496. *Unstable Intermediates. Part VIII.* Magnetic and Spectrophotometric Studies of Dilute Solutions of Sodium in Ammonia.*

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The shape, oscillator strength (0·65 ± 0·05), and temperature-dependence of the 6700 cm.$^{-1}$ band of solutions of sodium in ammonia are very similar to the corresponding properties of the *F*-band in alkali halide crystals. Addition of sodium iodide results in a small shift of this band to higher energies and the appearance of a new band at about 12,500 cm.$^{-1}$. At 77° K these solutions set to clear blue glasses without precipitation of metal. Their electron resonance spectra are single symmetrical lines centred on the free-spin value with a width between points of maximum slope of 4·6 gauss. Prolonged photolysis with a tungsten filament lamp has no effect on the glasses. The results are discussed in relation to current models for these solutions and it is concluded that they are best explained by the "solvent-cavity" theory.

Magnetic studies have shown that, for metal concentrations less than about 0·1M, at least two species are present in metal–ammonia solutions, one being diamagnetic (e_2 species) and one paramagnetic (e_1 species).[1,2] Below about 10^{-3}M the e_2 species is almost

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* Part VII, *J.*, 1959, 963.

[1] Freed and Sugarman, *J. Chem. Phys.*, 1943, **11**, 354.

[2] Hutchison and Pastor, *ibid.*, 1953, **21**, 1959.

completely dissociated. These species are characterised by electronic absorption bands at about 15,000 cm.$^{-1}$ and 6700 cm.$^{-1}$ respectively.[3,4]

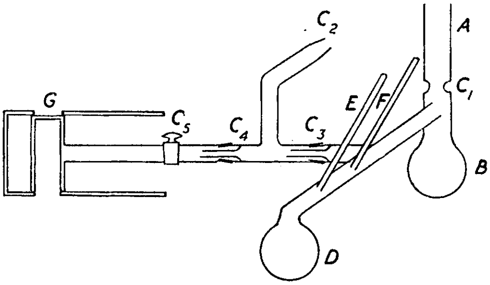
Of the many theories for these solutions, two seem to be suitable and widely accepted. The "expanded-metal" theory depicts the e_1 species (or "monomer") as a solvated sodium ion with the valency electron moving in an expanded orbital which embraces the cation and the first layer of oriented solvent molecules. The e_2 species is a weakly bonded "dimer" consisting of two such units having their valency electrons antiparallel in a molecular orbital covering both units.[5,6] The alternative "solvent-cavity" theory presents single or paired electrons in cavities defined by oriented solvent molecules and similar to the cavities which would remain if the negative ions of a dissolved electrolyte were removed from solution. In other words, the electrons occupy negative-ion vacancies and hence these resemble *F* and *F'* centres in alkali halide crystals.

Results of nuclear resonance [6] and *X*-ray scattering [7] studies have been interpreted in terms of the expanded-metal theory, but neither study could be extended to cover dilute solutions. This work was undertaken in an attempt to choose between the two models for the e_1 species, and was based on the following precepts: (i) That addition of a sodium salt to solutions of sodium in ammonia should favour the formation of monomer and dimer units at the expense of e_1 cavity units, and (ii) that if monomer units were present in relatively large concentration, electron spin resonance spectra of rigid solutions should show hyperfine lines characteristic of the nuclei of the cations.

EXPERIMENTAL AND RESULTS.

Preparation of Solutions.—The apparatus shown in Fig. 1 was used for the preparation and manipulation of sodium–sodium iodide–ammonia solutions.

FIG. 1. *Apparatus used for preparation of solutions of sodium in ammonia.*



The dried electrolyte was shaken into bulb *D*, and metallic sodium was placed in *A* which was then sealed off. The whole apparatus was evacuated through the B10 joint C_2, and well flamed to remove moisture. When gently heated, the metal ran into bulb *B* through constriction *C*, which was then sealed off. Ammonia, which had been dried by condensation on metallic sodium, was distilled into *D via* C_2, and was then allowed to melt and dissolve the electrolyte. By rotation of the apparatus about joint C_3, the ammonia solution was poured back and forth between bulbs *D* and *B*, until a blue solution of suitable optical density was obtained. Part of this solution was then poured into the optical cell *G*, this being of fused silica and with a light path of 0·1 mm. Surrounding the cell, with the exception of the light path, was a Perspex box containing a coolant, usually an alcohol–solid carbon dioxide mixture. After the cell had been removed for spectral measurements, the joint C_4 was stoppered and, with the remaining ammonia solution frozen, the apparatus was again evacuated through C_2. When the solution had melted, it was poured into the paramagnetic resonance sample tubes

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[3] Fowles, McGregor, and Symons, *J.*, 1957, 3329.
[4] Symons, *Quart. Rev.*, 1959, **13**, in the press.
[5] Becker, Linquist, and Alder, *J. Chem. Phys.*, 1956, **25**, 971.
[6] McConnell and Holm, *ibid.*, 1957, **26**, 1517.
[7] Schmidt, *ibid.*, 1957, **27**, 23.

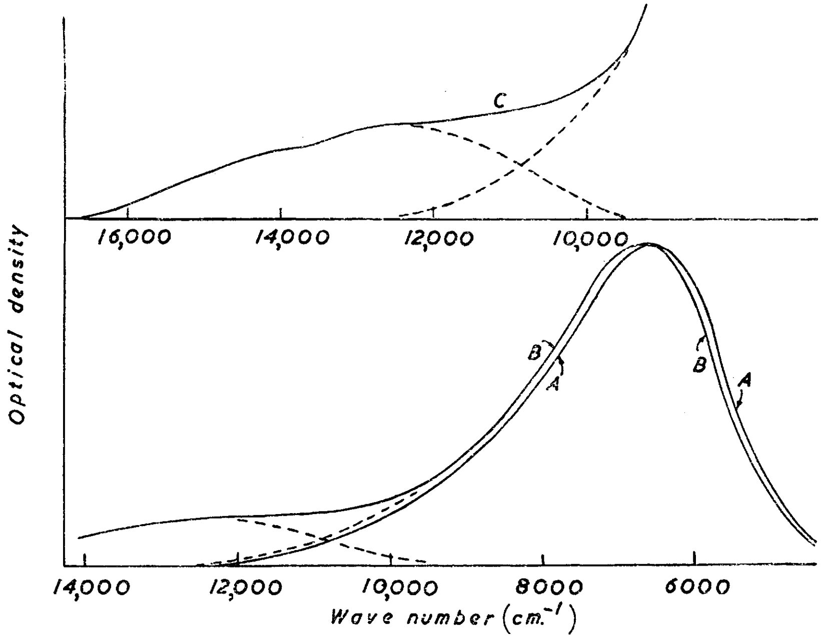
E and F which were then sealed off and removed. Spectral and paramagnetic resonance measurements were thus made on samples of the same solution.

Addition of sodium iodide reduced the stability of dilute metal solutions considerably, despite all precautions, and solutions nearly saturated with salt were too unstable for spectroscopy. All attempts to prepare stable solutions containing lithium salts failed.

Spectra.—The spectral measurements were made with a Cary model 14 recording spectrophotometer. During all measurements, dry nitrogen was passed through the cell compartment to prevent condensation of moisture on the optical windows.

Typical spectra are shown in Fig. 2. Even in the absence of sodium iodide the spectra are asymmetric, being broadened on the high-energy side. This asymmetry might be caused by very weak unresolved components at higher energies than the main band, but the recorded trace, which is plotted on a wavelength scale, is remarkably symmetrical throughout the whole of the band, and shows no sign of unresolved components. A similar phenomenon is found for F bands in alkali halide crystals, and may arise because of the dependence of oscillator strength on transition energy. An estimate of the bands responsible for the shoulders found in the spectra of solutions containing sodium iodide was obtained by subtracting the main band, it being assumed that the new band contributed nothing at 6700 cm.$^{-1}$. This new band is also markedly asymmetric, possibly because of the presence of a third band in the 15,000 cm.$^{-1}$ region.

FIG. 2. *Near-infrared spectra of solutions of sodium in ammonia.*



Curve A. Sodium in ammonia (5×10^{-4}M).
Curve B. Sodium in ammonia + sodium iodide (*ca.* 0·1M).
Curve C. Curve B extended to higher wavenumbers: optical density scale is doubled. The curves shown by dotted lines were derived by shifting Curve A until its peak coincided with that of B and then subtracting.

Extinction coefficients were estimated by direct comparison of optical densities and the areas under integrated electron spin resonance signals. We find $\varepsilon_{\text{max.}}^{6700} \approx 4 \times 10^4$. Hence, an oscillator strength for the 6700 cm.$^{-1}$ band of 0·65 ± 0·05 was measured by graphical integration of the whole spectrum. (In arriving at this value we have omitted the internal field correction, which should be quite small for these solutions.)

The concentration of metal in these solutions was about 5×10^{-4}M. With the cells available we were unable to study more concentrated solutions near the band maximum, but the short-wavelength edge of more concentrated solutions always showed a well-defined shoulder in the 15,000 cm.$^{-1}$ region.

Electron Spin Resonance.—The electron spin resonance measurements were made at 9000 Mc./sec. on a spectrometer in which a small modulation field at 10 kc./sec. was superimposed on the slowly varying main magnetic field, to give the derivative of the absorption line as the main field was swept through resonance. The 10 kc./sec. signal was mixed with a crystal-controlled 10·090 kc./sec. frequency and detected at 90 c./sec. with a mechanical, phase sensitive, chopper detector. The samples, in 5 mm. Pyrex tubes, were placed in the H_{102} rectangular cavity which was used in transmission and which could be maintained at 77° K by immersion in an insulated reservoir containing liquid nitrogen.

Frozen solutions containing sodium iodide were transparent blue glasses in contrast to solutions containing no added salt, which freeze to grey opaque masses containing small colloidal metal particles. Unfortunately the glasses invariably cracked so badly that their absorption spectra could not be recorded.

The electron spin resonance spectra were perfectly symmetrical gaussian curves centred on $g = 2{\cdot}002$ with no sign of hyperfine structure. The width between points of maximum slope (ΔH_{MS}) was 4·6 gauss, which is appreciably greater than the width for precipitated sodium (3·5 gauss).

Photolysis.—Glasses were irradiated at 77° K with light from a tungsten-filament lamp passed through several thicknesses of soda-glass. There was no gain or loss of colour after irradiation for 24 hr., and the electron spin resonance spectra were not altered.

Equilibria.—Becker *et al.* assumed equilibria (1) and (2) and found values for K_1 and K_2 from the magnetic data of Hutchison and Pastor [2] and Freed and Sugarman : [1]

$$\mathrm{M} \rightleftharpoons \mathrm{M}^+ + \mathrm{e}; \quad K_1 = [\mathrm{M}^+][\mathrm{e}]/[\mathrm{M}] \qquad (1)$$

$$2\mathrm{M} \rightleftharpoons \mathrm{M}_2; \quad K_2 = [\mathrm{M}_2]/[\mathrm{M}]^2 \qquad (2)$$

$$(\mathrm{M} = \text{monomer};\ \mathrm{M}_2 = \text{dimer})$$

K_1 for potassium was relatively insensitive to changes in temperature, and close to the value 0·05 estimated by Kraus from conductivity data.[8] K_2 increased markedly with decrease in temperature. No great weight can be placed on these figures, or on equilibrium concentrations estimated by their use, since concentrations have been used instead of activities.

Concentrations based on $K_1 = 0{\cdot}05$ and $K_2 = 10^3$.

No.	e	Na$^+$	M	M$_2$	Total Na
1	5×10^{-2}	5×10^{-2}	5×10^{-2}	2·5	2·6
2	$2{\cdot}2 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$	1×10^{-2}	0·1	0·132
3	1×10^{-2}	1×10^{-2}	2×10^{-3}	4×10^{-3}	$1{\cdot}6 \times 10^{-2}$
4	1×10^{-3}	1×10^{-3}	2×10^{-5}	4×10^{-7}	$1{\cdot}02 \times 10^{-3}$
5	1×10^{-4}	1×10^{-4}	2×10^{-7}	4×10^{-11}	$1{\cdot}002 \times 10^{-4}$
6	1×10^{-4}	1×10^{-1}	2×10^{-4}	$0{\cdot}4 \times 10^{-4}$	$3{\cdot}4 \times 10^{-4}$

However, a rough idea of the composition of various solutions can be obtained and some estimates are given in the Table, rounded values of 0·05 and 10^3 for K_1 and K_2 being used. The most significant conclusion to be drawn is that in very dilute solutions in the absence of added salt the concentrations of monomer and dimer are negligibly small.

DISCUSSION

Equilibrium (1) is an essential part of the expanded-metal theory since, without it, the high conductivities of dilute solutions of metals would be incomprehensible. The results show that the monomer is a minor constituent in dilute solutions. We conclude that the infrared band cannot be a property of the monomer because the very high oscillator strength of 0·65 is based upon the assumption that all the unpaired electrons are involved in the transition. Therefore this transition must be due to electrons which are not bound to sodium ions; these electrons are certainly bound in some way and we suggest that the e_1 cavity model is a good description of their ground state.

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[8] Kraus, *J. Chem. Educ.*, 1953, **30**, 86.

Taking this in conjunction with other considerations,[9] we can now present an overall picture of dilute solutions of metals in ammonia. That is, expanded-metal dimer units, responsible for the band at 15,000 cm.$^{-1}$,[9] dissociate on dilution, *via* monomer, into cations and e_1 cavities, the latter absorbing at 6700 cm.$^{-1}$. Further, we tentatively ascribe the 12,500 cm.$^{-1}$ band to monomer units, which are found in detectable amounts only in the presence of excess of cations.

This overall picture differs from that of Becker *et al.*[5] in that it retains the concept of electrons in cavities of oriented solvent molecules, and makes these units responsible for the 6700 cm.$^{-1}$ band instead of monomer units.

Some general consequences of this model will now be considered.

Spectra.—Any constraint favouring monomer must also favour dimer (cf. col. 6 of the Table). Most spectra showing the 12,500 cm.$^{-1}$ band also showed signs of a shoulder at 15,000 cm.$^{-1}$ which, we suggest, is due to very small concentrations of dimer (see Fig. 2).

The absorption spectra for corresponding alkali-metal atoms and dimeric molecules furnish a basis of comparison with the spectra assigned to monomer and dimer units. The atoms have intense transitions in the 14,000 cm.$^{-1}$ region ($P \longleftarrow S$) which fall between the $^1\Sigma_u{}^+ \longleftarrow {}^1\Sigma_g{}^+$ and $^1\Pi_u \longleftarrow {}^1\Sigma_g{}^+$ transitions of the corresponding molecules. There is a trend to lower energies on going from sodium to cæsium for all bands, and the two bands for the molecules converge. By analogy, one would expect a doublet for the dimer. However the separation between the two transitions for Cs_2 is only about 3000 cm.$^{-1}$, which is less than the width at half-height for the 15,000 cm.$^{-1}$ band.[10] This band could therefore be a closely spaced doublet.

Again, by analogy, the monomer should have a single intense band in the 15,000 cm.$^{-1}$ region, so that the tentative allocation of the 12,500 cm.$^{-1}$ band to this unit is not unreasonable. Although the spectra of dimer and monomer must be a function of the cation, nevertheless the orbitals are so diffuse that the major rôle of the cation must be to provide a positive centre, so the apparent independence of band maxima on the nature of the cation is not surprising.

Differences between cations become apparent in amine solvents: thus lithium and calcium in dilute solution in amine solvents have spectra which are dominated by the infrared band whereas solutions of the other alkali metals absorb largely in the 15,000 cm.$^{-1}$ region. We suggest that the monomer units must have a relatively high surface-charge density for the former, which may tend to reduce the probability of dimerisation.

Magnetism.—McConnell and Holm [6] estimated a value for P(Na), the density of the sodium nucleus at the unpaired electron, equal to $5 \times 10^{-3} \times P^{\circ}$(Na), the computed value for a 3*s* electron. From this, and the estimated value for the hyperfine splitting constant for sodium atoms [11] we find that an electron spin resonance spectrum consisting of four equally intense lines with an overall splitting of about 5 gauss should be observed if monomer units were the major paramagnetic component. Under conditions favouring rapid exchange processes such as (1) and (2) this hyperfine structure might be lost, but such reactions should not occur in a rigid glass. The shape and width of the observed single line are incompatible with this conclusion unless contact with hydrogen and nitrogen nuclei broaden the individual lines of the quartet beyond the limit of resolution.

Kaplan and Kittel [12] have shown that if the unpaired electrons existed in solvent cavities and moved in orbitals built up largely from 1*s* orbitals of the solvent hydrogen atoms on the periphery of the cavity then, in the absence of line narrowing due to fluctuations of the solvent molecules, a line width of 10ξ would be expected. (ξ is a measure of the effective *s* character of the molecular orbital on hydrogen and is probably close to unity.) The experimental width of 4·6 gauss is quite close to this estimate, so the line could be due to e_1

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[9] Symons, *J. Chem. Phys.*, 1959, **30**, in the press.

[10] Blades and Hodgins, *Canad. J. Chem.*, 1955, **33**, 411.

[11] Kip, Kittel, Levy, and Portis, *Phys. Rev.*, 1953, **91**, 1066.

[12] Kaplan and Kittel, *J. Chem. Phys.*, 1953, **21**, 1429.

cavity units of this type, though Knight shift studies do not seem in accord with this extreme situation.

McConnell and Holm [6] found relatively large Knight shifts for ^{23}Na and ^{14}N nuclear resonance lines but no shift for the ^{1}H line. Measurements could not be extended to cover concentrations less than about 0·1M, so the relative amount of paramagnetic species was always small. The shifts for sodium seem to provide good evidence for the existence of monomer units, and the decrease in P(Na) over the range 0·4—0·1M is in accord with equilibria (1) and (2).

Pitzer has shown that the large shift for nitrogen, and the small shift for hydrogen, could arise if NH_3^- ions are formed, the extra electrons moving in orbitals which are " 3*s*-like " for nitrogen.[13] If such an orbital had a node close to the hydrogen atoms then hyperfine contact interaction with protons would be small.[13] Further details are not given. Three extreme cases can be visualised. In one, the unpaired electrons move only on ammonia molecules directly solvating cations or on the periphery of cavities. Another would allow the electron freedom to move throughout the solution rather like a conduction electron. The third consists of NH_3^- ions as distinct entities, solvated in the normal way.

The " conduction-electron " model is not compatible with the results of spectrophotometric, conductimetric, or electron resonance studies.[4] The solvated NH_3^- model is similar to an e_1 cavity model with an ammonia molecule at the centre, since oriented solvent molecules are needed to provide bonding. We prefer the simple e_1 cavity model for the following reasons:

(i) If the Knight shift arises because of contact hyperfine interactions between electrons and single nitrogen nuclei then, when the solutions freeze, such units should cause marked hyperfine splitting of the electron spin resonance spectra. A rough estimate of the expected splitting can be derived by using the experimental value for P(N) of $4{\cdot}5 \times 10^{24}$ cm.$^{-3}$ obtained from the Knight shift.[6] Using $a = 2{\cdot}7\pi\mu_{\beta}\cdot\mu_{N}P(\mathrm{N})/I_{\mathrm{N}}$, where a is the hyperfine splitting constant in gauss, and the other symbols have their usual significance,[11] we obtain $a \gtrsim 75$ gauss. We conclude that each unpaired electron must be distributed over a fairly large number of ammonia molecules since a single narrow line is obtained.

(ii) On the basis of the solvated NH_3^- model one would predict an increase in P(N) on dilution which would parallel the decrease in P(Na). If, however, the electron, bonded primarily by the central positive charge due to either cations or oriented solvent molecules, moves, when sufficiently close, in the lowest-energy vacant molecular orbitals of the solvent molecules, then this insensitivity to changes in concentration is understandable.

If these orbitals are as Pitzer has suggested,[13] then the lack of shift for hydrogen is accommodated. However the general picture may still hold even if these orbitals do not have nodes at the hydrogen nuclei. The small shift does not necessarily mean that hyperfine contact interaction does not occur; indeed the results of Carver and Slichter, who studied the Overhauser effect in metal–ammonia solutions, seem to show that such interaction is quite strong.[14,15] The unpaired electron density for 1*s* electrons on hydrogen, P^0(H), is $2{\cdot}1 \times 10^{24}$ cm.$^{-3}$, which is less than the measured value for nitrogen. If the estimate [6] that $P(\mathrm{H})/P(\mathrm{N}) \leqslant 0{\cdot}4$ is correct for 0·1M-solutions, then no shift would have been detected even if the paramagnetism were due to free hydrogen atoms. Also, dipolar interaction between electrons and protons would shift the nuclear resonance spectra in a direction opposite to the Knight shift and would help to cancel any shift due to contact interaction. This is the case for the effect of certain paramagnetic ions on the hydroxyl-hydrogen atom of *n*-propyl alcohol.[16]

Photolysis.—It seems probable that if electrons are ejected from their bonding sites

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[13] Pitzer, *J. Chem. Phys.*, 1958, **29**, 453.

[14] Carver and Slichter, *Phys. Rev.*, 1956, **102**, 975.

[15] Van Vleck, *Nuovo cim.* (*Suppl.*), 1957, **6**, 1081.

[16] Phillips, Looney, and Ikeda, *J. Chem. Phys.*, 1957, **27**, 1435.

they return to the same type of site rather than choosing new ones. If sufficiently transparent glasses can be prepared, spectroscopy should decide this question. This is a surprising result in view of the high concentration of " monomer sites " in the glass, and may mean that the electrons are not totally ejected under the conditions used, or that concurrent photo-ionization of monomer units is more efficient. This result is in marked contrast with that of Linschitz, Berry, and Schweitzer [17] who found that photolysis of rigid solutions of lithium in mixed solvents containing methylamine resulted in very rapid bleaching of the band at 16,500 cm.$^{-1}$, paralleled by general increase in extinction in the near infrared region with a very broad maximum in the 12,000 cm.$^{-1}$ region. If the 16,500 cm.$^{-1}$ band is a property of the dimer, then the photolysis could follow various paths, the most probable being ejection of both electrons into shallow traps in the rigid solvent.

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[17] Linschitz, Berry, and Schweitzer, *J. Amer. Chem. Soc.*, 1954, **76**, 5833.