Unstable Intermediates. Part CIV.[1] Electron Spin Resonance Studies of Solutions of Lithium in Ethylamine–Diglyme Mixtures

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Solutions of lithium in ethylamine are characterised by two e.s.r. features, one, comprising nine hyperfine lines, assigned to coupling with four equivalent nitrogen nuclei, and another, a single narrow line, assigned to solvated electrons. Although no lithium hyperfine coupling was detected, the former unit is thought to be an electron associated with the ion $Li(EtNH_2)_4^+$. Addition of diglyme to such solutions gave an increase in the ^{14}N hyperfine coupling, but no change in the number of hyperfine lines in the concentration range for which the solutions were sufficiently stable for measurement ($\leqslant 0·56$ mol fraction diglyme). In contrast with pure ethylamine solutions, the ^{14}N hyperfine coupling from the diglyme solutions increased on warming. On cooling, clear blue glasses were formed, and the two e.s.r. signals merged into a single broad line with widths between points of maximum slope in the range 14—24 G. This is assigned to the solvated electrons, the widths being a measure of the overall hyperfine coupling to ^1H and ^{14}N.

Exposure of ethylamine–diglyme glasses to ^{60}Co γ-rays gave blue solids which, on bleaching with visible light, lost single e.s.r. lines having widths in the range 15—20 G. These units appear to be very similar to those obtained on freezing the lithium solutions.

THE observation that hyperfine features can be detected in the e.s.r. spectra of solutions of lithium in ethylamine[2] constituted an important step forward in our knowledge of metal solutions, since it has been clearly demonstrated[3] that these arise from hyperfine coupling to four ^{14}N nuclei. Although no hyperfine coupling to lithium nuclei (^7Li, 92·57, $I = 3/2$) was observed, it seemed certain that the four solvent molecules responsible for the interaction must be those of the solvated lithium ion, $Li(EtNH_2)_4^+$, since for solutions of other metals in this solvent, solvent exchange is very rapid and only exchange-narrowed lines are observed.[2,4] When ^6Li was used there was a small, but real, reduction in the line-widths, whence it was deduced that $A_{^7Li} \geqslant$ *ca.* ±0·05 G. We concluded[3] that the species responsible for the 9-line hyperfine pattern was probably not the monomer unit thought to be responsible for the e.s.r. spectra of the other alkali metals in ethylamine, whose e.s.r. spectra have relatively large and strongly temperature-dependent hyperfine coupling to the metal nuclei, but are better described as ion-pairs, in which the unpaired electrons are accommodated in cavities whose walls incorporate the solvated lithium ions. Perhaps the main reason for this assignment was the very large fall in the magnitude of the calculated spin-density on the cations on going to lithium, and the fact that there was no detectable increase in the coupling to lithium on warming, whereas for sodium or potassium marked increases are observed.[4] In order to explain the equivalence of the four solvent molecules bonded to lithium, we suggested that, in a relative sense, the unit rotates so that only one of the solvent molecules is involved with the unpaired electron at a given time. The remaining solvent molecules defining the electron's cavity then exchange rapidly, as usual.

The narrow central line was assigned to solvated electrons which are not associated with the cations. We have found, as required by equilibrium (1), that this central line is strongly favoured at very low metal

$$Li(EtNH_2)_4^+ + e^-_{solv} \rightleftharpoons Li(EtNH_2)_4^+e^-_{solv} \quad (1)$$

concentrations. For dilute solutions at low temperatures, this equilibrium is slow, and both species were detected. The broadening of all features at higher temperatures was assigned to the increased rate of exchange for (1). Again, for high concentrations, the life-times of specific ion-pairs falls below 10^{-6} s and only a single, broad line was detected.[3]

On going from ethylamine to butylamine the proportion of the single-line species fell nearly to zero, and the ^{14}N hyperfine coupling increased to about 4 G. Absence of the singlet accords well with equilibrium (1) since the less polar medium should strongly favour ion-pair formation.

The present work had two main aims: one was to examine the effect of a co-solvent upon the ^{14}N hyperfine coupling, and in particular to see if one or more of the solvent molecules responsible for the coupling could be displaced. Diglyme (diethylene glycol dimethyl ester) was therefore selected because it does not contain nitrogen, but is a good cation solvator.

The second aim was to probe the effect of freezing upon the e.s.r. spectra. We have endeavoured for many years to obtain solid metal–ammonia solutions having e.s.r. spectra assignable to the solvated electrons, but apart from a very narrow feature having a special environment, we have met with no success.[5] Even metal solutions in hexamethylphosphoramide, which freeze to blue glasses, had no clear e.s.r. features assignable to solvated electrons. Since ethylamine–diglyme solutions freeze to good glasses, it was expected that they would be ideal for such studies, and indeed, it seems that we have at last been successful in achieving this aim. This has enabled us to compare results with those for

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[1] Part CIII, M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 3205.

[2] K. Bar-Eli and T. R. Tuttle, *J. Chem. Phys.*, 1964, **40**, 2508.

[3] R. Catterall, M. C. R. Symons, and J. W. Tipping, *Pure Appl. Chem.* (Metal Ammonia Solutions Supplement), 1970, 317.

[4] R. Caterall, M. C. R. Symons, and J. W. Tipping, *J. Chem. Soc.* (*A*), 1967, 1234.

[5] R. Catterall, W. T. Cronenwett, R. J. Egland, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2396.

parallel radiation-damage studies. It has long been contended that there are close links between the trapped electron centres often formed in γ-irradiated glasses with those of solvated electrons in fluid solutions,[6] but no direct link has previously been obtained.

EXPERIMENTAL

Apparatus and techniques have been described.[7,8] Solvent composition was estimated by measuring the height of solvent induced into the calibrated main tube of the apparatus. Ethylamine was always introduced first. The amount of ethylamine in the vapour phase was calculated from the experimentally measured apparatus volume and the tabulated vapour pressure of ethylamine.[8] We assumed that the vapour pressure of ethylamine above the solvent mixture obeyed Raoult's law. Changes in the calculated mole fractions of digylme in the liquid phase in our samples were negligible within the temperature range in which observations were made.

Samples were irradiated with ^{60}Co γ-rays in a Vickrad source at a dose rate of about 4 Mrad h^{-1} for periods up to 1 h. E.s.r. spectra were obtained on Varian V4500-03 and E3 spectrometers.

RESULTS

Using a Pyrex apparatus we obtained e.s.r. spectra of dilute (*ca.* 10^{-4} mol l^{-1}) solutions of lithium in mixtures of ethylamine and diglyme between 182 and 239 K. We observed in all our experiments a nine-line pattern similar to that observed in previous studies of lithium ethylamine solutions [2,3] (Figure 1). This pattern was observed over only a restricted range of temperature. The nine lines broadened and merged into a broad single line at the extremes. As in the previous studies, we found the nitrogen hyperfine splitting constant of lithium–ethylamine solutions to be essentially independent of temperature, at least above the freezing range of the solution. However, the nitrogen hyperfine splittings of solvent mixtures had a marked positive dependence upon temperature and diglyme mole fraction. Our results are in Table 1. Figure 2 is a plot of nitrogen hyperfine splitting as a function of temperature for several solvent mixtures. The uncertainty in the measurements was greatest at the extreme temperatures.

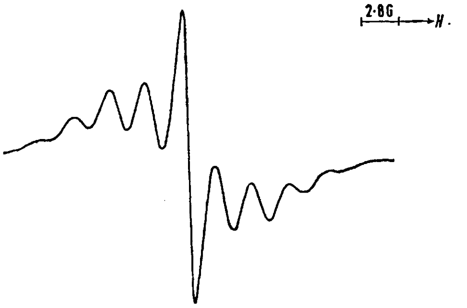

FIGURE 1 E.s.r. spectrum of ethylamine–diglyme mixture (0·32 mol fraction diglyme) containing lithium at 215 K

The presence of diglyme in lithium–ethylamine solutions greatly increased the rate at which they decomposed. We were unable to prepare blue solutions in 60% diglyme sufficiently stable to study. The measurements made upon the 56% diglyme solutions were much less reliable than the others because of rapid decomposition.

TABLE 1

Dependence of ^{14}N hyperfine coupling upon temperature for solutions of lithium in several ethylamine–diglyme mixtures; (1) and (2) represent distinct preparations

pure $EtNH_2$		6·8% diglyme (1)		6·8% diglyme (2)	
Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G
−89	2·41 ± 0·02	−91	2·74 ± 0·05	−88	2·48 ± 0·03
−80	2·50 ± 0·02	−85	2·57 ± 0·01	−83	2·53 ± 0·04
−70	2·51 ± 0·02	−79	2·58 ± 0·02	−79	2·63 ± 0·03
−63	2·52 ± 0·06	−74	2·58 ± 0·02	−73	2·67 ± 0·03
−58	2·53 ± 0·06	−69	2·66 ± 0·02	−69	2·68 ± 0·02
		−64	2·73 ± 0·02	−66	2·71 ± 0·04
		−59	2·73 ± 0·05	−64	2·74 ± 0·04
		−54	2·84 ± 0·11	−61	2·76 ± 0·04
		−49	2·78 ± 0·20	−59	2·77 ± 0·05
				−56	2·80 ± 0·04

15% diglyme		17% diglyme (1)		17% diglyme (2)	
Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G
−95	2·58 ± 0·02	−85	2·60 ± 0·03	−85	2·61 ± 0·03
−90	2·72 ± 0·02	−75	2·70 ± 0·03	−75	2·71 ± 0·02
−86	2·66 ± 0·02	−65	2·78 ± 0·04	−65	2·82 ± 0·05
−81	2·66 ± 0·03				
−76	2·70 ± 0·04				
−72	2·76 ± 0·04				
−69	2·77 ± 0·04				
−63	2·80 ± 0·04				
−60	2·86 ± 0·05				
−58	2·83 ± 0·07				
−55	2·88 ± 0·10				
−50	2·90 ± 0·05				

32% diglyme		42% diglyme		56% diglyme	
Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G	Temp./ °C	^{14}N h.f.s./G
−87	2·90 ± 0·03	−92	2·81 ± 0·06	−92	2·8 ± 0·2
−78	2·97 ± 0·03	−81	2·92 ± 0·04	−88	2·62 ± 0·07
−69	3·04 ± 0·02	−71	3·29 ± 0·03	−82	2·88 ± 0·05
−59	3·17 ± 0·04	−61	3·36 ± 0·04	−78	3·01 ± 0·03
−49	3·26 ± 0·05	−51	3·50 ± 0·06	−66	3·25 ± 0·05
−44	3·30 ± 0·06	−46	3·59 ± 0·04	−61	3·22 ± 0·05
−39	3·29 ± 0·18	−41	3·65 ± 0·03	−56	3·31 ± 0·04
−34	3·29 ± 0·14	−36	3·56 ± 0·15	−45	3·40 ± 0·04
				−36	3·46 ± 0·08

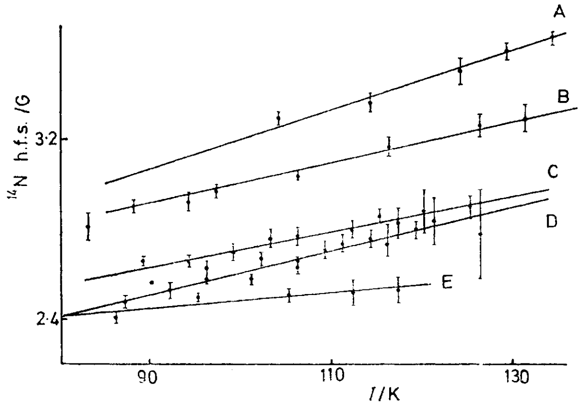

FIGURE 2 Variation in the ^{14}N hyperfine coupling for lithium–ethylamine solutions with temperature and added glyme; A, 0·42 mol fraction glyme; B, 0·32 mol fraction glyme; C, 0·152 mol fraction glyme; D, 0·068 mol fraction glyme; E, pure ethylamine

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[6] M. C. R. Symons, *Pure Appl. Chem.* (Metal Ammonia Solutions Supplement), 1970, 309.

[7] R. Caterall and M. C. R. Symons, *J. Chem. Soc.*, 1965, 6656.

[8] I. Hurley, Ph.D. Thesis, Brandeis University, 1970.

The hyperfine pattern persisted at temperatures considerably below the apparent f.p.s. At still lower temperatures a single-line spectrum was observed which broadened to a limiting value on further cooling and had the same *g*-value as that for the fluid solutions (Figure 3).

The *g*-value of the singlet in a 25% diglyme–ethylamine solution showed no variation with temperature below 240 K. This *g*-value agreed within experimental error with the *g*-value of the singlet of a lithium–ethylamine solution at 203 K (2·0009 ± 0·0001).

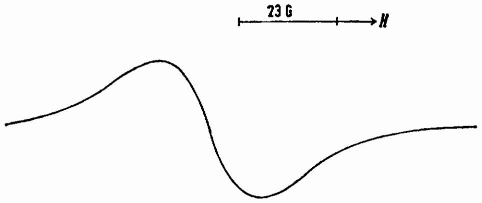

FIGURE 3 Typical e.s.r. spectrum for a lithium–ethylamine solution containing 0·068 mol fraction glyme at 77 K

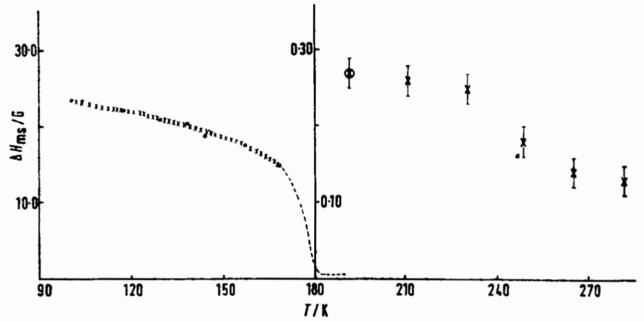

FIGURE 4 Variation in the width (ΔH_{ms}) of the singlet with temperature for a lithium–ethylamine solution containing 0·068 mol fraction glyme

The linewidth of the singlet in very dilute Li–EtNH$_2$ solutions ($\leqslant 10^{-5}$ mol l^{-1}) was found to increase with decreasing temperature (see Figure 4). The linewidth was measured at the lowest temperature at the beginning and end of the experiment and found to agree within 0·01 G, despite a loss of intensity by at least a factor of 10 during the experiment.

Some solid-state e.s.r. spectra, especially for the pure amines, had narrow lines characteristic of colloidal lithium superimposed upon the broad solvated electron line. The blue colours were not bleached on exposure to visible light from a tungsten filament lamp, in contrast with the results for the γ-irradiated materials. Exposure to light from a medium-pressure mercury lamp resulted in an increase in the intensity of the broad electron lines and a slight increase in width. These extra absorptions partially decayed in the dark.

TABLE 2

E.s.r. linewidths (ΔH_{ms}) for the singlet assigned to trapped electrons in γ-irradiated ethylamine–diglyme solutions and in solid solutions containing lithium

System	Li + EtNH$_2$	Li + BuNH$_2$						
Mol fraction of glyme			1·0	0·70	0·56	0·49	0·25	0·20
ΔH_{ms}	22 ± 5 [a]	23 ± 2	4 ± 0·5	4·5 ± 0·5	5 ± 0·5 [b] 15 ± 2	5·6 ± 1 [b] 15·5 ± 2	17·5 ± 2	19 ± 2
System	Li + EtNH$_2$ + glyme							
Mol fraction of glyme	0·068	0·152						
ΔH_{ms}	20 ± 2	23 ± 2						

[a] Varied with each preparation. [b] Two lines detected.

Irradiated samples had e.s.r. spectra at 77 K consisting of broad features of solvent radicals superimposed upon

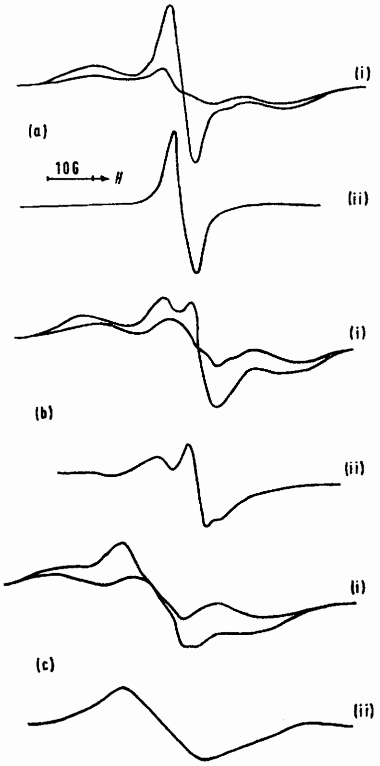

FIGURE 5 E.s.r. spectra (i) and difference spectra (ii) of γ-irradiated and bleached ethylamine–diglyme solid solutions at 77 K; (a) 1·0 mol fraction glyme; (b) 0·56 mol fraction; (c) 0·2 mol fraction

single central lines which were selectively lost on bleaching the blue glasses with light from a tungsten lamp (Figure 5). The widths of these singlets were estimated as described previously.[9] These are given for a range of solvent mixtures in Table 2. In the glyme-rich solutions two superimposed singlet lines were lost on bleaching, one having a width close to that for pure glyme and the other close to those for amine-rich solutions. This effect has previously

[9] W. T. Cronenwett and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 2991.

been observed in optical spectra, and probably reflects a partial phase separation on freezing to give regions of pure glyme.

DISCUSSION

Fluid Solutions.—The persistence of a nine-line hyperfine pattern indicated that there was no replacement of the four interacting amine molecules by ether molecules within the solvent composition range studied. The variation in nitrogen hyperfine coupling with solvent composition and temperature observed in solvent mixtures shows, nevertheless, that the paramagnetic species are considerably affected by the changes in composition.

These results seem to accord best with our ion-pair model, and certainly rule out the idea that the interacting amine molecules are part of the solvent shell of the electron with no specific interaction with lithium. Evidently, lithium ions are strongly preferentially solvated by ethylamine, and we have not been able to reach a concentration of glyme sufficient to effect partial displacement.

However, had the electron been closely bonded to this unit alone, we would not have expected the observed solvent sensitivity in A(N), which clearly shows that the paramagnetic entity is being modified. The increase in A(N) indicates that the electron is specifically attracted to the amine part of a well comprising amine and ether molecules. Thus the electron spends an increasing proportion of time close to the amines as the ether content increases. A similar model would explain the marked increase in A(N) as the bulk of the alkyl group R increases in RNH_2 solvents.[3]

Frozen Solutions.—Results for rigid solutions were not very reproducible, and features associated with fluid solutions were generally still found at temperatures several degrees below the rigidity point. This indicates partial phase separation, the extent of which depended upon the solvent composition and rate of freezing. Signals from the multiline species and the species responsible for the central line seemed to merge into single broad featureless lines which no longer displayed ^{14}N hyperfine structure. Despite the errors, the widths of these lines definitely decreased as the concentration of diglyme increased and, less clearly, as the percentage of the singlet species increased. The former result fits in with expectation that the solvent shells lose amine molecules in ether-rich solutions, and the latter shows that ^{14}N hyperfine coupling is certainly no smaller for the solvated electron than for the ion-pair unit.

γ-Irradiated Solvent.—The very similar widths and g-values for the curves subtracted on bleaching and the frozen metal solutions confirm the close similarity of these centres. We have long tried to establish this point for ammonia solutions unsuccessfully,[5] but the similarity certainly comes as no surprise.[6]

The radiolysis method has enabled us to study lithium-free solvents, but there is no marked difference, which supports our contention that all these species are structurally very similar, the role of the lithium cations being structurally minor. Also we have been able to move into the ether-rich regions in which lines of intermediate width between the 4 G for pure ether and *ca.* 15—20 G for pure amine were obtained. In some cases there were definite inflections on the e.s.r. derivative curves, suggesting the presence of hyperfine features separated by *ca.* 3—5 G but none was clear enough to warrant reproduction.

These results can be compared with those for γ-irradiated pyrrolidine[9] where, for the *N*-deuteriated material, clear ^{14}N hyperfine features were resolved. These showed that $A_{iso}{}^{14}N = ca.\ 5$ G and the anisotropy was small. Our present results confirm that anisotropic coupling to ^{14}N is not very significant, although that to the amino-protons is quite large.

Again, the value for A(N) for the lithium-containing species (2·5—4 G) is close to that for the electron in pyrrolidine (5 G). We suggest that, because of its tetrahedral structure, only two of the four amine molecules bonded to lithium are likely to interact with the electron in the ion-pair units at a given time. Relatively rapid rotation then averages these so that the observed, time-average, interaction would be half that for the static unit. This modification brings the results for the lithium complex and pyrrolidine remarkably close, again confirming the similarity of the units.

In complete contrast are the results for γ-irradiated triethylamine.[10] Here, lines about 4 G wide are assigned to trapped electrons. This width is the same as that observed for solid ethers, and suggests that $A(N) = 0$ in this case. It is significant that tertiary amines are not solvents for metals. It thus seems that N–H bonds are necessary for the appearance of a strong hyperfine coupling to nitrogen. This suggests that N–H bonding or antibonding σ-orbitals are involved, but brings us no closer to understanding the as yet unexplained result that the isotropic coupling to such protons is always small and negative.

The lack of photosensitivity of the frozen metal solutions in contrast with the ready bleaching of the γ-irradiated solvents is a surprising difference. It is probably connected with the fact that most of the colour in the frozen solutions is associated with electron pair units, whilst all the colour in the γ-irradiated solids is associated with electrons trapped singly. The sensitivity to u.v. light is probably associated with decomposition products such as amide ions, $EtNH^-$. It implies that there are still electron traps available in these rigid metal solutions, although their thermal sensitivity suggests that they are relatively shallow.

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[10] H. Tsujikawa, K. Fueki, and Z. Kuri, *J. Chem. Phys.*, 1967, **47**, 256.