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Effect of Added Electrolyte on the Electron Spin Resonance Spectra of Solutions of Metals in Ammonia*

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IT is commonly believed that there are two paramagnetic entities in solutions of alkali metals in ammonia, one being pictured, broadly, as a "solvated" electron (e_1), and the other as an "expanded" metal atom (M).[1] Details remain obscure, and it is not certain to what extent either entity is present in solutions of different concentrations. In an attempt to constrain possible equilibria between these species to favor type M, sodium iodide was added to solutions of sodium in ammonia.[2] In addition to a slight shift of the main band in the 6800 cm^{-1} region, a shoulder appeared at 12 500 cm^{-1} together with a possible further inflection on the high-energy tail of this shoulder.[2] It was suggested that this band might be due to species M, and therefore that the 6800 cm^{-1} band was due to e_1 species.[2]

We have extended these studies over a wide range of concentrations of metal and salt and at various temperatures, and although the presence of a shoulder at 12 500 cm^{-1} has been confirmed, the species responsible for this is apparently never a major constituent of these solutions. These results differ from those of Gold, Jolly, and Pitzer,[3] but we agree with these workers that any absorption by dimeric species must occur close to 6800 cm^{-1} rather than in the visible region as postulated earlier.[4]

TABLE I. Variation of g with salt concentrations.

Metal/salt	Salt concentration (molal)	$\Delta g(-70°)$
Na/NaI	0.60	9.0
	0.80	14.0
	1.20	20.5
	1.60	26.0
	1.90	27.0
K/KI	1.00	21.5
	1.40	31.0
	1.70	35.0
	1.90	40.0
Cs/CsI	1.00	29.0
	1.60	49.0
	3.25	87.0

TABLE II. Variation of g with temperature.

CsI concentration (Molal)	$\Delta g(-70°)$	$\Delta g(-23°)$	$\Delta g(21°)$
1.00	29.0	33.0	44.0
1.60	49.0	59.0	66.0
3.25	87.0	97.0	111.0

The main outcome of concurrent electron resonance studies is that when the concentration of added salt is greater than about 0.5m there is a detectable decrease is the g value coupled with an increase in linewidth. These trends have been measured over the temperature range 21° to −70° and for salt concentrations up to the limit of solubility. The results, given in Table I for −70°, show small but certain differences in Δg as the cation is varied: Δg being given by

$$\Delta g = 10^4(g_{\text{metal solution}} - g_{(\text{metal+salt})\text{solution}}),$$

our value for g in the absence of added salt being 2.0011 at this temperature. This was independent of the concentration of metal, which was generally about 0.30m. The variation of g with temperature is typified by the results given in Table II for solutions containing cesium and its iodide. The lowest g value recorded in this work was 1.9904.

The width between points of maximum slope (ΔH_{MS}) for metal solutions is about 45 mG. Under our conditions lines were broadened by field inhomogeneity and other instrumental factors to 0.3 G and solutions containing iodide up to about 1.0 m had absorption bands with this width. Above this concentration ΔH_{MS} increased markedly to a limit of between 2 and 3 G, which was almost independent of temperature.

No resonance was detected from frozen solutions other than that ascribable to precipitated metal.

Samples, which were quite stable during periods required for measurement, were prepared by the method of Dewald and Lepoutre.[5]

The significance of the spin resonance results is that they provide evidence for definite interaction between the unpaired electrons and the added cations. This is not apparent from the studies of optical spectra. Since the absorption band in the 6800 cm^{-1} region is probably largely due to diamagnetic species present in these solutions[3] it will require a careful quantitative comparison before optical spectra can be assigned to the paramagnetic species present. Changes in the g values can be compared with those for F centers in different alkali halides, but are remarkably large considering the relatively low concentration of cations and anions. Further discussion is deferred to a later publication.

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