689. *Unstable Intermediates. Part XXXI.* Solvated Electrons: Solutions of Europium in Ammonia*

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The blue solution that results when europium metal dissolves in ammonia has been studied by optical and electron spin resonance spectroscopy. It is found that dilute solutions can best be described in terms of europium(II) cations and solvated electrons. That separate spin resonance spectra can be observed for these two species leads to the conclusion that they are well separated in the form of loose ion-pairs rather than as centrosymmetric units similar to the monomer described by Becker, Lindquist, and Alder.[1]

Europium metal has been reported to dissolve in liquid ammonia to form a blue solution,[2] and one aim of this research has been to determine whether this solution is comparable to those of the alkali and alkaline-earth metals.[3] It has been suggested[2] that the solubility of europium is related to its relatively low density and high volatility, and to the high stability of the europium(II) ion ($4f^7$ configuration). This solution thus appears to be analogous to those of the alkaline-earth metals, but is unique in that the cation itself is paramagnetic.

A second aim has been to probe the nature of the paramagnetic, non-conducting species which has been postulated[4] to account for the magnetic[5] and conductometric[4] properties of metal solutions. Two models have been suggested for this unit, a loose ion-pair,[6] and a monomer[1] having a relatively high spin-density on the cation. Although recent nuclear magnetic resonance studies of ammonia solutions[7] and electron spin resonance studies of amine solutions[8] appear to favour a centrosymmetric monomer, this conclusion is not compelling.[9] Addition of excess of cations (as alkali halides) to the solutions in an attempt to constrain the equilibria was complicated by a strong electron–anion interaction.[10] In europium solutions, the paramagnetic cation can act as a probe for differentiating between the two models.[11]

Interactions between paramagnetic ions of opposite charge in aqueous solutions at room temperature have been studied by Pearson and Buch,[12] who used paramagnetic metal salts of diamagnetic anions and potassium nitrosyldisulphonate, $2K^+[ON(SO_3)_2]^{2-}$. The three narrow lines ($\Delta H_{ms} = 0{\cdot}35$ gauss, $|A|_N = 13$ gauss) obtained from the dilute nitrosyldisulphonate solutions are broadened by increasing concentration of paramagnetic cations [such as the hexa-aquochromium(III) ion] at an initial rate of about 1000 gauss mole^{-1}. This contrasts markedly with the initial self-broadening of 10 gauss mole^{-1} associated with increase of anion concentration in the absence of a paramagnetic cation. Lanthanide ions in general were much less efficient in broadening the anion resonance, with the exception of the hexa-aquogadolinium(III) ion [$4f^7$, isoelectronic with europium(II)], which showed a strong broadening effect identical with that of the transition-metal ions.

The ground state of the europium atom ($4f^7 5s^2 5p^6 6s^2$) and the bivalent ion ($4f^7 5s^2 5p^6$) are both spherically symmetrical ($^8S_{7/2}$). Hyperfine structure of the electron spin resonance absorption arising from interaction with the nuclear magnetic dipole was first observed by Bleaney and Low,[13] but fluid solutions have not been studied by this technique. Magnetic parameters for the ion in various host crystals are collected in Table 2. Individual hyperfine components in crystals are sufficiently narrow to allow resolution of two sextets from the two naturally occurring europium isotopes (Table 2).

The two broad absorption bands of the europium(II) ion in the near ultraviolet, which are attributed[14,15] to the $4f^7 \longrightarrow 4f^6 5d^1$, or possibly[14,16] to the $4f^7 \longrightarrow 4f^6 6s$ transitions, show a marked dependence on the nature of the host lattice.[14–17] The lower-energy band is characterised by a tail that extends into the visible and sometimes shows underlying

* Part XXX, M. J. Blandamer, L. Shields, and M. C. R. Symons, preceding Paper.

structure. In addition, sharp bands in the 31,000 cm.$^{-1}$ region have sometimes been recorded (Table 1).

Solutions of the europium(III) ion in water, methanol, and ethanol show characteristic visible absorptions [18] at 17,240, 19,050, and 21,510 cm.$^{-1}$.

Experimental

Materials.—Europium metal of 99·9% purity and reagent grade liquid ammonia were employed. The purification of the ammonia and the treatment of glassware have been described elsewhere.[10] Since europium metal cannot be distilled in Pyrex vessels, clean pieces of metal were cut and transferred under dry, oxygen-free petroleum ether, which was finally removed under high vacuum.

Preparation of Solutions.—Solutions of europium metal in liquid ammonia were prepared by conventional high-vacuum techniques and a modification of the method described for alkali-metal solutions.[10] The solutions strongly resemble those of calcium in their affinity for ammonia, and in their tendency to phase-separation at high temperatures. 0·1M-Solutions were prepared by mixing known amounts of ammonia and metal; more dilute solutions were prepared by dilution of 0·1M-solutions, or by decomposition of metal solutions to the amide. Samples for optical and electron spin resonance spectroscopy were sealed in 4 mm. diameter Pyrex tubing and stored at 77°K.

Solutions of europium(II) iodide were prepared under conditions of high vacuum by decomposing solutions of the metal in liquid ammonia with an approximately equimolar quntity of ammonium iodide. A bulky, yellow, crystalline solid was precipitated, leaving a pale yellow solution. The iodide was observed to be considerably more soluble at higher temperatures, and samples for spectroscopy were prepared by decanting the saturated solution at −78°. More dilute samples were prepared from these solutions by the addition of an approximately five-fold excess of ammonia. Samples were sealed in 4 mm. diameter tubing before being warmed to room temperature. It has been observed that europium(II) salts decompose slowly in aqueous solution,[14] but no such behaviour was observed in liquid ammonia, and samples were stored at room temperature.

Electron Spin Resonance Apparatus.—The 3 cm. apparatus used has been described previously.[10,19] Measurements at −23 and −78° were made by surrounding the microwave cavity with a bath of solid–liquid carbon tetrachloride or of solid carbon dioxide ethanol.

Optical Absorption Measurements.—Optical spectra from the near ultraviolet to the near infrared were measured at room temperature with a Unicam S.P. 700 double-beam, recording spectrophotometer. The position of the infrared maximum was located by reference to the ammonia absorptions near 5000 cm.$^{-1}$. Samples were contained in cylindrical Pyrex cells of approximately 4 mm. internal diameter, the reference beam passing through a similar cell (made from the same length of tubing) containing liquid ammonia.

Results

Europium(II) Iodide Solutions.—Optical absorption spectra. The solutions showed a weak absorption band at 27,400 cm.$^{-1}$ with a broad, structureless, low-energy tail extending into the visible. This band is identified with the lower-energy transition reported previously for the europium(II) ion (Table 1) and has an extinction coefficient of approximately 4: the work of Low [15] indicates a value of about 10. A sharp band at 31,400 cm.$^{-1}$, similar to bands observed in aqueous solutions [14] and in calcium fluoride [15] (Table 1), is attributed to a weak, forbidden transition within the f^7 configuration of europium(II). The optical cut-off at 34,000 cm.$^{-1}$ is presumably due to the intense iodide charge-transfer-to-solvent absorption [20] (37,000 cm.$^{-1}$ at room temperature in liquid ammonia), the higher-energy europium(II) absorption, and solvent absorption.

No visible absorption bands characteristic of the europium(III) ion were observed.

Electron spin resonance spectra. The parameters (Table 2) derived from the resolved hyperfine components of the spectra at room temperature and −78° (Figures 1*a* and *b*) are very similar to those found for the europium(II) ion in other media (Table 2). These spectra are identical with those obtained by Lorentzian reconstruction (Figure 1*c*) from the observed hyperfine splitting constants and *g*-factor (Table 2) and line-widths of 15

TABLE 1

Absorption bands of the europium(II) ion in various media

Medium	$\nu_{max.}$ ($cm.^{-1}$) Strong, broad bands I	II	Weak, narrow bands		Ref.
CaF_2	29,000	45,050	24,200	32,300	15
			35,400	37,000	
CaF_2	27,150	45,050			16
SrF_2	27,870	43,480			16
BaF_2	28,470	42,700			16
NaCl	29,410	41,530			*a*
KCl	29,730	41,370			*a*
KCl	29,150	40,130			17
KBr	29,730	38,140			*a*
KBr	29,000	40,210			17
$SrCl_2$	30,570	—			*b*
H_2O	31,200	40,320	30,960	31,200	14
			31,450	31,700	
EuI_2–NH_3	27,400	*c*	31,400		*d*
Eu metal–NH_3 [e]	27,400				*d*

[a] J. Kirs and L. A. Niilisk, *Trudy Inst. Fiz. i Astron. Akad. Nauk Est., S.S.R.*, 1962, **18**, 36. [b] S. Freed and S. Katcoff, *Physica*, 1948, **14**, 17. [c] Masked by absorption of iodide ions and solvent. [d] This work. [e] An additional band, at 5600 $cm.^{-1}$, arises from a transition of the solvated electron.

and 25 gauss, respectively. The widths of the hyperfine components in solution are appreciably greater than those observed for the ion in strontium sulphide [13] (4 gauss) and in barium fluoride [21] (6 gauss).

Europium Metal Solutions.—Decomposition products. The fading of the blue colour of dilute solutions is accompanied by the precipitation of an orange, flocculent solid, presumably europium(II) amide. No trace of the optical absorptions of amide or of europium(II) ions could be detected in the fully decomposed solutions. Also, no electron spin resonance absorption due to the europium(II) ion could be found. We conclude that the solubility of the decomposition products is negligible for the purpose of this work.

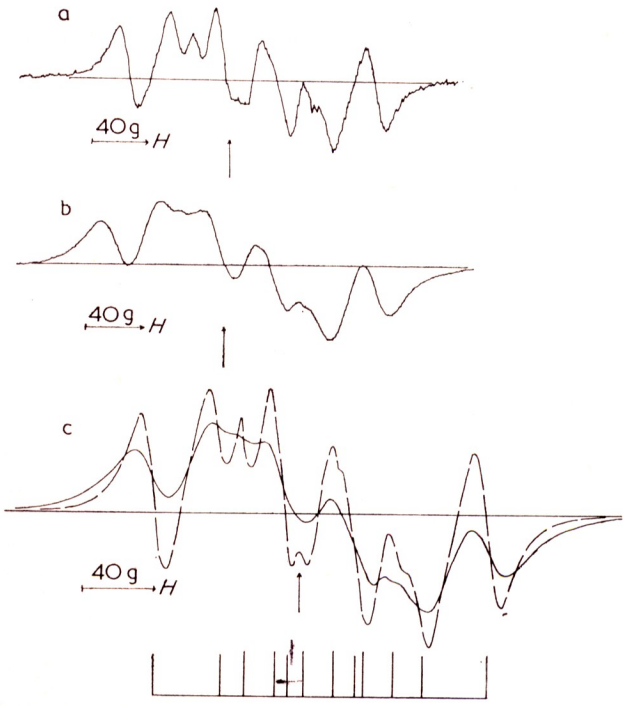

FIGURE 1. Electron spin resonance spectra of dilute solutions of europium(II) iodide in liquid ammonia: *a*, room temperature; *b*, −78°; *c*, obtained by Lorentzian reconstruction from the observed hyperfine splitting constants and *g*-factor (Table 1) and line widths of 15 and 25 gauss; $g = 2{\cdot}000$ is indicated by the vertical arrow.

TABLE 2

Electron spin resonance characteristics of the europium(II) ion in various media

Medium	Temp. (°K)	g-Factor	^{151}Eu|A| [a] (10^{-4} cm.$^{-1}$)	^{153}Eu|A| [b] (10^{-4} cm.$^{-1}$)	Ref.
SrS	R.T.[c]	1·9912(10) [d]	30·82(20)	13·79(20)	13
BaF_2	77	1·993(1)	33·5(6)	14·9(6)	21
CaF_2	13	1·9926(3)	34·3263(4)	15·2350(8)	*e*
EuI_2–NH_3	R.T.	1·9921(4)	32·90(10)	14·60(10) [f]	*g*
EuI_2–NH_3	195	1·993(1)	33·0(3)	—	*g*
Eu metal–NH_3	R.T.	1·992(1)	33·1(3)	—	*g*
Eu metal–NH_3	195	1·9922(4)	32·96(10)	—	*g*

[a] ^{151}Eu; natural abundance 47·77%, nuclear spin × $(h/2\pi) = 5/2$, nuclear moment × $(eh/4\pi) = 3·4$. [b] ^{153}Eu; natural abundance 52·23%, nuclear spin × $(h/2\pi) = 5/2$, nuclear moment × $(eh/4\pi) = 1·5$. [c] Room temperature, 21° ± 2°. [d] Figures in parentheses denote the original authors' estimate of the uncertainty in the last figure. [e] J. M. Baker, J. P. Hurrell, and F. I. B. Williams, "Paramagnetic Resonance," ed. W. Low, Academic Press, New York, 1963, **1**, 202; J. M. Baker and F. I. B. Williams, *Proc. Roy. Soc.*, 1962, *A*, **267**, 283. [f] ^{153}Eu|A| calculated from the measured ^{151}Eu|A| and the hyperfine splitting ratio determined by electron nuclear double resonance; *e* above. [g] This work.

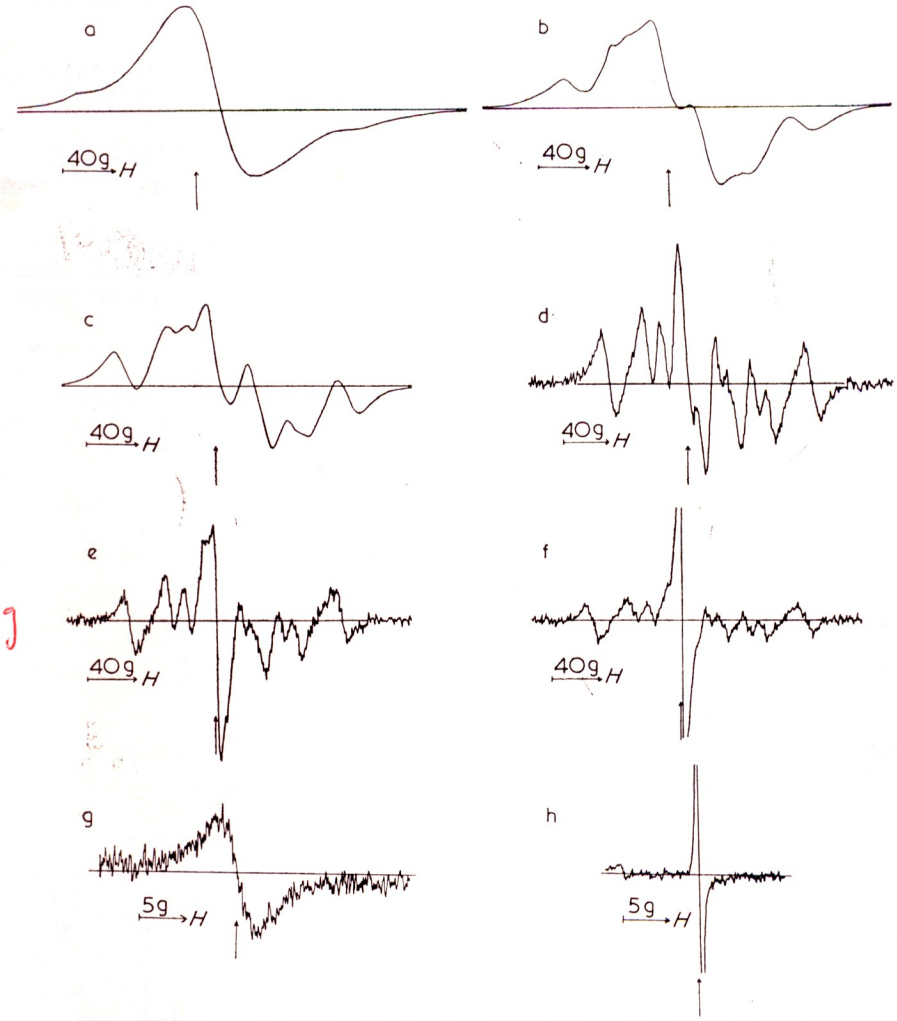

FIGURE 2. Electron spin resonance spectra of solutions of europium metal in liquid ammonia at room temperature: *a*, 0·1M; *b*, 0·001M; *c* to *f*, progressive dilution; *g*, approximately 5 × 10^{-5}M; *h*, approximately 10^{-7}M; $g = 2·0004$ is indicated by the vertical arrow.

Optical absorption spectra. Solutions of europium metal had a very strong absorption in the near infrared at all concentrations up to 0·1M (the most concentrated solution examined). This absorption had a maximum at 5600 cm.$^{-1}$ and a broad high-energy tail extending into the visible and giving rise to the blue colour. The band was completely absent in the decomposed solutions. A second optical band at 27,400 cm.$^{-1}$, detected only in the more concentrated solutions, was identical with the lower-energy transition of the europium(II) ion (Table 1).

Electron spin resonance spectra. The spectra were strongly dependent on both concentration and temperature. The effect of changing metal concentration is illustrated in Figure 2 for solutions below 0·1M at room temperature. The resonance signal obtained from a 0·3M-solution consisted of a symmetrical, Lorentzian line having $\Delta H_{ms} = 28{\cdot}5$ gauss and $g = 1{\cdot}9925 \pm 0{\cdot}0004$. Solutions 0·1M in metal had asymmetric spectra ($\Delta H_{ms} = 42{\cdot}6$ gauss, $g = 1{\cdot}9857$) (Figure 2*a*) and showed traces of the outermost ^{151}Eu hyperfine components. Below this concentration, the asymmetry was lost (Figures 2*b* and *c*), the spectra being similar to those obtained from europium(II) iodide solutions, except for an enhancement of one of the inner lines (Figure 1). On further dilution, this feature was better resolved (Figures 2*d* and *e*) and finally the europium(II) spectrum became too weak to detect, leaving a single, symmetrical line (Figure 2*g*) having ΔH_{ms} ~4 gauss, $g = 2{\cdot}0004 \pm 0{\cdot}0002$, which narrowed on further dilution to about 0·3 gauss, without any change in the *g*-factor, before also becoming undetectable.

This line strongly resembles that observed for solutions of alkali metals in ammonia. Hutchison and Pastor [5] found widths of about 0·025 gauss and a *g*-factor of $2{\cdot}0012 \pm 0{\cdot}0002$ for potassium solutions, but we have recently [22] compared electron spin resonance spectra for all the alkali metals at 0·1m and find the *g*-factors somewhat lower, and markedly greater line-widths for cæsium solutions (0·2 and 0·4 gauss at 0·1 and 0·2m, respectively).

Metal:	Li	Na	K	Rb	Cs	Eu	Ca, Ba, Sr [a]
g-Factor [b] (room temp.)...	2·0006	2·0004	2·0006	2·0004	2·0002	2·0004	2·001
,, (−78°)	2·0008	2·0008	2·0009	2·0005	2·0005	—	—

[a] K. D. Voss, Ph.D. Thesis, Michigan State University, 1962 (estimated error ±0·001). [b] Estimated error ±0·0002, with reproducibility ±0·00005.

The effect of lowering the temperature for a 0·001M-solution may be seen by comparing Figures 2*b* and 3. The 0·1M-solutions showed a very similar improvement in resolution,

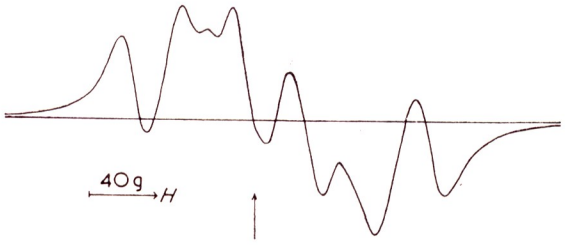

FIGURE 3. Electron spin resonance spectrum of a 0·001M-solution of europium metal in liquid ammonia at −78°. $g = 2{\cdot}000$ is indicated by the vertical arrow.

and spectra at −23° had intermediate resolution. This improvement in resolution with decreasing temperature contrasts with the decreasing resolution in europium(II) iodide solutions (Figure 1).

Correlation of optical and electron spin resonance spectra. The decay of europium metal solutions was followed in the extremely dilute range by concurrent optical and electron spin resonance spectroscopy. The relationship between electron spin resonance line-widths and optical density at 5600 cm.$^{-1}$ was almost linear. If an extinction coefficient of 10^5 is assumed,[9] the optical data can be used as a measure of concentration and hence the equation

$$\Delta H_{ms} = 0{\cdot}30 + (7{\cdot}8 \times 10^4)\text{M}$$

can be derived, M being the concentration of the solution between 5×10^{-5} and 10^{-7}M.

Discussion

The Nature of Europium Metal Solutions.—The present results are in good accord with the concept that the metal in dilute solutions of europium in ammonia is fully converted into europium(II) cations and solvated electrons. Thus, the hyperfine coupling constant, the *g*-factor, and the optical spectra indicate extensive formation of europium(II). Europium atoms are known to have a smaller hyperfine coupling constant,[23] whilst europium(I) and europium(III) would not be expected to give rise to detectable electron spin resonance spectra in fluid solutions. Absence of the latter ion is confirmed by the absence of its optical absorption bands.

In addition, electron spin resonance results are characteristic of solvated electrons in ammonia, except that the resonance spectra are considerably broader than usual for all but the most dilute solutions. The optical spectra in the near-infrared region also show no differences and, in particular, the unusual band-shape thought to be characteristic of solvated electrons [24] is a prominent feature of the europium solutions. The following discussion is accordingly based on the concept that the metal ionises completely to europium(II) and solvated electrons. We stress that, although the solutions slowly decomposed, this did not give rise to an accumulation of europium(II) ions, since the product of decomposition, presumably the amide, was quantitatively precipitated.

Cation–Electron Interactions.—The properties of alkali-metal solutions in ammonia are generally discussed in terms of the equilibria

$$M^+ + e^-_{solv.} \rightleftharpoons M \quad (1)$$

$$M \rightleftharpoons \tfrac{1}{2}M_2 \quad (2)$$

$$e^-_{solv.} \rightleftharpoons \tfrac{1}{2}(e_2^{2-})_{solv.} \quad (3)$$

$$M + e^-_{solv.} \rightleftharpoons M^- \quad (4)$$

where M^+ is an alkali-metal cation, M is either an " ion-pair " ($M^+_{solv.}$ - - $e^-_{solv.}$) [6] or the expanded metal monomer of Becker *et al.*[1] M_2 is either a cluster of four ions,[9] the electrons in separate cavities being paired, or an expanded metal dimer.[1] The species $(e_2^{2-})_{solv.}$ comprises two electrons paired in a single solvent cavity,[24,25] and M^- the two-electron, spin-paired analogue [26] of the ion-pair ($e^-_{solv.}$ - - - $M^+_{solv.}$ - - - $e^-_{solv.}$), or of the monomer. These species can be suitably modified to accommodate a bivalent cation such as calcium(II) or europium(II), M then being written as $M(II)^+$ and M^- as M(II).

Currently, equilibria (1) and (2) are generally invoked to explain magnetic and conductometric results, though it has been suggested [26] that the additional equilibrium (4) is necessary to reconcile the equilibrium constants derived from the two approaches. Also, O'Reilly [27] has used a scheme involving equilibria (1) and (3) or (4) to accommodate his recent nuclear magnetic resonance results.

Just as the observation of hyperfine coupling to a single cation nucleus in various alkali-metal–amine solutions [8] seems to show that monomer formation is the dominating mode for cation–electron interaction in those solvents, so the detection of separate electron spin resonance spectra for europium(II) ions and solvated electrons in europium solutions under conditions of extensive ion-pairing shows, in contrast, that in ammonia, cation–electron interaction involves loose ion-pairing. The marked broadening, as the concentration is increased, of the singlet assigned to solvated electrons confirms that such weak interaction is occurring.

We conclude that centro-symmetric monomer units are not important constituents of these solutions, and hence that they are even less likely to be significant in solutions of univalent metals.

Electron–Electron Interactions.—The present results also give some information about electron pairing in solutions of metals in ammonia. Thus we find that the unit $Eu^{2+}_{solv.}$ - - - $e^-_{solv.}$ does not give rise to a singlet or a triplet state, but remains effectively as two doublet-state species. If the electron-paired species were either $(Eu^{2+}_{solv.}$ - - $e^-_{solv.})_2$

r $e^-_{solv.}$ - - $Eu^{2+}_{solv.}$ - - $e^-_{solv.}$, it would be difficult to understand why the two $e^-_{solv.}$ units hould " combine " to give a deep singlet state (deep because the triplet level of the unit ; not thermally populated), whilst neither electron interacts in this way with the eighbouring europium(II) cations. If this conclusion is correct, we are forced to consider he $(e_2^{2-})_{solv.}$ species as being of importance. Other factors in favour of this unit, which vill, of course, generally be loosely associated with cations, will be presented later.[28]

Line-broadening Factors.—The mechanism by which the electron spin resonance lines re mutually broadened presumably arises from magnetic dipole forces since, for the loose on-pair, spin-exchange effects will be unimportant.

The marked broadening of the electron spin resonance line assigned to the solvated lectrons is similar to that found for the anion $[ON(SO_3)_2]^{2-}$ in the presence of various aramagnetic cations,[12] but the rate of broadening with increase in concentration is far reater (80,000 gauss $mole^{-1}$ compared with 1010 gauss $mole^{-1}$). This is presumably due oth to the greater mobility of solvated electrons and to their far greater delocalisation elative to the unpaired electron in $[ON(SO_3)_2]^{2-}$.

By arbitrarily assuming a line-width of about 5 gauss for the solvated electron in the on-pair, the relative concentrations of free and ion-paired solvated electrons in europium olutions can be estimated very roughly and compared with those in alkali metal solutions.

Europium solutions

Concentration (M)	10^{-6}	10^{-5}	3×10^{-5}	5×10^{-5}
$\frac{100[M]}{[e^-] + [M]}$	4	11	16	42

Alkali-metal solutions

Concentration (M)		5×10^{-4}	5×10^{-3}	$1{\cdot}25 \times 10^{-2}$	0·4
$\frac{100[M]}{[e^-] + [M]}$	(i) from conductance data [a]	4	12	13	30
	(ii) from magnetic data [b] ...	1·5	9	13·5	30

[a] D. S. Berns, G. Lepoutre, E. A. Bockelman, and A. Patterson, jun., *J. Chem. Phys.*, 1961, **35**, 1820. [b] Ref. 1.

Concentrated Solutions.—The onset of marked broadening and asymmetry of the electron spin resonance band as the concentration of metal is increased is taken as an indication of the formation of solvent-deficient ion-clusters that are of sufficient size to have the character of colloidal metal particles. This occurs for europium solutions at a far lower concentration than is found for solutions of alkali metals (Figure 2), but the behaviour seems to be comparable with that of calcium solutions.[29]

It is significant that this onset moves to higher concentrations of metal as the temperature is lowered. Since at lower temperatures electron-pairing is favoured, this result is somewhat surprising. It is presumably a result of the decrease in the dielectric constant of the solvent on warming, with a consequent increase in ion-clustering.

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[1] E. Becker, R. H. Lindquist, and B. J. Alder, *J. Chem. Phys.*, 1956, **25**, 971.
[2] J. C. Warf and W. L. Korst, *J. Phys. Chem.*, 1956, **60**, 1590.
[3] M. C. R. Symons, *Quart. Rev.*, 1959, **13**, 99.
[4] C. A. Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 1323; 1921, **43**, 749.
[5] C. A. Hutchison, jun., and R. C. Pastor, *J. Chem. Phys.*, 1953, **21**, 1959.
[6] C. A. Kraus, *J. Chem. Educ.*, 1953, **30**, 83.
[7] H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 1957, **26**, 1517; J. V. Acrivos and K. S. Pitzer, *J. Phys. Chem.*, 1962, **66**, 1693.
[8] K. D. Vos and J. L. Dye, *J. Chem. Phys.*, 1963, **38**, 2033; K. Bar-Eli and T. R. Tuttle, jun., *ibid.*, 1964, **40**, 2508.
[9] M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1962, **84**, 2264; M. Gold and W. L. Jolly, *Inorg. Chem.*, 1962, **1**, 818; C. Hallada and W. L. Jolly, *ibid.*, 1963, **2**, 1076.
[10] R. Catterall and M. C. R. Symons, *J.*, 1964, 4342.

[11] R. Catterall and M. C. R. Symons, *J. Chem. Phys.*, 1965, **42**, 1466.
[12] R. G. Pearson and T. Buch, *J. Chem. Phys.*, 1962, **36**, 1277.
[13] B. Bleaney and W. Low, *Proc. Phys. Soc.*, 1955, *A*, **68**, 55.
[14] F. D. S. Butement, *Trans. Faraday Soc.*, 1948, **44**, 617.
[15] W. Low, *Nuovo cim.*, 1960, **17**, 607.
[16] A. A. Kaplyanskii and P. P. Feofilov, *Optics and Spectroscopy*, 1963, **13**, 129.
[17] R. Reisfeld and A. Glesner, *J. Opt. Soc. Amer.*, 1964, **54**, 331.
[18] E. V. Sayre, D. G. Miller, and S. Freed, *J. Chem. Phys.*, 1957, **26**, 109.
[19] J. A. Brivati, N. Keen, and M. C. R. Symons, *J.*, 1962, 237.
[20] T. R. Griffiths and M. C. R. Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125.
[21] V. M. Vinokurov, M. M. Zaripov, V. G. Stepanov, G. E. Chirkin, and L. Ya Shekun, *Fiz. Tver. Tela.*, 1963, **5**, 1936 (translation in *Soviet Physics-Solid State*, 1964, **5**, 1415).
[22] R. Catterall and M. C. R. Symons, unpublished results.
[23] P. G. H. Sandars and G. K. Woodgate, *Proc. Roy. Soc.*, 1960, *A*, **257**, 269.
[24] M. J. Blandamer, R. Catterall, L. Shields, and M. C. R. Symons, *J.*, 1964, 4357.
[25] S. Freed and N. Sugarman, *J. Chem. Phys.*, 1943, **11**, 354; R. A. Ogg, jun., *ibid.*, 1946, **14**, 114
[26] E. Arnold and A. Patterson, jun., "Metal–Ammonia Solutions," eds. G. Lepoutre and M. J. Sienko, Benjamin, New York, 1964, p. 285.
[27] D. E. O'Reilly, *J. Chem. Phys.*, 1964, **41**, 3729.
[28] R. Catterall and M. C. R. Symons, unpublished results.
[29] R. A. Levy, *Phys. Rev.*, 1956, **102**, 31; D. Cutler and J. G. Powles, *Proc. Phys. Soc.*, 1962, **80**, 13(

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