, up to the limit defined by the system, the extent of the cation-electron interaction is modified by equal amounts for each diglyme molecule added. On the basis of the present model, it can easily be shown that this symmetrical form for the $A$ function is expected only if $P_i$ (and therefore $P_j$) changes in equal steps upon successive additions of diglyme molecules.

Since any property $X_{obs}$ of the monomer can be written as

$$X_{obs} = P_i X_i + P_j X_j$$

the observation, from $A_{iso}(39,K)$ values, that $P_i$ and $P_j$ values change by equal steps with successive addition of diglyme molecules, leads to the conclusion that the asymmetric functions for $X = \Delta g, \Delta H(m_{1})$ and $\Delta H(0)$ are due to irregular changes in $X_i$ and $X_j$ with successive addition of diglyme molecules, as has been assumed in the preceding discussion.

The structures of the ion-pairs discussed in the present work resemble those proposed by Slates and Swarc$^{135}$ to explain their optical results for the ion-pair, $B^-Na^+$ (where $B^-$ represents the biphenyl radical anion) in glyme (E)/tetrahydropyran (or methyltetrahydrofuran) solvent mixtures, viz.
178.  

\[ B^{-}Na^{+} + E \rightleftharpoons B^{-}Na^{+}E \]
and \[ B^{-}Na^{+} + E \rightleftharpoons B^{-}ENa^{+} \]
with \( B^{-}Na^{+} \) corresponding to \( e^{-}K^{+} \) in the present work.

In conclusion, the present model for the monomer has the same weakness as all previous models in that, although qualitatively attractive, it is incapable of rigid quantitative analysis. Thus, the behaviour of \( \Delta H(m) \) can be fit on the basis of a two-state model, but these states can be either temperature-dependent species, as discussed in the present chapter, or solvent composition-dependent species, as discussed in Chapter 7, and, at the present moment, there is no way of distinguishing between the two.

6. In Table 10.2, the properties of the potassium monomeric species in ethylamine and tetrahydrofuran are compared with the corresponding properties in ammonia.
A comparison of the properties of the potassium monomeric species in ethylamine, tetrahydrofuran and ammonia.

<table>
<thead>
<tr>
<th>Property</th>
<th>THF</th>
<th>EtNH₂</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{K^+ e^-}$ (secs)</td>
<td>$1 \times 10^{-7}$</td>
<td>$3 \times 10^{-7}$</td>
<td>$\sim 10^{-12}$</td>
</tr>
<tr>
<td>$d_{K^+ e^-}$ ($\text{Å}$)</td>
<td>--</td>
<td>$4.4$</td>
<td>$6.9$</td>
</tr>
<tr>
<td>$A_{iso}^{(39K)}$ (gauss)</td>
<td>$29.7$</td>
<td>$9.3$</td>
<td></td>
</tr>
<tr>
<td>$\frac{dA_{iso}^{(39K)}}{dT}$ (C deg)</td>
<td>$0.123$</td>
<td>$0.116$</td>
<td>$\rightarrow 0$</td>
</tr>
<tr>
<td>$\Delta g$</td>
<td>$0.0010$</td>
<td>$0.0005$</td>
<td>$\rightarrow 0$</td>
</tr>
</tbody>
</table>

- $K^+$ - solvent interaction: fairly weak, strong, very strong.
- $e^-$ - solvent interaction: weak, weak, strong.

Spin-pairing interaction:
- dominant at $C \sim 10^{-6} \text{ M}$
- dominant at $C \sim 10^{-5} \text{ M}$
- negligible at $C < 10^{-3} \text{ M}$

Schematic representation of proposed structures.
39. J. Jortner, S.A. Rice, and E.G. Wilson, Colloque Weyl I (as ref. 13), P. 222.


52. R. Catterall, Colloque Weyl 11, Cornell Univ., June 1969; Pure and Appl. Chem. (Metal-Ammonia Symposium supplement) 1970 (paper 6) to be published.


54. R. Catterall, M.C.R. Symons and J.W. Tipping, Colloque Weyl 11, (as ref. 52), paper 25.


62. R. Catterall, L.P. Stodulski and M.C.R. Symons, Colloque Weyl 11, (as ref. 52), paper 9.


84. E.C. Evers and R. Haynes, Colloque Weyl 11, (as ref. 52), paper 10.
89. L.R. Dalton, unpublished result.
113. R. Catterall, private communication.
121. R. Catterall, *Nature*, to be published.
126. (as ref. 123), page 12.
ABSTRACT.

Solutions of potassium in ethylamine, tetrahydrofuran, diglyme and a series of solvent mixtures have been studied by electron spin resonance and optical spectroscopy.

Optical spectra consisted of a single maximum at 14,000 cm$^{-1}$ for solutions prepared in pyrex vessels, at 11,000 cm$^{-1}$ for solutions prepared in quartz vessels. Electron spin resonance spectra, in pure solvents and solvent mixtures, consisted of an equally-spaced quartet, attributed to the "monomer", $K_{\text{solv}}^+$, and a central singlet, attributed to the solvated electron, $e^-_{\text{solv}}$. For some solvent systems, a marked dependence of hyperfine quartet line-widths upon nuclear magnetic quantum number, $m_I$, was observed.

The dependence of the optical spectrum upon vessel material and the magnitude of electron spin resonance line-widths have been discussed in terms of the steady-state composition of the solutions. On the basis of results obtained in pure solvents and solvent mixtures, it is proposed that the monomer, in amine and ether solvents, is best represented as a solvent-separated ion-pair whose structure is modified at higher temperatures.