

836. *Unstable Intermediates. Part XXII.* Solvated Electrons: The Effect of Added Electrolytes on the Electron Spin Resonance Absorption of Solutions of the Alkali Metals in Liquid Ammonia.*

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The electron spin resonance absorption of solutions of alkali metals in liquid ammonia has been studied as a function of the concentration of metal and of added alkali-metal halides. When the concentration of metal is small ($<10^{-2}m$) there are small negative deviations in the g -factor for added chlorides and bromides but very large negative deviations for added iodides, the shifts for a given salt molality being then a function of the cation. These shifts are enhanced at higher metal concentrations and higher temperatures, and are accompanied by a marked increase in line-width.

The visible and near infrared absorption spectra of some of these solutions have been measured and the appearance of a shoulder in the $12,500\text{ cm}^{-1}$ region has been confirmed.

These results are discussed in terms of a specific interaction between unpaired electrons and iodide ions.

MAGNETIC and conductometric results for solutions of metals in ammonia are generally discussed in terms of equilibria of the form:



where M is used to denote either the ion pair,¹ $M^+e^-_{\text{solv.}}$ or the expanded metal atom species described by Becker, Lindquist, and Alder,² and M_2 the corresponding ion cluster ($M^+e^-_{\text{solv.}}$)² proposed by Gold, Jolly, and Pitzer,³ or the expanded metal dimer.² The symbol $e^-_{\text{solv.}}$ is used to denote some form of solvated electron.

In an attempt to constrain equilibrium (i) to favour M , Clark *et al.*⁴ studied the effect of added sodium iodide on the electron spin resonance and optical absorption of sodium in ammonia. No modification of the electron spin resonance was noticed but a shoulder at

* Part XXI, *J.*, 1964, 536.

¹ Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 1323.

² Becker, Lindquist, and Alder, *J. Chem. Phys.*, 1956, **25**, 971.

³ Gold, Jolly, and Pitzer, *J. Amer. Chem. Soc.*, 1962, **84**, 2264.

⁴ Clark, Horsfield, and Symons, *J.*, 1959, 2478.

12,500 cm^{-1} appeared on the high-energy side of the 6800 cm^{-1} optical absorption band which was discussed in terms of the formation of M.

Since then Gold and Jolly⁵ have systematically studied the effect of changing the concentration of metal on the visible and infrared absorption, and have concluded that the M_2 species has an absorption very similar to that of the M and $e^-_{\text{solv.}}$ species. They were unable to detect any additional absorption in the 12,500 cm^{-1} region for solutions containing added salt. The effect of added sodium iodide on the optical absorption of solutions of sodium in ethylenediamine has also been studied⁶ but no modification was detected.

In fact both the g -factor and the line-widths of the electron spin resonance absorption, and the optical absorption of solutions of metals in ammonia are modified by the addition of high concentrations of alkali halides⁷ and these results are now reported in detail.

EXPERIMENTAL

Purification of Materials.—*Alkali metals.* Sodium and potassium (reagent grade) were melted through a capillary under vacuum to remove oxide impurities and then drawn up into 1–3 mm. bore Pyrex tubing under dry, oxygen-free, nitrogen. Rubidium and caesium metals of 99.9% purity were supplied in sealed ampoules. The ampoules were opened at 77°K under an atmosphere of nitrogen introduced into the vacuum system and the metals melted and drawn up into Pyrex tubing. From data on densities of the alkali metals, lengths of the metal-filled glass tubing could be selected to contain any required weight of metal. Oxide formation was small and restricted to the ends of the tube for sodium and potassium. Rubidium and caesium tubes were cut and stored under liquid nitrogen and introduced into the apparatus against a counter-current of dry, oxygen-free, nitrogen. Further purification of the metals is described later.

Ammonia. Reagent grade liquid ammonia was purified by storing as the potassium solution at -78° for not less than 48 hr. Evolved hydrogen was removed at intervals.

Alkali-metal halides. Salts were generally of reagent or AnalaR grade. They were dried at 140° in air for not less than 24 hr. before introducing a known weight into the apparatus. Rubidium and caesium salts contained up to 1% of the other metal but preliminary experiments with 99.9% caesium iodide showed that the impurity had no detectable effect on the electron resonance absorption of the solutions.

Nitrogen. Oxygen-free nitrogen was passed over molecular sieves to remove water and other impurities immediately before use.

Glassware.—Apparatus fabricated from Pyrex tubing was aged for 12 hr. in concentrated nitric acid, thoroughly rinsed with de-ionised water and dried under vacuum. Earlier experiments using other cleaning solutions had indicated that the critical factor in the preparation of stable solutions was not the cleaning procedure, but the “baking-out.”

Preparation of Solutions.—A known weight of alkali metal contained in a glass tube was placed in the open end of a multiply-constricted side arm against a current of purified nitrogen, and the end closed. After evacuation the metal was distilled past the constrictions, each portion of the tube being removed during the process, and was finally evaporated to the side wall of a tube containing a known weight of the required salt. After sealing at the final constriction a known quantity of ammonia was admitted and condensed as a liquid on the metal film. After the resulting solution had run down on to the salt, the vessel together with a side arm was removed from the vacuum line by sealing at a further constriction. Finally, an aliquot part of the solution was tipped into the side arm which was constructed of capillary bore tubing. This was then sealed and the solutions stored in liquid nitrogen pending electron resonance measurements. The use of capillary tubing was necessary to avoid excessive damping of the microwave cavity. A similar technique was used for optical studies.

Electron Resonance Apparatus.—The apparatus used was described previously.⁸ The magnetic field was measured using the method described by Horsfield *et al.*⁹ with a modification

⁵ Gold and Jolly, *Inorg. Chem.*, 1962, **1**, 818.

⁶ Windwer and Sundheim, *J. Phys. Chem.*, 1962, **66**, 1254.

⁷ Catterall, Corset, and Symons, *J. Chem. Phys.*, 1962, **38**, 272.

⁸ Brivati, Keen, and Symons, *J.*, 1962, 237.

⁹ Horsfield, Morton, and Moss, *J. Sci. Instruments*, 1961, **38**, 322.

by Brivati,¹⁰ which gave an accuracy of ± 5 parts in 10^5 . Because the proton resonance probe was not in exactly the same magnetic field as the cavity, g -factors were corrected by measurements on charred dextrose prepared according to the method of Hoskins and Pastor,¹¹ a g -factor of 2.0023 being assumed. The accuracy of the g -factor measurements is estimated to be ± 1 part in 10^4 .

Optical Absorption Measurements.—Optical spectra throughout the visible and near infrared regions were measured on a Unicam S.P. 700 recording spectrophotometer. The temperature of the absorption cell, contained in a vacuum-jacketed cell-box, was regulated and maintained by a stream of pre-cooled nitrogen, and measured by a thermocouple in contact with the absorption cell. The positions of the absorption maxima were found by the method of rectilinear diameters and absolute values calculated by extrapolation from the ammonia absorption peaks at 5012 and 4464 cm^{-1} .

RESULTS

Electron Resonance Absorption.— g -Factors. We define the change in the g -factor with increasing salt concentration by $\Delta g = 10^4 (g_{\text{soln}} - 2.0012)$, where g_{soln} is the observed g -factor for the solution and 2.0012 is the concentration-independent g -factor recorded by Hutchison and Pastor¹² for sodium and potassium solutions in the absence of added salt.

The results at room temperature for solutions dilute ($< 10^{-2}\text{m}$) in metal and containing added iodide are shown in Fig. 1. In all cases a trend to lower g -factors is observed with

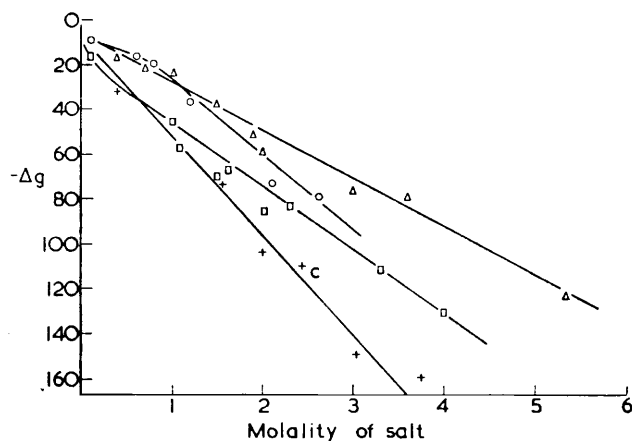


FIG. 1. The variation in g -factor at room temperature for dilute solutions of the alkali metals containing added alkali iodides.

○ Sodium solutions containing sodium iodide. Δ Potassium solutions containing potassium iodide. + Rubidium solutions containing rubidium iodide; Point "c" sodium solution containing rubidium iodide. \square Caesium solutions containing caesium iodide.

increase in salt concentration. Although all the iodides show the same general trend, small differences are apparent at all concentrations. A sample 2.44m in rubidium iodide and 10^{-2}m in sodium metal showed behaviour characteristic of rubidium solutions.

The corresponding variation in Δg at -78° is shown in Fig. 2. The trends are very similar to those at room temperature, but $-\Delta g$ is consistently smaller. Results for potassium and rubidium bromides at -78° , and for sodium, potassium, rubidium, and caesium bromides at room temperature are in Fig. 3. The solubility of sodium and caesium bromides at -78° was so small that significant results could not be obtained. Within experimental error all the bromides showed identical behaviour. At both temperatures the g -factor fell to 2.0000 at about 0.5m and remained constant to saturation, except in the case of very concentrated rubidium bromide solutions.

Representative results for sodium, potassium, and caesium iodides in dilute metal solutions at -23° are in Table 1 from which it can be seen that their g -factors are intermediate between those for the two temperatures studied in detail. Values of Δg for mixtures of salts in dilute solutions of the metals are in Table 2 and compared with the expected g -shift assuming additivity. The agreement is only approximate.

¹⁰ Brivati, unpublished work.

¹¹ Hoskins and Pastor, *J. Appl. Phys.*, 1960, **31**, 1506.

¹² Hutchison and Pastor, *J. Chem. Phys.*, 1953, **21**, 1959.

FIG. 2. The variation in g -factor at -78° for dilute solutions of the alkali metals containing added alkali iodides.

○ Sodium solutions containing sodium iodide. Δ Potassium solutions containing potassium iodide. + Rubidium solutions containing rubidium iodide; Point "c" sodium solution containing rubidium iodide. □ Cæsium solutions containing cæsium iodide.

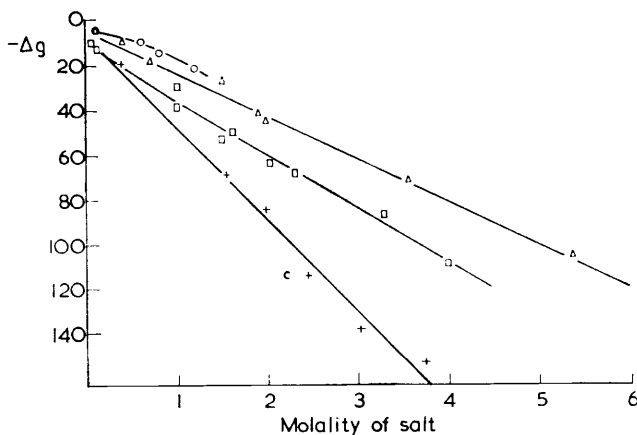


TABLE 1.

Representative values of Δg at -23° .

Metal	Concn. (m)	Salt	Concn. (m)	$-\Delta g$		
				Room temp. ^a	-23°	-78° ^a
Na	0.10	NaI	0.603	18	12	10
Na	0.01	NaI	0.805	23	15	13
Na	0.01	NaI	1.201	35	27	23
Na	0.20	NaI	1.602	49(70) ^c	60	b
Na	0.20	NaI	1.899	62(83) ^c	82	b
K	0.10	KI	1.007	28	23	22
K	0.20	KI	1.405	37	33	32
K	0.20	KI	1.722	44	39	36
K	0.01	KI	1.901	48	45	41
Cs	0.01	CsI	1.599	68	62	53
Cs	0.01	CsI	3.287	112	95	89

^a Values of $-\Delta g$ at room temperature and -78° are taken from a smoothed curve drawn through the dilute metal solution points. ^b Sodium iodide saturation solubility at -78° is about 1.3m. ^c Values in parentheses are for the smoothed data for 0.2m-sodium solutions.

TABLE 2.

The effect of mixtures of salts on the g -factor of dilute solutions of the alkali metals.

Metal	Salt(1)	Salt(2)	Temp.	Salt(1) (m)	$-\Delta g(1)$	Salt(2) (m)	$-\Delta g(2)$	$-\Delta g(1) + \Delta g(2)$	$-\Delta g(\text{obs.})$	ΔH_{ms}
Na	NaI	KI	Room	1.517	46	2.036	50.5	96.5	78	0.5
			-78°	1.3 ^a	27 ^a	2.036	43	70	62	1.1
Na	NaI	RbI	Room	1.216	36.5	1.512	74.5	111	63	0.5
			-78°	1.216	23.5	1.512	66	89.5	55	0.9
Na	NaI	CsI	Room	1.517	46	1.516	66	110	107	0.9
			-78°	1.3 ^a	27 ^a	1.516	52	79	87	2.3
K	KI	RbI	Room	1.544	40	1.568	77	117	54	0.3
			-78°	1.544	34	1.568	68	102	43	0.5
K	KI	RbI	Room	1.586	41	1.588	78	119	94	0.4
			-78°	1.586	34.5	1.588	69	103.5	74	1.5
K	KI	CsI	Room	1.500	39	1.503	65.5	104.5	88	0.7
			-78°	1.500	33	1.503	51.5	85.5	79	3.4
Rb	RbI	CsI	Room	1.462	73	1.512	66	139	156	1.4
			-78°	1.462	64	1.512	52	116	132	7.0
K	KI	KBr	Room	1.517	39.5	1.514	13.5	53	47	0.3
			-78°	1.517	33.5	1.514	12	45.5	48	1.3

^a Solution is saturated in sodium iodide. Δg measured at estimated saturation concentration of 1.3m.

Studies of the effect of added chloride ion were restricted to sodium solutions. In all cases Δg was found to be very small and negative (see Table 3).

Widths. The widths of the electron resonance spectra are markedly dependent on salt

TABLE 3.
Values of Δg at room temperature for sodium solutions containing added sodium chloride.

Salt (m)	0.27	0.62	0.70	0.78	1.05	1.4
Metal (m)	0.001	0.02	0.1	0.1	0.1	0.01
$-\Delta g$	3	4	4	4	5	6

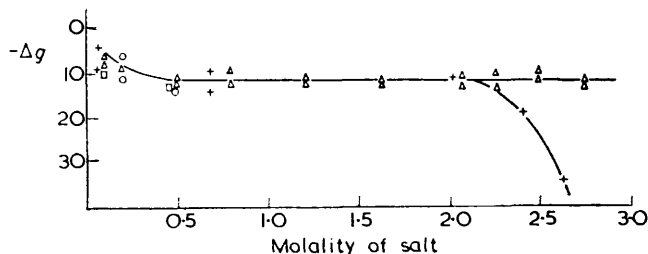


FIG. 4. The widths at room temperature of the electron resonance signals from dilute solutions of the alkali metals containing added alkali halides.

○ Na + NaI, 0.2m. ● Na + NaI; △ K + KI; ▽ K + KBr; × Rb + RbI; + Rb + RbBr; □ Cs + CsI.

a, Data of reference ¹² for sodium and potassium solutions; b, Limit of resolution for the spectrometer.

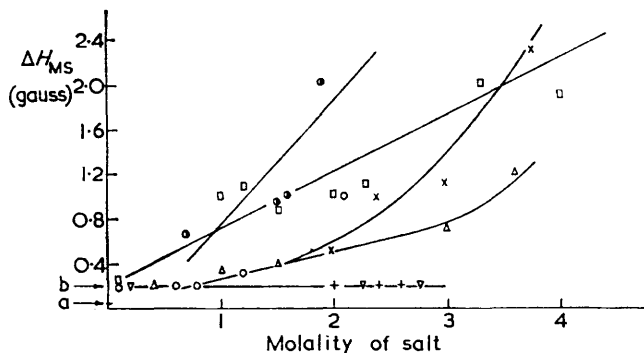
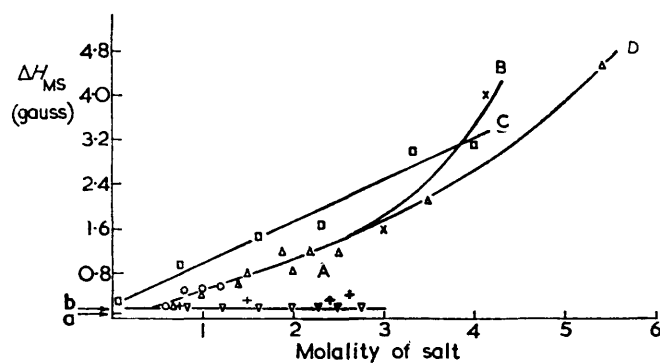


FIG. 5. The widths at -78° of the electron resonance signals from dilute solutions of the alkali metals containing added alkali halides.

○ Na + NaI, 0.2 molal Na + NaI (curve A); △ K + KI (curve D); ▽ K + KBr; × Rb + RbI (curve B); + Rb + RbBr; □ Cs + CsI (curve C).

a, Data for reference ¹³ for a 0.08m-potassium solution at -70° ; b, Limit of resolution for the spectrometer.



concentration, the width at a given salt concentration being greater by a factor of about 2—3 at the lower temperature. The variation of the width with concentration of added salt for dilute metal solutions is shown in Figs. 4 and 5 for room temperature and -78° , respectively. The increase for iodides is practically linear up to 2m but is more rapid at higher concentrations. With the possible exception of caesium solutions the widths approach our experimental limiting

value of 0.2 gauss at about 0.8m and extrapolation to the value in the absence of added salt¹² is reasonable. Hutchison and Pastor¹² found minimum widths for potassium solutions at -25 , 0 , and -33° to be 20, 30, and 44 milligauss, respectively, while at -70° Levy¹³ found the width to have increased to 100 milligauss. Sodium solutions showed very similar trends.¹² The only recorded values for rubidium ($<0.15\text{m}$) and caesium (0.8m) solutions¹³ are 0.16 and 0.40 gauss, respectively, at -70° . The solutions containing bromides have widths of 0.2 gauss,

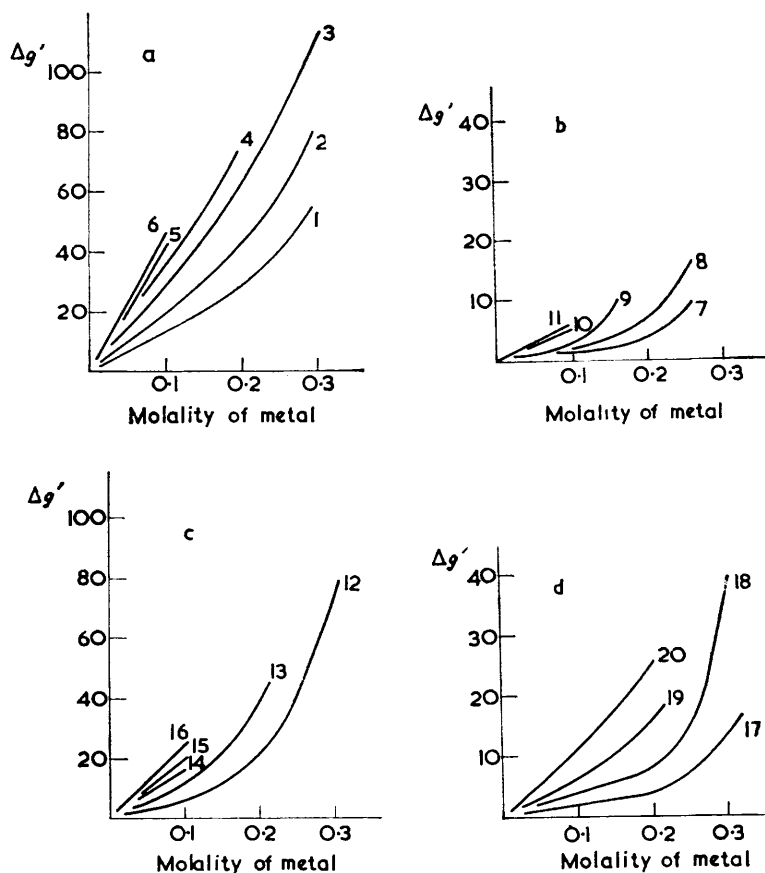


FIG. 6. The g -factor of metal solutions at room temperature as a function of metal and salt concentrations.

a, Rb + RbI, molality of salt, 1, 0.2; 2, 0.4; 3, 0.8; 4, 1.2; 5, 1.9; 6, 2.6. *b*, Rb + RbBr, molality of salt, 7, 0.1; 8, 0.2; 9, 0.5; 10, 0.9; 11, 1.6. *c*, Cs + CsI, molality of salt, 12, 0.2; 13, 0.5; 14, 1.0; 15, 2.0; 16, 3.0. *d*, Na + NaI, molality of salt, 17, 0.2; 18, 0.5; 19, 1.0; 20, 2.0.

the experimental limit at both temperatures, with the exception of rubidium bromide solutions at -78° , where the trend to lower g -factor is paralleled by a slight increase in width to 0.4 gauss.

Solutions more concentrated in metal. The effect of added salt on the g -factor of more concentrated metal solutions has been investigated and the results at room temperature are presented in Fig. 6. We define the change in g -factor with increasing metal concentration at a given salt concentration by $\Delta g' = \Delta g_{m(0)} - \Delta g_m$, where $\Delta g_{m(0)}$ and Δg_m are the values of Δg observed for metal concentrations $<10^{-2}$ and "m," respectively. At this temperature, solutions containing added iodide showed an increase in $\Delta g'$ with increasing metal concentration, the increase being

¹³ Levy, *Phys. Rev.*, 1956, **102**, 31.

more marked at high concentrations of metal and of salt. Similar but much smaller trends in $\Delta g'$ were observed for sodium bromide (Table 4) and rubidium bromide (Fig. 6b) solutions. At

TABLE 4.

Values of Δg at -78° and room temperature for sodium solutions containing up to 0.2m sodium and added sodium bromide.

Salt (m)	0.20	0.49	0.80	1.23
Metal (m)	0.01	0.01	0.20	0.20
$-\Delta g$ (-78°)	6.3	7.0 ^a	—	—
$-\Delta g$ (room temp.)	11.5	15	36	54
$\Delta g'$ (room temp.) ^b	—	—	23	43

^a Saturated solution, concentration estimated 0.25m (Heymer and Schneider, *Z. anorg. Chem.*, 1959, **302**, 306 give 0.28m at -75°). ^b Calc. from eqn. in text, assuming $\Delta g_{m(0)} = -12$.

-78° , however, the g -factors for solutions containing up to 0.3m metal showed no divergence from the curves in Fig. 2 for solutions dilute in metal.

Solutions relatively concentrated in both iodide and metal have spin-resonance curves which are asymmetrically broadened (Fig. 7). The broadening (Fig. 4) and asymmetry increase with

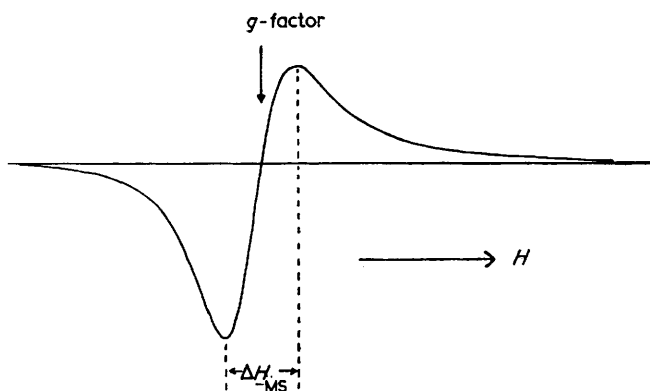


FIG. 7. Asymmetric spin resonance absorption obtained from solutions concentrated in alkali metal or salt. Metal concentration greater than 0.1m.

increase in concentration of either component, and with increase in temperature, provided that the concentration of metal is not less than about 0.1m. It appears that the low-field edge of the absorption curves remains relatively unchanged and thus the additional g -shift ($\Delta g'$) is largely a manifestation of the asymmetric broadening. This asymmetry was not reported for concentrated (1m) solutions of sodium and potassium¹² in ammonia but has been found for concentrated caesium solutions,¹⁴ when again the effect is greatly reduced on cooling. Levy¹³ reported no asymmetry at -70° for a 0.8m caesium solution. The phenomenon is presumably associated with delocalised electrons in large ion-clusters since it resembles that found for bulk alkali metals.¹⁵ On cooling the solutions, the ion-clusters tend to break down owing to the increased solvating power of the medium, so that this "conduction electron" effect is greatly diminished.

Solutions of sodium, potassium, and rubidium show a characteristic phase separation at low temperatures, and this phenomenon in the case of sodium solutions is greatly enhanced by the presence of sodium iodide.¹⁶ Caesium solutions, however, do not show phase separation.¹⁶ Although the presence of bromide and iodide salts in potassium and rubidium solutions also favoured the formation of two liquid phases, we found no indication of phase separation in solutions of caesium, even in the presence of high concentrations of caesium iodide. When phase

¹⁴ Catterall and Symons, unpublished results.

¹⁵ Feher and Kip, *Phys. Rev.*, 1955, **98**, 337.

¹⁶ See, e.g., T. P. Das, "Advances in Chemical Physics," Interscience Publishers, New York, 1962, Vol. IV, p. 303; Das and Sienko, "Metal Ammonia Solutions: Physico Chemical Properties," Mémoires et Travaux des Facultés Catholiques de Lille, France, W. A. Benjamin, Inc., New York, 1964, p. 23.

separation occurs in the microwave cavity the narrow, symmetrical, dilute solution line is seen superimposed on the broader, asymmetrical line from the concentrated phase. It is suggested that the electron resonance technique would be a very sensitive probe in the investigation of phase separation in these solutions, especially when the appearance of very small amounts of the dilute phase in concentrated solutions is of interest.

Optical Absorption.—The visible and near infrared absorption spectrum of an approximately 1m solution of sodium iodide in a 2.8×10^{-3} m sodium solution has been recorded from -13 to -73° . The presence of a well-defined shoulder, reported earlier ⁴ at $12,500 \text{ cm.}^{-1}$ on the main 6800 cm.^{-1} absorption band, was confirmed. The temperature dependence of the position of maximum absorption of the main band was found to be linear within experimental error and to fit the equation $\nu_{\text{max.}} (\text{cm.}^{-1}) = 7147 - 10.86t$ where t is the centigrade temperature, 7147 cm.^{-1} the value of $\nu_{\text{max.}}$ at -80° found by extrapolation, and $-10.86 \text{ cm.}^{-1} \text{ deg.}^{-1}$ the mean experimental temperature coefficient. Temperature coefficients in the absence of added salt have been recorded by Douthit and Dye ¹⁷ ($-9.7 \text{ cm.}^{-1} \text{ deg.}^{-1}$) for sodium solutions, by Blades and Hodgins ¹⁸ ($-9.1 \text{ cm.}^{-1} \text{ deg.}^{-1}$) for potassium solutions, and by Gold and Jolly ⁵ ($-12.7 \text{ cm.}^{-1} \text{ deg.}^{-1}$) for solutions of all the alkali metals.

DISCUSSION

Anion Effect.—For a given cation, it is found that iodide gives a large, negative Δg , bromide a small negative Δg , whilst chloride and also amide give a negligible shift.

Cation Effect.—The effect of varying the cation for a given anion is only really noticeable for iodides (Figs. 1 and 2). Even in these instances the effect appears to be subsidiary to that of the anion, and the order of the cations does not follow any simple trend.

It is concluded that equilibrium (i), although not completely ruled out, must contribute little to the observed g -shift.

Interaction between Electrons and Anions.—For simplicity we consider only interactions between electrons and solvated anions or anions which are "paired" to cations. Interactions between electrons and ion-clusters, while obviously important in the solutions of high salt concentration, would be expected to differ only slightly from those between electrons and ion-pairs with respect to Δg . For solvated anions, it seems reasonable to suppose that the intimate interaction required in order that a g -shift be detected, arises from states in which the unpaired electron occupies a vacant orbital of the solvated anion. Such orbitals are strongly defined by the surrounding polarised solvent ^{19,20} and may be depicted as linear combinations of anion orbitals, such as the vacant $6s$ level for iodide, and F -centre type expanded orbitals ²¹ defined by the polarised solvent. Indeed the outer part of these orbitals may be very similar in form to that of "solvated" electrons in ammonia. ²² The lowest of these orbitals is expected to be an s -state, so that in order to obtain the required orbital momentum, excited states must be involved. Since the g -shift is negative, a state involving the outer $6p$ level of the anion is the most reasonable choice.

Interaction between solvated electrons and anions in ion-pairs will presumably be similar except that the electrons may also be constrained to occupy outer levels of the cations and, especially for heavy cations, this could give rise to an additional g -shift. It is not sufficient to assign the shift to monomer units having a neighbouring anion which could modify the electron's orbital by mixing in p -character, since this would be largely independent of the nature of the anion. There may also be a "crystal-field" lowering of the energy of the halide $p\sigma^*$ level, and hence halide ions in ion-pairs may induce a Δg different from that induced by the solvated ions. In view of the uncertainty associated with the structure of ion-pairs in various solvents, more detailed consideration of the

¹⁷ Douthit and Dye, *J. Amer. Chem. Soc.*, 1960, **82**, 4472.

¹⁸ Blades and Hodgins, *Canad. J. Chem.*, 1955, **83**, 411.

¹⁹ Platzman and Franck, *Z. Physik*, 1954, **138**, 411.

²⁰ Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338, 346.

²¹ Gourary and Adrian, *Solid State Physics*, 1960, **10**, 127.

²² Griffiths and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125.

structure of $(IP)^-$ does not seem to be warranted. The formation of *contact* ion-pairs in iodide solutions²³ as evidenced by the cation dependence of the first iodide absorption band, only occurs in solvents of low dielectric constant (such as carbon tetrachloride) and is not thought to occur to any significant extent in liquid ammonia.²³ Hence we expect Δg arising from interaction between the electron and solvent separated ion-pairs and clusters to be quite close to that from interaction with solvated halide ions, $(Hal^-)^-$, but to depend slightly on the cation, as found. The small shift for bromide solutions must arise in part because of the smaller spin-orbit coupling constant for bromine compared with that for iodine, but since bromide ions seem to give a relatively large negative Δg for F centre electrons (cf., e.g., the g -factors for F centres in potassium chloride, bromide, and iodide of 1.995, 1.980, and 1.971, respectively), this is probably not the only factor. In our view, an important aspect is that the acceptor level for the solvated bromide ion is considerably higher in energy than for the solvated iodide ion. Although no datum for the absorption of bromide ions in liquid ammonia is available (the band being masked by solvent absorption), the difference in energy²⁴ is greater than 12.7 kcal. mole⁻¹ and probably is similar to the corresponding differences in water^{22,24} and methyl cyanide^{24,25} (19.4 and 14.3 kcal. mole⁻¹, respectively). Hence states which give rise to orbital momentum are much less important for bromide ions, either alone or paired to cations. This conclusion is justified if the "confined" model for the outer orbital is a good approximation,²² and will be still more applicable to chloride solutions.

Equilibria.—The ion-pair dissociation constant for sodium iodide in liquid ammonia²⁶ at 25° is 6.7×10^{-4} . If activity coefficients are neglected, this means that the percentage of solvated sodium ions falls from nearly 10 at 0.1m to 3 at about 1m. Since the curves of Figs. 1 and 2 are linear for salt concentrations greater than 0.8m, we discuss the data in terms of effectively complete conversion to ion-pairs.



Using concentrations $(b - x)$, $(a - x)$, and x for the equilibrium concentrations of unpaired electrons, ion-pairs, and $(IP)^-$ ions, respectively, b and a being the initial concentrations of electrons and ion-pairs, we have

$$K = x/(b - x)(a - x) \quad (a)$$

In practice, $a \gg b$, so

$$x = abK/(1 + aK) \quad (b)$$

and, provided $K \ll 1$, this gives

$$x = abK \quad (c)$$

In order to relate this result to the observed g -shifts we write

$$g(\text{obs.}) = 2.0012(b - x)/b + g(IP)^-(x/b) \quad (d)$$

2.0012 being the g -factor for dilute metal solutions in the absence of salt. This weighted average g -factor will be found rather than separate lines for the two species provided there is rapid interconversion, that is, provided the rate constants for equilibrium (iii) are large.

Then since $10^{-4}\Delta g = g(\text{obs.}) - 2.0012$, we have

$$10^{-4}\Delta g = (x/b)[g(IP)^- - 2.0012] \quad (e)$$

which, with (c) gives

$$10^{-4}\Delta g = aK[g(IP)^- - 2.0012] \quad (f)$$

This requires that a plot of Δg against a be linear and have a slope independent of the

²³ Griffiths and Symons, *Mol. Phys.*, 1960, **3**, 90.

²⁴ Blandamer, Shields, and Symons, *Trans. Faraday Soc.*, 1964, **60**, 1524.

²⁵ Kosower, Martin, and Meloche, *J. Chem. Phys.*, 1957, **26**, 1353.

²⁶ Gunn and Green, *J. Chem. Phys.*, 1962, **36**, 368.

metal concentration. Both requirements are fulfilled for solutions having metal concentration in the 10^{-4} — 10^{-2} m region. It may be concluded either that only one type of ion-pair is formed under these conditions²³ or that the relative concentrations of different types of ion-pair does not alter in the range studied.

Temperature Effect.—For all solutions studied there was a decrease in $-\Delta g$ on cooling. For a temperature change of approximately 100° this shift was between 10 and 20%. If our assumption that in the linear region (Figs. 1 and 2) shifts are due entirely to interactions between electrons and ion-pairs (or more complex ion-clusters), then we cannot invoke the ion-pair equilibrium, $M^+ + Hal^- \rightleftharpoons IP$, to explain this trend. However, if equilibrium (iii) moves on cooling to disfavour $(IP)^-$ then the average g -factor should tend to that for solvated electrons, as is observed.

One reason for this shift of equilibrium (iii) could be that the vacant orbital on the halide ion is destabilised on cooling. This has already been suggested to explain the temperature effect on the spectrum of iodide in ammonia.²⁰ This destabilisation, as well as modifying equilibrium (iii), will also make the excited p -level less accessible to the electron, thus decreasing $-\Delta g(IP)^-$ and further reducing the observed $-\Delta g$.

Line-widths of Dilute Metal Solutions.—In contrast with solutions which are concentrated in metal, dilute solutions containing added iodide show a symmetrical broadening of the electron resonance absorption, the shape of the line remaining closely Lorentzian. This increase in width roughly parallels the decrease in the g -factor (cf. Figs. 1 and 2 with Figs. 4 and 5). Since this large broadening is unique to iodide salts it is probably due to a hyperfine interaction with one or more ^{127}I nuclei. The width will then be a function of the number of iodide ions in each ion-cluster and the rate of electron transfer from one iodide anion to another. The individual hyperfine components are doubtless also broadened by the large quadrupole moment of ^{127}I . It is noteworthy that the percentage increase in line-width on cooling is comparable with that found for dilute metal solutions in the absence of salt,¹² and hence may arise from a decrease in motional narrowing. The increase in line-width with increase in salt concentration may also be linked with the expected increase in the size of ion-clusters.

It might be argued that the line-width increment is associated with the large shift in the g -factor and is due to spin-orbit-lattice relaxation. This, however, would decrease on cooling and would lead therefore to a sharpening of the absorption line. We conclude that this mechanism is of minor significance.

Optical Spectra.—From the studies of Gold and Jolly⁵ it seems that solvated electrons have comparable absorption spectra in the presence or absence of neighbouring cations or when paired with neighbouring electrons. It is noteworthy that another property of these spectra, namely the temperature coefficient of the absorption maximum is hardly modified by the addition of high concentrations of salt. This would be in accord with the postulate³ that the immediate environment of the electron is only slightly changed by ion-pairing.

The new band which appears under certain conditions as a shoulder in the $12,500\text{ cm}^{-1}$ region, which was originally ascribed to monomer,⁴ is probably better assigned to the species described as $(IP)^-$ and detected by electron spin resonance. This new band always appears as a shoulder and was not detected by Gold and Jolly⁵ in solutions relatively concentrated in metal. Presumably in their conditions the band was hidden under the absorption edge of the infrared band.

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