Unstable Intermediates. Part XCIX.[1] Solvated Electrons in Solid Metal–Ammonia Solutions

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Rapid freezing of metal–ammonia solutions, containing added salt to inhibit solvent crystallisation, gave blue solids whose e.s.r. spectra were generally characterised by three distinct features: (i) an intense narrow, line with g 1·9992 and ΔH_{MS} 0·035 G; (ii) a broad singlet associated with colloidal metal particles; and (iii) a triplet probably associated with ^{14}N nuclei.

The narrow line is thought to have considerable significance since there must be rapid effective nuclear exchange in order that the expected hyperfine coupling to ^{1}H and ^{14}N nuclei of the solvent be averaged almost to zero. We suggest that electron transfer between one- (e_1) and two-electron (e_2) centres: $e_1 + e_2 \rightleftharpoons e_2 + e_1$, is rapid, even at 77 K, and that this leads to effective nuclear averaging without limiting the spin lifetimes. Possible assignments for the triplet are discussed.

SOLIDIFICATION of dilute metal–ammonia solutions normally results in phase separation, the solutions being effectively destroyed. However, it was reported [2] that addition of alkali-metal salts to metal–ammonia solutions helped to prevent phase separation, and solids with definite blue colours were obtained. Nevertheless, the predominant e.s.r. absorption for these frozen solutions was caused by colloidal metal, and so new information relating to the structure of the solutions resulted.

We now describe the results of studies to prevent phase separation sufficiently for e.s.r. spectra associated with solvated electrons to be obtained. It was hoped that the results would help to link the extensive studies of fluid solutions to those of u.v.- or γ-irradiated glasses such as hydrated sodium hydroxide,[3] ethanol,[4] and ethers,[4] all of which are thought to give rise to electron centres which closely resemble those in fluid solution.[5] A preliminary report of some aspects of our studies has appeared.[6]

EXPERIMENTAL

Solutions of alkali metals in ammonia containing various alkali-metal halides were prepared *in vacuo* as outlined previously.[7] All the alkali metals except rubidium were used, together with a range of their chloride, bromide, and iodide salts. These were cooled to 77 K by the following procedures: (i) by sealing in very thin-walled Pyrex capillary tubes *in vacuo*, cooling initially to 195 K, and then plunging into liquid nitrogen, (ii) as (i), but the tips of the capillaries were removed and the solutions sprayed into liquid nitrogen to give minute blue beads, (iii) solutions were prepared in air, and pipetted into liquid nitrogen to give blue beads, or (iv) solutions were pipetted on a copper block at 77 K and the resulting blue film scraped off under nitrogen into the e.s.r. sample tubes.

Metal amide solutions were prepared by allowing the corresponding metal–ammonia solutions to decompose completely. These were exposed to ^{60}Co γ-rays at 77 K at dose rates of 0·14 Mrad h^{-1} for several hours.

E.s.r. spectra at X-band frequencies were obtained by use of Varian V 4052 and E 3 spectrometers, and the widths of the narrow features were measured on the V 4052 instrument by use of a superherteodyne technique to eliminate broadening from the 100 KHz modulation. Temperatures were controlled with a Varian variable temperature accessory. S-Band spectra were obtained with a spectrometer constructed in these laboratories and described elsewhere.[8]

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[1] Part XCVIII, M. C. R. Symons, preceding paper.

[2] H. C. Clark, A. Horsfield, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 2478.

[3] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4352.

[4] M. J. Blandamer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 1127.

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

[6] R. Catterall, *Phil. Mag.*, 1970, **22**, 779.

[7] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4342.

[8] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

RESULTS

Results are summarised in the Figures and Tables. Feature *A* consists of a very narrow singlet having *g* 1·9992. Feature *B* is a pair of shoulders having the form expected for parallel features, separated by 76 G, and probably associated with at least part of the central portion of the spectrum, which varied with the nature of the salt and is labelled collectively, *C*. Feature *D* is a triplet of relatively narrow lines separated by *ca.* 14 G, which only appeared close to the softening region of the glasses. Feature *E* is a singlet whose width depended upon the nature of the metal.

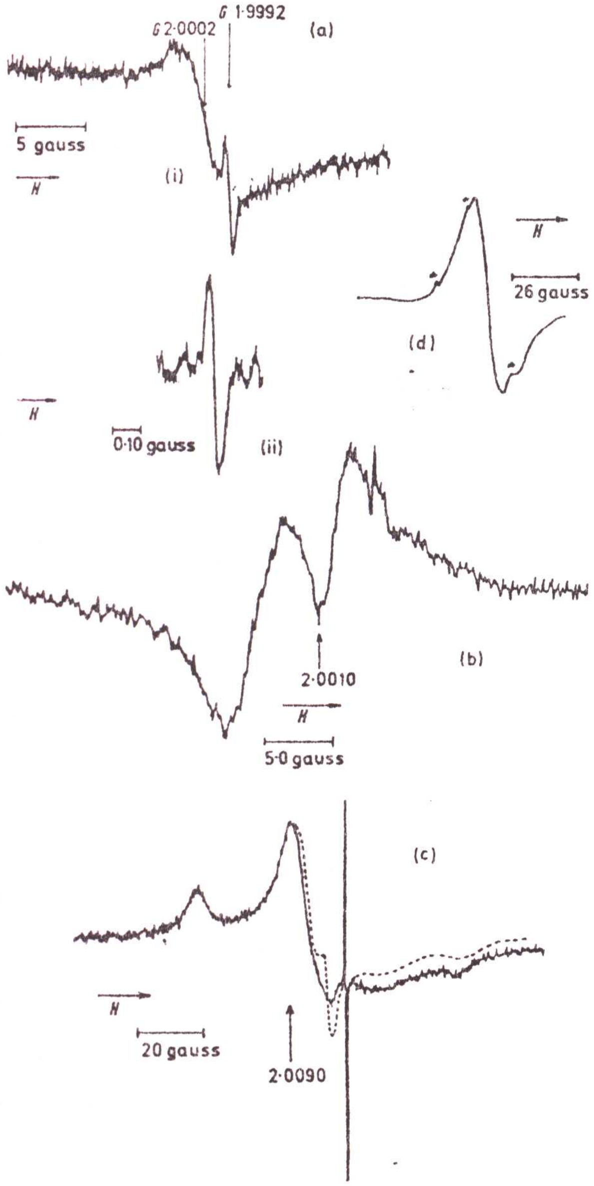

FIGURE 1 First-derivative e.s.r. spectra for various frozen metal–ammonia solutions. (a) Potassium + potassium bromide in ammonia, prepared *in vacuo*, showing mainly species *A*, *C*, and *E* (77 K). (b) Sodium + sodium iodide in ammonia, showing, from left to right, species *C*, *E*, and *A* (77 K). (c) Potassium + potassium bromide (full line) and potassium iodide (dashed line), both showing species *B* (outer shoulders), together with species *C* and *E*, and *A* (77 K). (d) Potassium + potassium bromide at 170 K showing species *D* (three narrow lines marked with an asterisk)

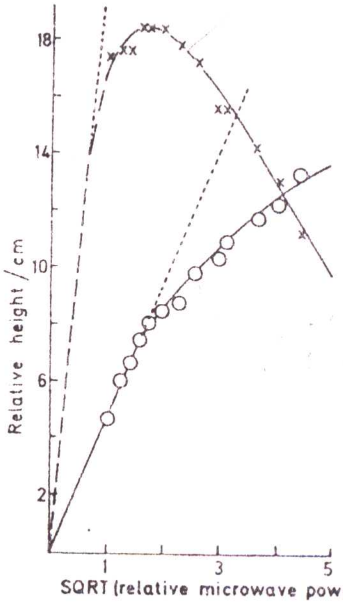

FIGURE 2 Saturation behaviour of the narrow line (species *A*) (crosses) and the central line (species *C* + *E*) (open circles), for solutions of potassium and potassium bromide in ammonia at 77 K

TABLE 1

E.s.r. parameters at 77 K of colloidal metal species in sodium–ammonia solutions containing added salts

Metal concn.[a]	Salt concn.[b]		ΔH_{MS}/G[c]	*g*-Value[d,e]
0·1			2·12	2·0011
0·3	NaI	0·40	2·33	2·0010
0·2	NaI	1·51	2·57	2·0012
0·1	NaI	2·13	5·55	2·0015
0·001	NaI	2·63	2·24	2·0012
0·01	NaBr	0·20	2·18	2·0010
0·2	NaBr	0·80	2·28	2·0013
0·2	NaBr	1·23	2·40	2·0010
0·01	NaI	1·52	2·21	2·0016
0·01	$NaNH_2$		2·0	2·0009

[a] Molality, ±25%. [b] Molality, ±10%. [c] ±0·1 G. [d] ±0·0002. [e] All lines were Lorentzian except where stated. [f] Asymmetric.

TABLE 2

E.s.r. parameters for species *B* obtained at *X*- and *S*-band frequencies, together with typical results for NO_2^{2-} radical ions

Matrix	*T*/K	$A_{\parallel}$/G	$A_{\perp}$	$g_{\parallel}$	$g_{\perp}$
NH_3[a]	77	38 ± 0·5	~0 ± 4 G	2·0020 ±0·0005	2·006 ±0·002
NH_3[a]	184[b]	A_{iso} = 13 ± 0·5		g_{av} = 2·0040 ± 0·0002	
KCl[c]	77	30·9	6·0 ± 1	2·0038	2·0099
KCl	R.T.	A_{iso} = 13·7			2·0070

[a] This work. [b] Narrow lines, ΔH_{MS} = 1·5 G, formed reversibly on warming from 77 K. Parallel and perpendicular features reappear on cooling. [c] C. Jaccard, *Phys. Rev.*, 1961, **124**, 60; P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 1962, 4794.

When solutions of metals in hexamethylphosphoramide, prepared as described previously[9] were rapidly cooled to 77 K, blue solids were obtained, but the e.s.r. signals were simply characteristic of colloidal metal. No narrow singlets resembling *A* were detected.

The e.s.r. spectra obtained from γ-irradiated amide solutions were dominated by hyperfine features characteristic of NH_2 radicals, but on exposure of the solids to light from a tungsten filament lamp features corresponding to those labelled *B* and *C* were lost. There was no evidence for the formation of trapped electrons.

A variety of attempts to bleach or photolyse the blue solids were made, using visible or u.v. light, but to no avail. In no instance was the colour diminished, as judged visually, and the e.s.r. spectra were not modified. Similarly, careful annealing before or after such exposure to light produced no detectable change.

In a further set of experiments, layers of water were deposited at 77 K on frozen sodium–ammonia solutions which had an e.s.r. spectrum characteristic of colloidal sodium. On carefully controlled annealing followed by rapid recooling to 77 K, the onset of reaction gave no extra e.s.r. lines. Similar negative results were obtained using ethanol in place of water.

The narrow feature *A* was very readily saturated, as indicated in Figure 2. The other features were only affected at much higher powers, being comparable in this respect with normal radicals.

DISCUSSION

Quite the most interesting and unexpected feature of these results is the detection of the very narrow line, *A*. This feature was only detected when the concentration of metal was quite high (*ca.* 0·4M) and when good blue glasses were formed. Despite its prominence in some spectra (*cf.* Figure 1c) it only represents a very small proportion of the total paramagnetic material, and the species responsible for it is certainly not also responsible for the blue colour, although it could contribute. The e.s.r. absorption lines for fluid metal solutions are very narrow because hyperfine interactions, especially to ^{14}N nuclei which are known to be large from n.m.r. measurements, are completely destroyed by very rapid exchange processes. Also, all dipolar interactions are averaged to zero both by these exchange processes and by rapid tumbling of the interacting solvent molecules. It is hard to believe that direct exchange of solvent molecules can be rapid in the solid state at 77 K. We therefore expected to obtain e.s.r. lines broadened both by scalar and dipolar hyperfine interactions to ^{1}H and ^{14}N nuclei, and possibly also by interactions with the cation and anion nuclei of the added salts. Such broadening is certainly detected when electrons are trapped at anion vacancies in alkali-metal halide crystals, or in cavities in solid alcohols, ethers, *etc.*[3-5] Furthermore, very narrow lines have never been detected in such irradiated systems, so far as we are aware. It is this contrast with which we are primarily concerned.

The difference between the present system and those just discussed is that by far the major concentration of 'solvated' electrons in the fluid, and presumably also in the solid solutions, is in some diamagnetic form. There is considerable controversy regarding the structure of the spin paired species in metal ammonia solutions, the four main models being the e_2^{2-} or confined cavity model,[10] the M^- model,[11] the $(M^+e^-)_2$ model,[12] and a model which has been described as arising primarily from long-range spin-exchange interactions between e_1 centres.[13] We will describe this as the 'spin-exchange' model.

We have previously presented arguments against the M^- concept for metal–ammonia solutions, and in favour of the e_2^{2-} model,[10] which strongly resembles the *F′* centre in alkali-metal halides. This model seems to provide a key to understanding our present solid-state results, providing the cavities containing two electrons closely resemble those containing single electrons. That this could be the case seems reasonable: the size of the cavities is, we believe, largely controlled by the medium, depending strongly upon the number of solvent molecules that can conveniently describe the required sphere without producing too great solvent–solvent repulsions or too much disruption of solvent structure. The dielectron cavity could be smaller than that of single electrons if the electrostrictive forces dominate, or somewhat larger if electron–electron repulsion dominates. The fact that the optical absorption is hardly modified on pairing strongly suggests that these effects largely cancel, and the two types of cavity remain comparable.

If this is accepted, then the reaction

$$e_1^{(\alpha)} + e_2^{(\alpha\beta)} \rightleftharpoons e_2^{(\alpha\beta)} + e_1^{(\alpha)} \qquad (1)$$

should be facile both in the liquid and solid states. Provided the concentration of e_2 centres is sufficiently high, which will certainly be the case for the relatively concentrated solutions needed to give the narrow singlet, then reaction (1) will lead to conservation of electron spin (α), but very rapid exchange of nuclei. Electron–electron spin–spin broadening will be unimportant since the concentration of e_1 centres undergoing exchange is very low, and the e_2 centres are all diamagnetic.

Thus it seems that our previous theory involving e_1 and e_2 species can be invoked to give a reasonable explanation for the narrow singlet (*A*). The more controversial 'spin-exchange' model can also be modified so as to accommodate the results. This has been outlined by one of us elsewhere,[6] and therefore will not be elaborated here.

Although equilibrium (1) serves to explain the very small linewidth, it does not, so far as we are aware, provide an explanation for the low *g*-value, which is quite

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[9] R. Catterall, L. P. Stodulski, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 790.

[10] R. Catterall and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 13.

[11] S. Golden, C. Guttman, and T. R. Tuttle, *J. Amer. Chem. Soc.*, 1965, **87**, 135.

[12] M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1962, **84**, 2264.

[13] J. L. Dye, ref. 5, p. 1.

clearly less than that for fluid solutions, even when the low temperature is taken into consideration. Certainly, alkali-metal halides cause negative g-shifts, but these increase markedly on going from chloride to iodide,[7] and there is a parallel increase in linewidth. In contrast, the present shift was independent of both the metal and the nature of the added salt, and the width was invariant at 0·035 G. The shift may be associated with a change in the size or form of the cavities on freezing, and we hope to probe this aspect by studying the near-i.r. and visible spectra of the glasses. If the unpaired electrons are moving rapidly over a range of sites as implied by equation (1), then the measured g value is probably an average. Nevertheless, its remarkable constancy implies the formation of very precise units, in which the component ions of the added salts are not intimately involved. It is possible that some phase-separation has occurred on freezing, despite the precautions taken. We stress that, if equation (1) is operative, the unpaired electron will be predominantly in cavities stemming from e_2 species in the fluid solutions. These may differ sufficiently from the e_1 cavities to cause the small extra negative g-shift.

The features labelled B, C, and D have proven most difficult to identify. The S-band results show clearly that the outer shoulders (B) and the triplet (D) are caused by hyperfine interaction rather than by g-value variations. Initially, we looked for a fourth feature, since coupling to metal nuclei (both ^{23}Na and ^{39}K have $I = \frac{3}{2}$) was expected, but none could be found. It is certainly possible that the weak triplet (D), which shows marked broadening on the high-field side (Figure 1d) is really part of a quartet, the highest-field line being too broad to detect. This could arise because of selective relaxation effects, but since coupling to alkali metals is usually almost isotropic it seems unlikely.

We favour the postulate that both B (together with part or all of C) and D are associated with a radical containing one strongly interacting ^{14}N nucleus, the former being stationary and the latter rapidly tumbling. In that case we deduce from B and C that $A_{\parallel}(^{14}\text{N}) = 38$ G, $g_{\parallel} = 2{\cdot}002$, $A_{\perp}(^{14}\text{N})$ *ca.* 0 and $g_{\perp} = 2{\cdot}005$. This gives A_{iso} *ca.* 13 G and $g_{\text{av}} = 2{\cdot}004$, whilst D gives $A_{\text{iso}} = 13$ G and $g_{\text{av}} = 2{\cdot}004$. The fact that both sets of lines were obtained in some instances in the same e.s.r. spectrum can be understood in terms of the softening process for such solids, which frequently results in zones of fluid co-existing with solid. This seems to confirm our earlier contention that some phase-separation occurs on freezing.

The nature of the species responsible for these features is unknown. We do not believe it to be a fundamental property of metal solutions, since in some experiments especially using method (i) it was not formed, but, rather, a radical formed from what must be a common impurity. One possibility which we suggest very tentatively is NO_2^{2-} (see Table 2), which would be formed from any nitrogen dioxide present in, for example, liquid nitrogen. Unfortunately, we have been unable to prepare solutions containing NO_2^{2-} in ammonia because its salts are insoluble.[14] They are, however, soluble in hexamethylphosphoramide, but the resulting e.s.r. spectra always comprised a very broad singlet rather than the expected triplet. Thus the narrow lines obtained in this work (Figure 1d) are remarkable. If our contention is correct, that this species is purely a red herring so far as the present investigation is concerned, then we feel that further discussion is unwarranted.

It is most probable that the lines labelled E are caused by the formation of colloidal metal. The results (Table 1) are similar to Levy's,[15] who also noted a marked, and unexpected, temperature dependence for the line associated with potassium.

This leaves a residual feature, in the free-spin region, which is usually hidden by the central part of the ^{14}N triplet and the colloidal metal line, C. Its properties seem to be markedly dependent upon the nature of the added salt, and, although it could possibly be a property of the elusive solid-state e_t species responsible for the liquid-phase absorption line, it is more likely to be associated with some further unidentified impurity. Its formation was not very reproducible and because of masking by other features, its characteristics were difficult to obtain. We do not consider that detailed interpretation of the line-width in terms of an e_t unit is warranted.

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[15] R. A. Levy, *Phys. Rev.*, **1956**, **102**, 31.