

Solvated electrons: electron paramagnetic studies of solutions of lithium in ethylamine*

Martyn C. R. Symons^a and Fatai A. Taiwo^b

^a Department of Chemistry and Physics, Faculty of Applied Sciences, De Montfort University, The Gateway, Leicester, UK LE1 9BH

^b Department of Pharmacy, Faculty of Applied Sciences, De Montfort University, The Gateway, Leicester, UK LE1 9BH

Lithium metal dissolves in ethylamine to give stable blue solutions the EPR spectra of which showed the presence of a singlet assigned to solvated electrons, together with a nine-line spectrum assigned to $\text{Li}^+_{\text{solv}}\text{e}^-_{\text{solv}}$ ion pairs. The hyperfine splitting of *ca.* 2.5 G is assigned to four equivalent ^{14}N nuclei. There is no detectable coupling to lithium nuclei. In the region of 50% diglyme there is extensive displacement of two of the four amine ligands. Thus, in addition to the solvated electron centres, two ion pairs were detected, one showing hyperfine coupling to four ^{14}N nuclei and one to two ^{14}N nuclei. The hyperfine splitting remained constant at *ca.* 2.5 G. This result strongly supports a model in which it is the lithium ligands that give rise to coupling in the ion pairs. The diglyme displaces two amines at a time. There was no increase in the singlet, so the displacement of the second pair of amine ligands is not favourable.

One of the most remarkable chemical entities is the solvated electron. This species, in various forms, is unique in that, at least for most models, there is no 'central' set of nuclei around which the electrons occupy specific orbitals.¹ [The major exception is the model that places the unpaired electrons into orbitals centred on one (or more) solvent molecules, $\text{H}_2\text{O}^{\cdot-}$ being a key example.^{2,3}]

The earliest known system is that of dilute alkali metals in liquid ammonia.^{4,5} The resulting blue solutions are remarkably stable, but unfortunately the EPR spectra comprise single narrow lines which provide no structural information. However, solutions in amines, ethers and other aprotic solvents, though far less stable, have EPR spectra with some very informative hyperfine features, as summarised in Table 1. For the amines, hyperfine coupling to $^{23}\text{Na}^+$ and other metal nuclei is large, and increases markedly on heating.⁶ Only lithium fails to give any metal splitting, but, in contrast, the lithium solutions uniquely give hyperfine features from solvent ^{14}N nuclei.^{7,8} This is a unique result, and it was sometime before a model that could explain it was constructed. This model is essentially an ion pair (solvent shared ion pair⁹), in which one or two solvent molecules are shared. This is just one of many proposals for the structure of ion pairs involving solvated electrons. An alternative model comprises solvent-shared and more distant ion pairs,¹⁰ and expanded metal units.^{7,11,12} The former comprise fully solvated cations adjacent to fully solvated electrons. These are in contact for 'solvent shared' units, but more distant units are also considered. The latter comprise normal solvated cations, with the electron moving in an expanded orbital centred on the cation.

Our results rule out the former since these units are 'encounter' ion pairs with very low lifetimes. They also rule out the latter, since no hyperfine coupling to the lithium cations was obtained. However, the solvent-shared model is strongly supported by the present results. In this novel entity, shown in Fig. 1, the Li^+ ions are tetrahedrally solvated by four amine molecules (this is the normal mode of solvation for Li^+ ions) and the adjacent electron is solvated by about six solvent molecules, one or two of which are bridged between Li^+ and the electron. (In the following discussion we invoke two bridging solvent molecules, but there may only be one.)

Table 1 Hyperfine coupling to alkali-metal cations in amine solvents together with estimated spin densities

Nucleus	Hyperfine coupling (MHz)	$T/^\circ\text{C}$	% Atomic character
^7Li	0		0
^{23}Na	8.86	-30	1.0
	18.6	+10	2.1
	29.2	+29	3.3
^{39}K	26.6	-30	11.5
	28.2	+10	12.2
	36.2	+50	15.7
^{85}Rb	100.2	-30	9.9
	134.6	+10	13.3
	212.5	+50	21.0
^{133}Cs	317.2	+10	13.8

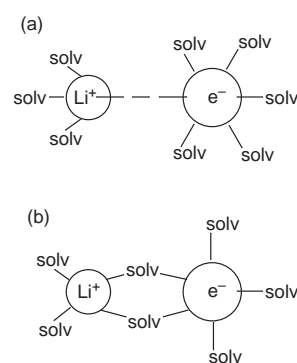


Fig. 1 Representations of the lithium cation–electron ion-pair species

Results and Discussion

EPR Spectral analysis

In the present extension we have analysed the EPR spectra for solutions of lithium in ethylamine–diglyme (2,5,8-trioxanonane) mixtures in the hope of detecting a change in the nitrogen-14 splitting from four equivalent nitrogen nuclei (for the experimental methods used see ref. 8). The solutions became progressively unstable as the concentration of diglyme increased and *ca.* 56% diglyme was the upper limit for EPR studies. The absence of metal hyperfine coupling in marked contrast with the results for the other alkali-metal cations shows

* Non-SI unit employed: $G = 10^{-4} \text{ T}$.

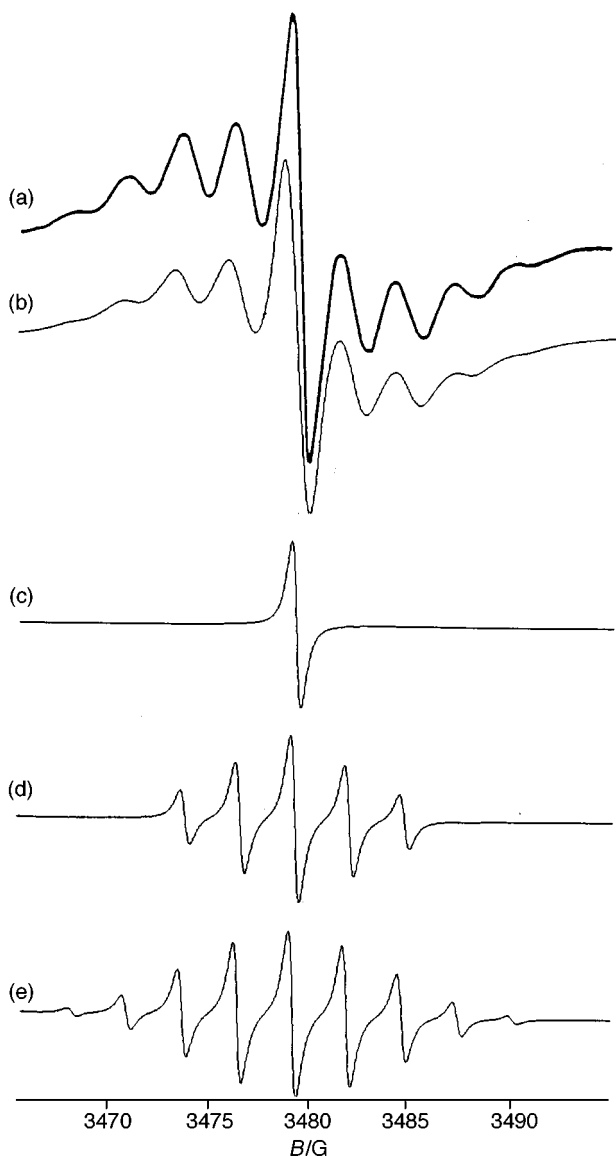


Fig. 2 (a) First-derivative EPR spectrum for the lithium–electron ion pair in a 56% diglyme–44% ethylamine solution, showing ^{14}N hyperfine features for the $(\text{EtNH}_2)_4$ and $(\text{EtNH}_2)_2$ complexes. (b) A computer simulation using a ratio of 4:3 for the $(\text{EtNH}_2)_4$ and $(\text{EtNH}_2)_2$ complexes; $A(^{14}\text{N})$ is invariant at 2.5 G. (c) A computer simulation of the narrow singlet for solvated electrons not in ion-pair species. (d) A computer simulation of the five-line spectrum for $(\text{EtNH}_2)_2$ complexes. (e) A computer simulation of the nine-line spectrum for $(\text{EtNH}_2)_4$ complexes. The best fit was obtained with a linewidth of 0.5 G

that these units must be separated ion pairs and not centrosymmetric units. Since the solvated electron centres for non-ion-pair units give a narrow singlet EPR spectrum, the interacting solvent molecules must be the shared molecules not the remainder, which will still exchange rapidly with bulk solvent. Since four equivalent ^{14}N nuclei are detected, these must be the primary solvent shell for Li^+ cations, which, because of the strong bonding to lithium, have long lifetimes on the EPR time-scale. This concept is fully supported by the results for solutions containing diglyme. These molecules solvate the Li^+ cations strongly, in a chelated unit. Hence only two ethylamine molecules remain, and only two bridging molecules with strong interaction with the unpaired electron are detected. Hence we suggest that for the pure ethylamine solution the $\text{Li}(\text{EtNH}_2)_4^+$ units rotate relative to the electron, so that all four become equivalent. When the chelating diglyme molecules add this still occurs, but now there are only two ^{14}N nuclei with hyperfine coupling.

A typical EPR spectrum for a 56% diglyme solution is shown in Fig. 2. This comprises a singlet from e^-_{solv} , a nine-line set

from the $\text{Li}(\text{EtNH}_2)_4^+$ solvates, but also a quintet of lines assigned to the unit $(\text{diglyme})\text{Li}(\text{EtNH}_2)_4^+$. The best simulation requires a ratio of 4:3 for the $\text{Li}(\text{EtNH}_2)_4^+$ solvates to the $(\text{diglyme})\text{Li}(\text{EtNH}_2)_2^+$. The contribution from the narrow singlet is quite noticeable. In the simulation for Fig. 2 we include the narrow singlet that is obtained for dilute solutions of lithium, together with the nine-line spectrum obtained for concentrated solutions in pure ethylamine, and the five-line spectrum that grows in with added diglyme. In arriving at this fit we used a range of widths, greater and smaller than those finally used which gave the best fit of all.

These results strongly support the model proposed, confirming that the amine and the diglyme are co-ordinated to the lithium ions, but that only two amine molecules bridge to the electrons. The contrast with the results for the other alkali metals is remarkable, with a complete switch from ^{14}N hyperfine splitting to hyperfine coupling to the metal nuclei. Thus it seems probable that for the latter species the electrons move extensively into the cation–solvent system, partially occupying the outer s orbitals of the cations. The spin densities on these cations increase markedly on heating, and on increasing the bulk of the alkyl groups. However we were unable to detect a clear change with temperature for the lithium solution.

These lithium solutions represent the limit in which this movement of the electrons to the cations is almost totally blocked by the strengths of the lithium–solvent bonds. However it is this strength that makes solvent exchange relatively slow, so that well resolved spectra result. Unfortunately, our results do not distinguish between one or two bridging solvent molecules. However, in view of the long lifetime required for the ion-pair units, two seems more probable. This is supported by comparison with our pyrrolidine results.

Comparison with irradiated pyrrolidine

When pyrrolidine glasses are exposed to ionisation radiation at 77 K they become deep blue, and display a strong EPR spectrum containing nine hyperfine features from four equivalent ^{14}N nuclei.¹³ This centre was identified as an electron trapped at a solvent cavity comprising four suitably located solvent molecules.

It is noteworthy that the ^{14}N hyperfine splitting was 5 G, which is exactly twice the value found for the lithium solutions discussed above. This again nicely fixes the number of shared ethylamine molecules as two. Thus, since all four of the liganded amines interact with the electron, ‘rotation’ must be rapid. Hence the hyperfine coupling should be 50% of the true coupling. This gives 5 G for the true value, exactly equal to the pyrrolidine value.¹³

References

- 1 M. C. R. Symons, *Chem. Soc. Rev.*, 1976, **5**, 337; F. S. Dainton, *Chem. Soc. Rev.*, 1975, **4**, 323.
- 2 H. F. Hameka, G. W. Robinson and C. J. Maesden, *J. Phys. Chem.*, 1987, **91**, 3150.
- 3 T. R. Tuttle and P. Graceffa, *J. Phys. Chem.*, 1971, **75**, 843.
- 4 W. Weyl, *Pogg. Ann.*, 1864, **121**, 601; **123**, 350.
- 5 C. A. Krauss, *J. Am. Chem. Soc.*, 1908, **30**, 1323.
- 6 R. Catterall, M. C. R. Symons and J. W. Tipping, *J. Chem. Soc. A*, 1967, 1234.
- 7 K. Bar-Eli and T. R. Tuttle, *J. Chem. Phys.*, 1964, **40**, 2508.
- 8 R. Catterall, M. C. R. Symons and J. W. Tipping, *Pure Appl. Chem.*, 1970, 317.
- 9 T. Griffiths and M. C. R. Symons, *Mol. Phys.*, 1960, **3**, 90.
- 10 R. Catterall, M. C. R. Symons and J. W. Tipping, *J. Chem. Soc. A*, 1966, 1529.
- 11 R. Catterall and P. P. Edwards, *J. Phys. Chem.*, 1975, **79**, 3010.
- 12 R. Catterall and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1972, 139.
- 13 W. T. Cronenwett and M. C. R. Symons, *J. Chem. Soc. A*, 1968, 2991.

Received 16th January 1998; Paper 8/00471D