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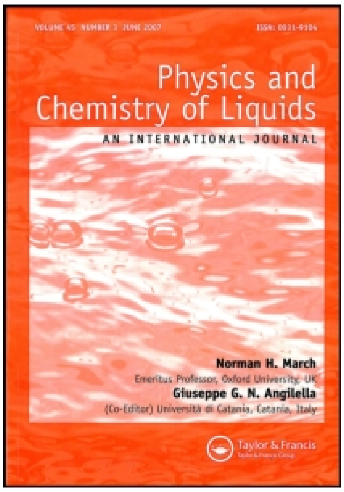

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The Electronic Properties of Metal Solutions

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Review Article

The Electronic Properties of Metal Solutions

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The introduction of sodium metal into anhydrous liquid ammonia produces an intensely coloured blue solution in which localised excess electrons, sodium cations, and various agglomerates of these species co-exist in equilibrium. With increasing metal concentration the system transforms into a bronze metallic conductor. In the transitional range, cooling of the (homogeneous) sample can give rise to a remarkable liquid-liquid separation in which both dilute (blue) and concentrated (bronze) phases co-exist. The apparent experimental simplicity of this system which permits the localisation of the fundamental unit of electrical change in dilute solutions, and its itineracy in concentrated solutions, has attracted a considerable amount of study from both chemists and physicists during the last 100 years.

In this article we discuss the recent advances made not only in the study of metals in liquid ammonia, but also in solutions of metals in various other solvents, for example, amines and ethers. The review attempts to cover the properties of metal solutions in the dilute and concentrated ranges, as well as the nature of the Metal-non-Metal transition in these systems.

1 INTRODUCTION

In the absence of catalysts, alkali, alkaline—earth and certain lanthanoid metals dissolve freely in anhydrous liquid ammonia to yield highly conducting solutions—blue and salt-like in the dilute regime; bronze and metallic in the concentrated range. Their intense blue or metallic-bronze colours, their two liquid phases and, as Cohen and Thompson[1] put it, "to say nothing of one's initial surprise at their very existence," perhaps excuse their initial treatment as scientific curiosities following their discovery by Weyl[2] in 1863. However, the physical properties of these intriguing liquid systems have been studied in considerably more serious vein[3–5] by both chemists and physicists since the 1920's. At the present time this interest continues unabated. The recent Colloque Weyl V Conference on Metal-Ammonia Solutions and Excess Electrons in Liquids[3e] brought together some 150 scientists from all disciplines. In a review of some 40 pages long one cannot expect to do justice to the sheer depth and extent of investigations into these systems.[5] However, our aim here is to provide a general background discussion centred around recent advances in studies of metals not only in ammonia, but also in various other solvents. To this author, *the* important feature to emerge from investigations of metal solutions in the last two decades has been the striking advances made possible from studies of metals in solvents other than ammonia. As Dye suggests,[6] in any description of metal solutions we invariably return to the ammonia system for guidance. Certainly in this solvent we have, at the present time, most data on physical and chemical properties. However, in contrast to the ammonia system, metal solutions in amines and ethers are rich in information about *distinguishable* species existing in solution. Section 2 will outline certain recent developments in these solvent systems which have led to a fairly detailed picture of *localized* electronic states in the dilute range.

Similarly there has been considerable interest recently in the study of the transition from localized-to itinerant-electron states in solvents other than liquid ammonia. In particular, a substantial body of experimental data is now emerging for the Metal-non-Metal transition in the lithium-methylamine system which allows a direct comparison with the situation existing in metal-ammonia solutions. (Section 3).

In the concentrated region, lithium-ammonia solutions have a conductivity exceeding that of liquid mercury. In contrast, the conductivity of saturated lithium-methylamine solutions is almost two orders-of-magnitude smaller than the value in ammonia solutions. However, a variety of properties are completely different from those expected for normal liquid metals. In Section 3 we briefly review recent studies of concentrated solutions, and consider the corresponding "expanded-metal" compounds, $Li(NH_3)_4$ and $Li(CH_3NH_2)_4$ formed by slow-cooling of the fluid solutions.

2 DILUTE SOLUTIONS

A Metals in liquid ammonia

In dilute solutions the accumulated evidence for the electrolytic nature of these systems is overwhelming—metal atoms spontaneously dissociate into excess electrons and positive ions

$$Na \rightarrow Na^+ + e^-, \tag{1}$$

(recall that the corresponding process[7] in the *gas-phase* requires some 2–4 eV!). Drawing upon analogous "conventional" electrolyte solutions, e.g. aqueous salt solutions, one infers that both species are "solvated" in that they polarise the surrounding dipolar solvent molecules in their own Coulombic field. This idea of "solvating" a fundamental particle is indeed intriguing. Kraus[8] first proposed that the excess electron existed in a "cavity" in the solvent in which one or more of the ammonia molecules have been excluded, thereby accounting for the extremely low density of the solutions.

However, it was Gibson and Argo[9] who were the first to apply the term "solvated electrons" for the excess electron states.

Jortner, in a milestone contribution,[10] elaborated on this simple physical picture. He supposed that the electron resided in a cavity of radius (R) approx. 3.2–3.4 Å in the solvent. The liquid ammonia in the vicinity of the cavity is polarised by the electron, producing a binding energy potential given by

$$V(r) = \frac{-\beta e^2}{R}[H(R - r)] - \frac{\beta e^2}{r}[H(r - R)] \tag{2}$$

where $H(x)$ is a step function, $\beta = K_{\infty}^{-1} - K_{\mathrm{st}}^{-1}$ and K_{∞} and K_{st} are the high- and low-frequency dielectric constants, respectively. Other polarization terms are added after the variational solution of the ground ($1s$) and first excited state ($2p$) of the electron in this potential well are calculated. On this approach the solvent is assumed to be a continuum, with the majority of the electron binding energy originating in the long-range electron-medium interaction.

More elaborate treatments for calculating the electronic energy levels and eigenfunctions for the excess electron have since been developed which attempt to introduce certain microscopic features of the local molecular environment. Among such approaches, the semi-continuum models proposed by Copeland, Kestner and Jortner[11] are the most popular, and the reader is referred to Refs. 12 and 13 for recent reviews. For illustrative purposes we will utilise the simple adiabatic model of Jortner[10] because of its obvious transparency in relating the major features of solvent properties to the energy levels and wave functions of the solvated electron.

The derived potentials, energy levels and wave functions for the solvated electron in two representative solvents, $MeNH_2$[14] and hexamethylphosphoramide† (HMPA)[15] are compared in Figure 1. The characteristic broad optical absorption band in the near infra-red is generally associated with the 1s → 2p transition of the electron within the potential well. Theory predicts,[11b,16] and experiments confirm,[14,17] a high transition probability for this excitation. Whatever the pecularities of the local structure around e_s^-, the energy of the optical transition does seem to be *coarsely* related to the binding energy of the excess electron in the dielectric medium. HMPA is taken as representative of a large, bulky aprotic solvent[15] in which electron and, indeed, any anion solvation is very weak. Methylamine is representative of a solvent in which the electron binding energy is considerably larger.[14,16,17] Within the cavity the electron wavefunction assumes its maximum value, outside the cavity the wavefunction asymptotically approaches zero. Although there is obviously a high degree of charge confinement within the

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† HMPA, $[(CH_3)_2N]_3PO$.

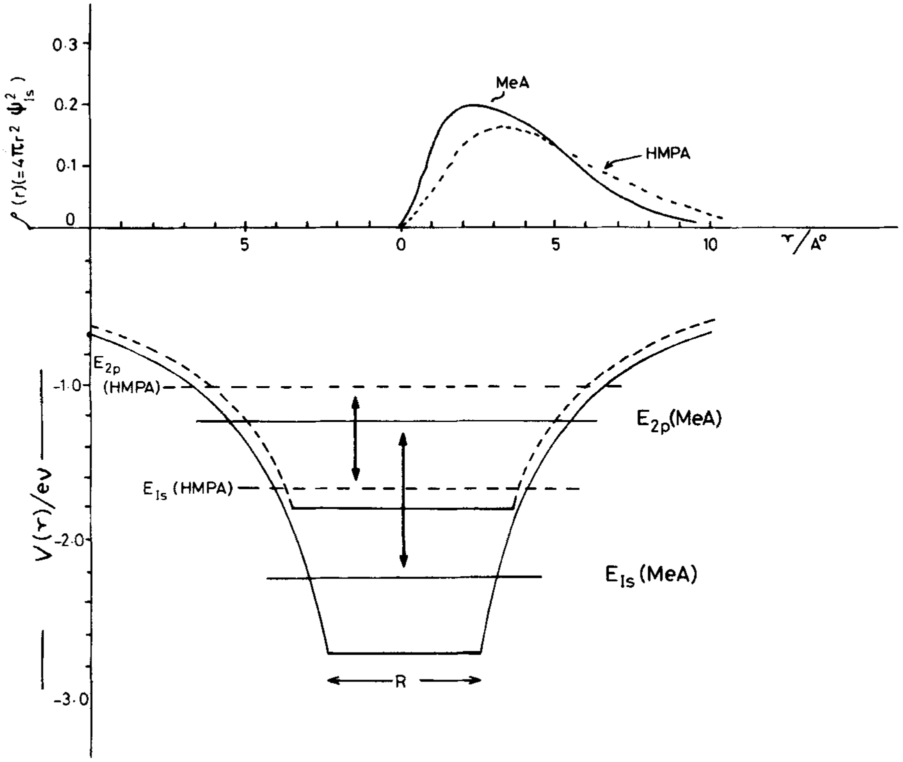

FIGURE 1 Energy levels and wavefunctions for the isolated solvated electron in methylamine (MeA) and hexamethylphosphoramide (HMPA).

cavity, there is also a considerable amount of change dispersion far beyond the first solvation layer. In this region the overall binding potential is obviously small, but nevertheless significant.

i) *Electron-cation interactions* As with any electrolyte, various aggregate species are expected to form as the concentration of solute increases. In particular, both the electrical conductivity and (metal) n.m.r. data signal the appearance of neutral species at metal concentrations 10^{-3} to 10^{-2} mole percent metal (MPM)[18]; the conductivity via a Morse-like behaviour in the equivalent conductance, the magnetic resonance via a finite Knight shift for the metal nucleus.[1] As expected for a high dielectric solvent, the ion-pairing association

$$M_s^+ + e_s^- \rightleftharpoons M_s \qquad (3)$$

is best viewed as a simple (and very short lived,[19] ca. 10^{-12} sec) ionic aggregation involving a complex in which there is negligible distortion of either the solvated electron or solvated cation wavefunction. The quite small Knight shift at the metal nucleus (ca. 1% of the free atom value) does indeed indicate a weakly-interacting association complex.

In this concentration range where the ion-pairing process is quite clearly indicated by the conductivity and n.m.r. data, the optical absorption peak shows certain minor modifications.[1,17,20] The precise origins of these changes are still a matter of some controversey.[17,20,21] An excellent, and timely review by Seddon and Fletcher[21] highlights recent advances in the study of optical properties, and at the same time establishes the inherent difficulties associated with the precise resolution and interpretation of metal solution spectra.

Another important property, the apparent molar volume of the solvated electron, is essentially unaffected by the electron-cation and, indeed, the electron-electron interaction.[1] The appellation "loose ion-pair" is therefore a particularly apt description for the association complex in metal-ammonia solutions.

ii) *Electron spin-pairing* The nature of the interaction which leads to electron spin-pairing is far less clear.[22] Figure 2 shows paramagnetic spin concentrations[23] for metal-ammonia solutions at 298 K, 273 K, and 240 K. The rapid decrease in the molar spin susceptibility of metal-ammonia solutions at 240 K in the concentration range 10^{-3} to 1 MPM below that expected for an assembly of localised electrons has been taken as direct evidence for the formation of diamagnetic complexes having an even number of electrons in a singlet ground state.[1,5] For example, at 0.1 MPM, at least 90% of the electrons are spin-paired at 240 K and the diamagnetic state is apparently several times kT lower in energy than the triplet or dissociated doublet states. In addition, lower temperatures favour the diamagnetic state.

In the weak interaction model[24] advocated to explain ion-pairing, aggregation interactions involving M_s^+ and e_s^- are relatively weak and leave the isolated, solvated electron properties relatively intact. This type of approach is consistent with the insensitivity to metal concentration of so many properties in the dilute regime.[1,22] However, a major difficulty[22] with this type of model arises when one considers the precise nature of the spin-pairing interaction in ammonia solutions. It is worth expanding on this issue, because it probably remains one of *the* fundamental dilemmas[22] of metal-ammonia solutions in the dilute range.

The mere existence of diamagnetic states in dilute $M-NH_3$ solutions in themselves present no direct threat to the weak-interaction model; spin-spin

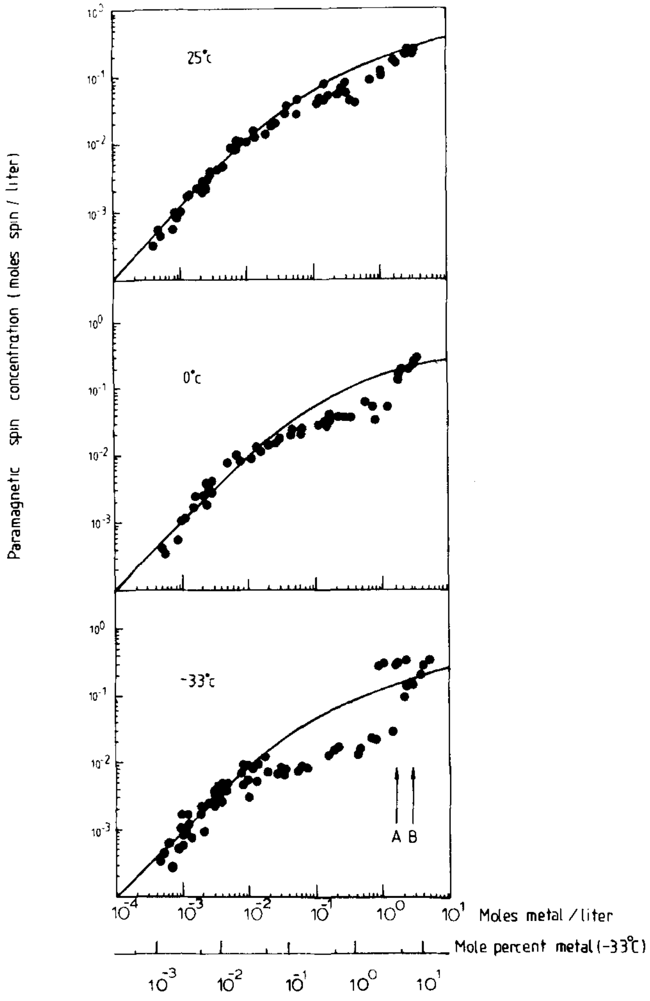

FIGURE 2 Paramagnetic spin concentrations for metal-ammonia solutions at three temperatures. The points represent experimental data from a variety of investigations (for a complete tabulation, see Refs. 23 and 27). The solid line indicates the predicted spin-pairing behaviour for non-interacting electrons. The arrow A denotes the onset of the Metal-non-Metal transition; B denotes the end of the transition (Ref. 1).

interactions could conceivably be incorporated into an ion-cluster model[24] where spin-pairing occurs via collision complexes, or long-range interactions between the isolated solvated electrons, possibly mediated via an intermediate cation. Indeed, a major result of a recent study[25] of solvated electron interactions is that the ground, singlet state is separated from the lowest triplet state by kT at distances of separation as large as 10.5 Å.

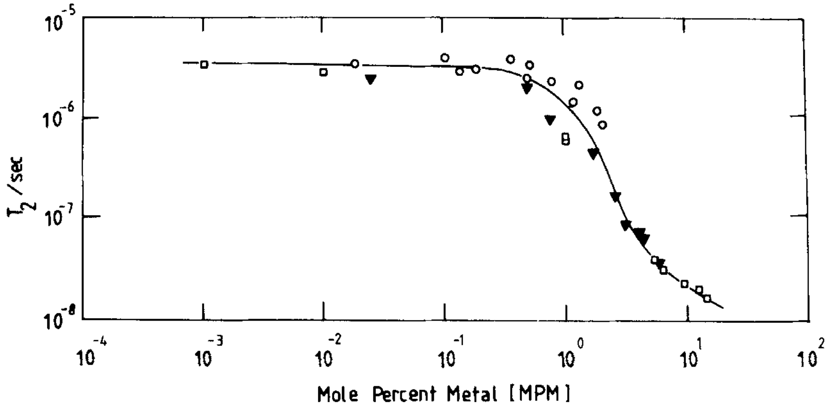

FIGURE 3 Electron spin-spin relaxation times (T_2) of metal-ammonia solutions at 238 K. Experimental data from a variety of sources; adapted from *U.* Schindewolf, *Zeit. für Physik. Chemie*, **112**, 153 (1978).

However, this type of scheme does run into some difficulty when one considers the exceptionally long lifetime (ca. 1μ sec) of the electron-electron spin-pairing interaction required to maintain the electron spin-state lifetimes, as detected by electron spin resonance (e.s.r.).[22,26] Measured electron spin-spin relaxation times (T_{2e}) for solutions in the concentration range 10^{-4} to 10^1 MPM are given in Figure 3. These spin resonance linewidths are among the narrowest known and, particularly for the lighter alkali metals, are essentially constant over the composition range (10^{-2} to 0.5 MPM) in which the spin susceptibility reveals that extensive spin-pairing is taking place (Figure 2). A long-range interaction between solvated electrons in the 10^{-3} to 10^{-2} MPM concentration range (with average separations ca. 90 to 180 Å) might be expected to produce relatively weakly bound diamagnetic units (but see comments in the preceding paragraph) which would rapidly separate into two individual e_s^- units. This should lead to considerable uncertainty in the electron spin lifetime and an electron spin relaxation rate which is markedly composition dependent. The effect is *not* observed (Figure 3). The extremely narrow ESR, with its attendant long T_{2e} in the μsec range,[26,44] then requires[22] that processes of the type

$$e_1 + e_1 \rightleftharpoons e_2 \tag{4}$$

have encounter lifetimes exceeding 10^{-6} seconds (recall that the corresponding lifetime of $M_s^+ e_s^-$ encounter ion-pairs in ammonia is only[19] ca. 10^{-12} sec). Thus the singlet state, once formed, must apparently exist for a microsecond or so, before conversion into a dissociated pair of electrons.

It has been suggested[22] that the exceptionally long lifetime of the singlet state may still arise from weak, long-range interactions, but with the lifetime requirements being satisfied through additional electron-exchange processes of the type

$$e_1^\alpha + \begin{bmatrix}\text{diamagnetic}\\ \text{cluster}\end{bmatrix} \rightleftharpoons \begin{bmatrix}\text{diamagnetic}\\ \text{cluster}\end{bmatrix} + e_1^\alpha \ldots \qquad (5)$$

However, this scheme does present major conceptional difficulties, and has been criticised recently.[28] In particular, the formation of specific diamagnetic (cluster) units at these very low metal concentrations might be considered unrealistic in view of the large (average) electron-electron separation (ca. 100 Å) and the isolation from the metallic state, with associated clustering phenomena[1,29,30] (occurring around ca. 4MPM for Na–NH_3).

Even without the complexities of electron-exchange processes of the type outlined above, the fundamental nature of the interaction between two solvated electrons leading to spin-pairing has yet to be firmly established. A treatment of the bonding in terms of a valence bond approximation has been attempted by Schettler and Lepoutre,[25] stressing the diffuse nature (Figure 1) of the trapping potential for the solvated electron. However, this treatment takes no account of the (rapidly) varying electron density with metal composition. A superexchange type process, involving an intermediary metal cation, is implicit in the recent suggestion by Mott[31] for the spin-paired species in ammonia. While there is some evidence for "ion-triples," $e_s^- M_s^+ e_s^-$, in a recent study of lanthanoid metals in ammonia,[32] the suggestion has also come under some criticism.[33] Clearly, charge neutrality must demand some cation involvement, but the details of the interactions remain to be firmly established.

Mott,[31] in an interesting contribution, has recently argued that the presence of phase separation in M–NH_3 solutions (Section 3.C), for compositions close to the Metal-non-Metal (M–NM) transition, demands spin-paired entities which are essentially "bipolarons"[34] involving two separate cavities (each containing an electron) associated with a cation, rather than two electrons within the same cavity in the solvent. The rationale behind this type of argument is that phase separation in liquid systems *at the M–NM transition* is only to be expected[31] when localised electron states are not engaged in strong homopolar bonding, e.g. Hg_2 in the case of Hg.

In a slightly different area, the recent progress into the theoretical description of single and interacting hydrogen impurities in metals[35,36] may, in future, provide some guidelines for describing the nature of the spin-pairing interaction in M–NH_3 solutions. A general picture to emerge[35] in free-electron like metals is that interactions between impurities can be discussed in terms of bonding (σ_g) and antibonding (σ_u^*) molecular orbital states. The primary effect of the metal conduction electrons is to fill the antibonding σ_u^* orbitals, thereby reducing the molecular dissociation energy at metallic densities compared to the "vacuum" value. This type of description has been extended by Ferraz *et al.*[36] in a study of the metal-molecular crystal phase transition from metallic H to solid H_2. Such a description is particularly attractive in the context of M–NH_3 solutions, where the transition from the metallic state gives rise to a lattice of predominantly diamagnetic states in the localised-electron regime (Figure 2). The picture of M–NH_3 solutions in terms of a "matrix-bound" analogue of the H/H_2 situation was advanced some time ago by Pitzer[37] (see also Section 3c) and may warrant further consideration. Similarly, Mott's detailed exposition[38] of the nature of the Metal non-Metal transition in M–NH_3 solutions is also based on the description of *localised* electrons in spin-paired states, the molecular bipolarons.

In this context it is also interesting to note that spin-pairing in Na–NH_3 is prevalent in the concentration range 10^{-3} to 1MPM, but as the system moves through the M–NM transition, the paramagnetic susceptibility rapidly approaches the predicted value for an assembly of degenerate electronic states[1] (Figure 2).

The time is indeed ripe for more detailed experimental and theoretical investigations into the spin-pairing phenomenon in metal solutions. Indeed, a considerable portion of the experimental data in this controversial area dates back to the late 1950's; and for some data,[39] even earlier!

B Solutions in amines, ethers and other solvents

One underlying theme to have (hopefully) emerged from the previous section is the lack of *specific* information[6] about distinguishable species in dilute M–NH_3 solutions. This might be anticipated to be a natural consequence for aggregate species in a host solvent with a large dielectric constant ($K_{st} \sim 17$ at 300 K). The properties of dilute M–NH_3 solutions are then best characterized[7,16] in terms of an assembly of isolated fragments (M_s^+ and e_s^-) in which the solvated electron forfeits *any* parentage in the electronic states of the gas-phase alkali atom.

In contrast to ammonia solutions, in which the alkali metal cation merely assumes a "bystander" role in the formation of aggregate species, metal solutions in the low-dielectric amines and ethers ($K_{st} < 10$ at 300 K) show a multitude of metal-dependent species, both paramagnetic and diamagnetic. The general body of experimental information requires the presence of *at least* three distinct species in solution[6,40,41]

$$M_s^+ + e_s^- \rightleftharpoons M_s \rightleftharpoons M_s^-, \tag{6}$$

the solvated, electron, the aggregate species of e_s^- and M_s^+, generally described as a monomer, (M_s) and a dielectron species, now well characterised in these systems as a centrosymmetric (solvated) alkali metal anion.

The association of (solvated) cation and electron (Eq. 3) can no longer be described as a weakly interacting ion-pair species; in these solvents we have immediately recognisable changes in the electronic properties of the aggregate species compared to its constituent partners. A problem of classification now enters,[40,43] when, for example, terms such as "loose", "tight", "solvent-separated", ion-pairs are introduced to describe the association complex.[42] However, we may make the general comment that the majority of aggregate species are more "tightly-bound" than in ammonia solutions; as anticipated from the decrease in the solvent dielectric constant. By this we mean that the electron-cation interaction can be sufficiently strong to introduce a noticeable metal dependence into the electronic properties.

This metal dependence also carries over to the spin-paired species. In the lower dielectric solvents these can no longer be represented in terms of weak, long-range interactions possibly mediated by an intervening cation, but are now distinct, new molecular species.[40,43]

In the following sections we outline a small portion of the spectroscopic information regarding these distinguishable species.

i) Paramagnetic states. Alkali metal monomers: ion-pairs to solvated alkali metal atoms

a) Fluid solutions Perhaps the most telling information regarding the nature of the monomer species, M_s, Eq. (3), arises from e.s.r. studies. The e.s.r. spectrum of the isolated, solvated electron consists of a single, narrow line with a g_e-factor close to the free-spin value, e.g. in ammonia the resonance has a width of ca. 30 mG and $g_e = 2.0016$.[44] Given the possibility of an interaction with an alkali cation (Eq. 3), an appreciable electron (spin) density *can* exist at the metal nucleus. Provided this electron-cation pair has a sufficiently long lifetime, then a hyperfine interaction ($A\mathbf{I} \cdot \mathbf{S}$) is possible,[19,45] resulting in $(2I + 1)$ lines in the e.s.r. spectrum, where I is the nuclear spin of the cation. In fact, the observation[46] of metal-hyperfine splitting in metal-amine solutions provided the first unambiguous identification of the atomic stoichiometry of the monomeric species M_s.

The separation (A) of the hyperfine lines in the e.s.r. spectrum represents a direct measure of the average s-electron density of the electron at the particular nucleus.[47] When this splitting is compared to that of the free (gas-phase) atom, we obtain a measure of the "percent atomic character" of the monomer. The percent atomic character in all these fluid systems increase

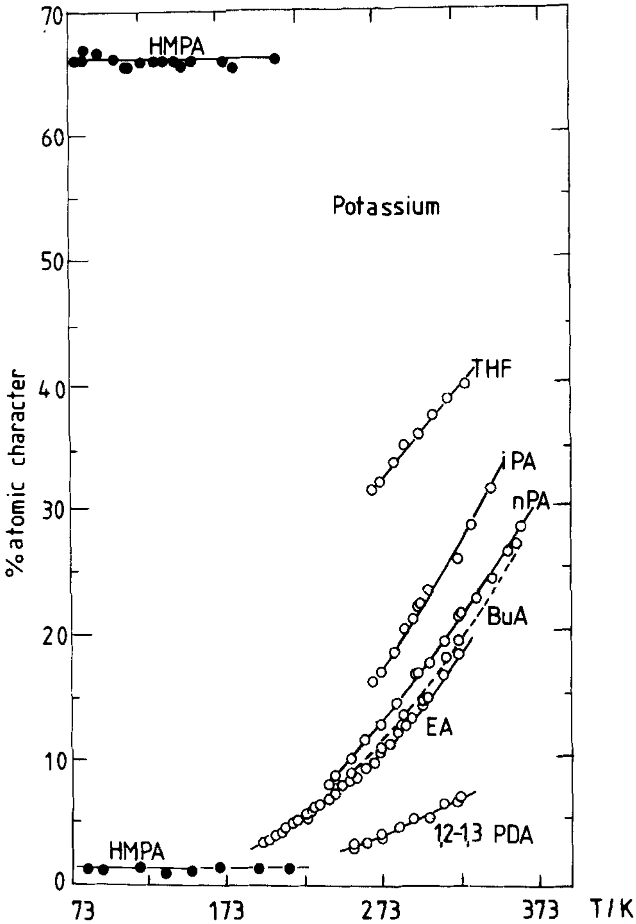

FIGURE 4 A comparison of temperature dependent changes in the metal hyperfine coupling constant (expressed in terms of percent atomic character) for fluid and frozen solutions of potassium in various solvents. Solvent identification: HMPA-hexamethylphosphoramide; THF-tetrahydrofuran; iPA-isopropylamine; nPA-n-propylamine; BuA-butylamine; EA-ethylamine; 1,2-1, PDA-1,2 and 1,3 propanediamine.

markedly with temperature, and under certain circumstances the monomer almost takes on "atomic" characteristic (Figure 4).[6,7,40] At the present time it is still not possible to unequivocably distinguish between the two models proposed to explain this type of behaviour;[45]—a rapid equilibrium among distinct (temperature-independent) species, or a single species whose electron distribution is markedly dependent upon temperature and solvent.[48]

The striking effect of the solvent upon the e.s.r. spectra of metal solutions is illustrated in Figure 5 for solutions of K, Rb and Cs in three solvents.

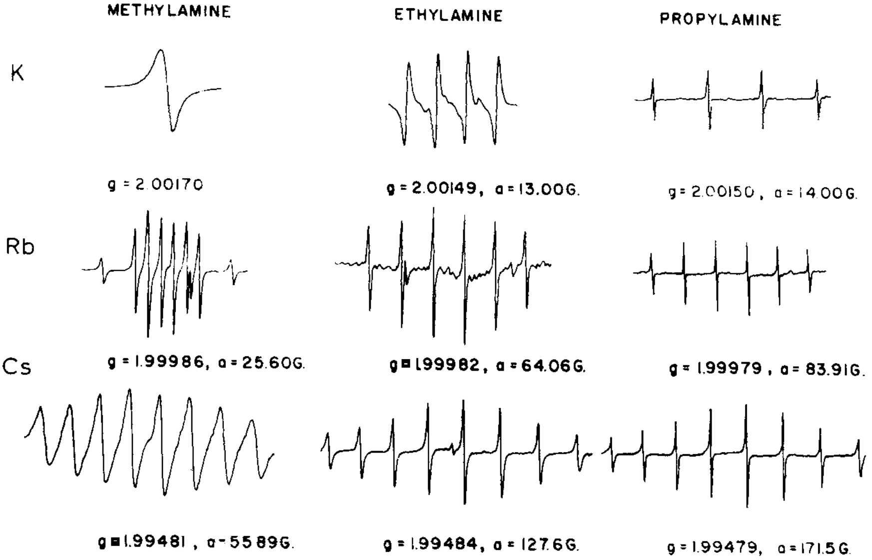

FIGURE 5 Some ESR spectra of K, Rb and Cs in three solvents (adapted from J. L. Dye, *Pure and Appl. Chem.*, **49**, 3 (1977)). Note the change in scale from pattern to pattern as indicated by the hyperfine splitting given.

A simple ion-pairing treatment is quantitatively capable of predicting the form of the ESR spectrum in the wide variety of metal-solvent systems.[19,40,45] Briefly, two parameters are critical in determining the spectra obtained,[19] the effective lifetime (τ_M) of the (primary) electron-cation encounter process (Eq. 1, calculated from diffusion-controlled encounter theory) and A_M, the metal hyperfine coupling constant, expressed in hertz. The product $P_c = \langle \tau_M A_M \rangle$ defines the form of the ESR spectra. For the high-dielectric solvents (NH_3, HMPA, etc $P_c \ll 1$ and a "time-averaged" signal of both paramagnetic species (e_s^-, M_s) is observed. In the lower-dielectric solvents, $P_c \ll 1$, and the encounter lifetime is sufficiently long to permit the conversion of the "loose" ion-pair to a centrosymmetric species representing something like an "expanded metal atom".[48] The latter species has the capability (in a low-dielectric solvent) of a large hyperfine coupling to the metal nucleus and Figure 6 shows the established[19] P_c values and observed features of the e.s.r. spectra.[45]

The success of this type of approach emphasises once again that, despite the unique nature of e_s^-, and the various types of association complexes formed with solvated alkali metal cations, a standard ion-pairing treatment does indeed give a reasonable semi-quantitative description of the magnetic and electrical properties of dilute solutions,[1,22]

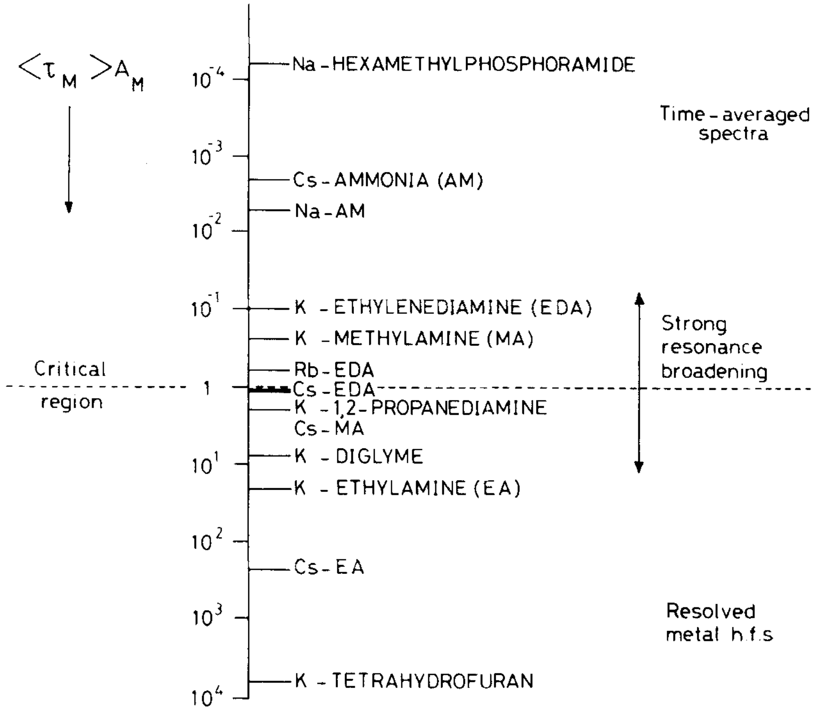

FIGURE 6 Classification of ESR spectra of fluid metal solutions on the basis of the product $\langle \tau_M \rangle A$.

Optical spectra of fluid amine and ether solutions contain a band in the near infra-red, similar in shape and position to the e_s^- band in ammonia solutions, and two additional bands at higher energies, whose positions are dependent primarily upon the alkali metal.[21,49] One of these metal-dependent bands has been assigned to solvated alkali metal anions[56] whilst kinetic studies have demonstrated that the other, *transient* band (observed via fast detection techniques, e.g. pulse radiolysis) arises from the monomeric species M_s[21]. The position of the M_s optical absorption exhibits a distinct blue shift from that of e_s^- observed in the same solvent. Furthermore, a close correlation has been established[50,51] between the magnitude of this shift and the per cent atomic character of the species M_s as determined by e.s.r. studies. Figure 7 shows optimal and e.s.r. data for potassium and caesium monomeric states in a variety of host matrices.[52] This correlation extends over the entire range from ion-pair-like species in the high dielectric solvents (NH_3, CH_3NH_2, etc.) through to atom-like variants in the non-polar rare-gas matrices.

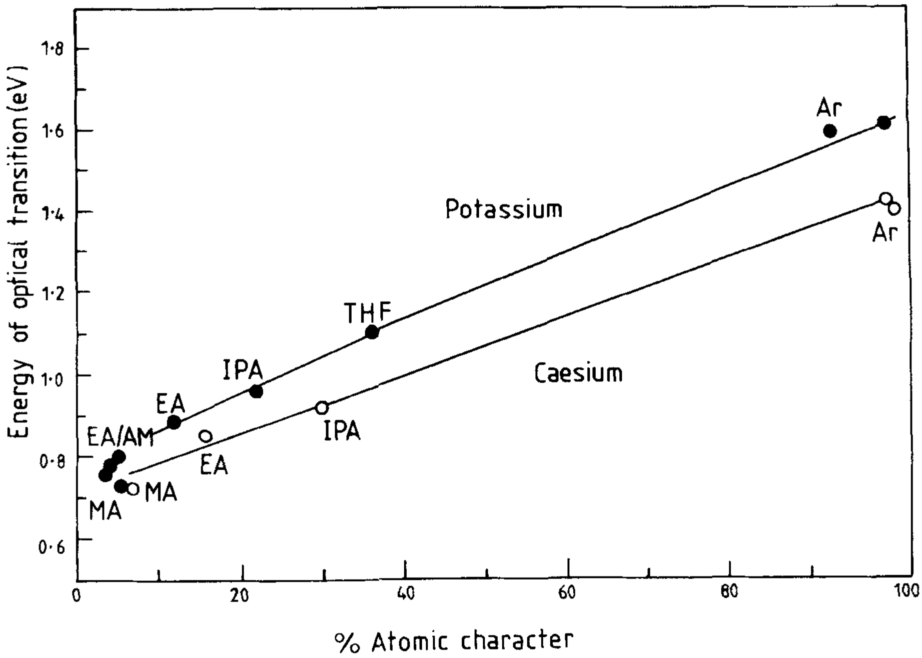

FIGURE 7 Correlation of optical and e.s.r. data for potassium and caesium monomeric states (M_s) in a variety of host matrices. Solvent identification as in Figure 4.

A recent communication[7] addresses the problem of just how the interaction between solvent and solute actually modifies the energy levels of the resulting monomeric species. The fundamental tenet was that the process of "solvation" of the alkali metal atom in many ways resembles the production, in vacuo, of an electronically excited form of the solute species, an analogy first drawn by Wannier[53] in 1937. The existence of a variety of (solvent-induced) local potential fields around the alkali atom in the condensed system[52] essentially reproduces the overall behaviour of the valence (ns) electron of the isolated (gas-phase) alkali atom in its *excited* electronic configuration. Drawing upon recent spectral data for gaseous excited states of the alkali atoms, it was possible[7] to set relative values to the energy levels in both situations (Figure 8). Thus, bonding of solvent to the metal atom necessarily[48] destabilises the orbital containing the alkali valence electron by an amount depending upon the degree of (solvent) lone-pair electron donation to the cation. Ultimately, the degree of donation in certain solvents (e.g. ammonia) is sufficient to fully "ionize" the valence electron into the host conduction band, producing the isolated, solvated electron.

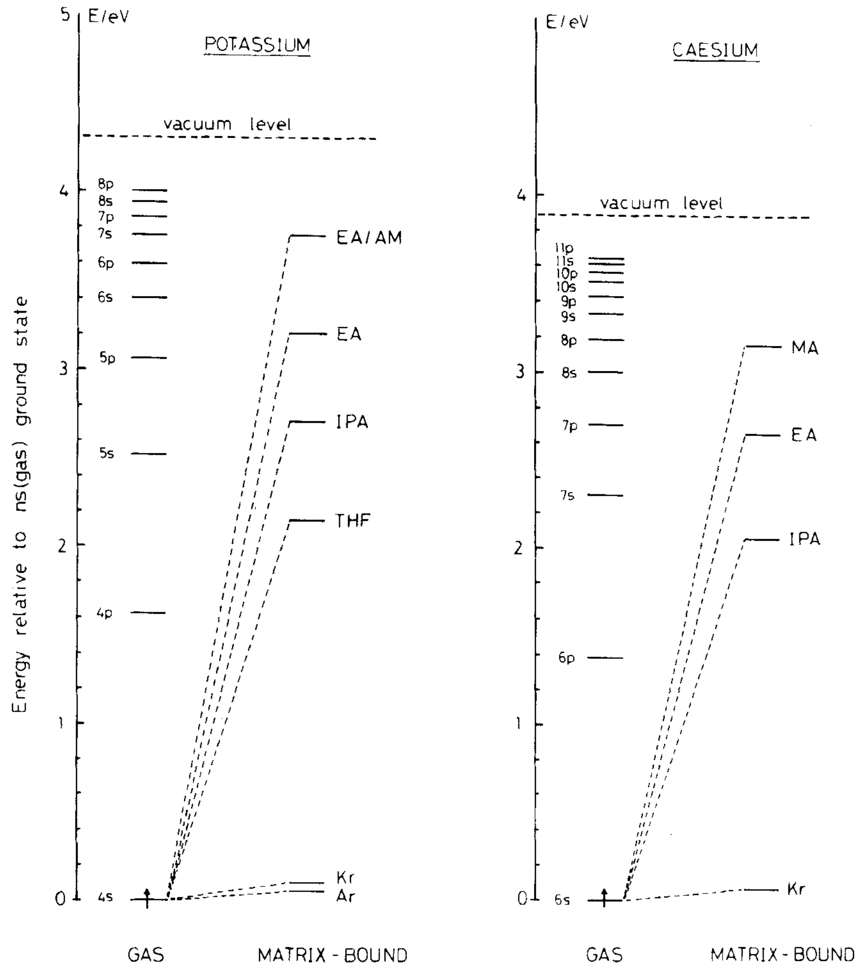

FIGURE 8 A comparison of the relative energy levels for gaseous excited and solvated ground states of potassium and casesium atoms. Taken from reference 7.

This type of mechanism, involving almost an "excitation" process, may be part of the underlying mechanism for the dissolution process in the NH_3 system, which involves the spontaneous ionisation of the valence electron from the solute metal (Eq. 1).

b) *ESR studies of quenched metal-HMPA solutions* These rapidly frozen solutions reveal a wealth of distinct, localised-electron states.[45,48,52,54] These range from 'atom-like' solvated-atom centres, with up to ca. 70% of the electron spin density on the cation, to weakly localized, ion-pair states

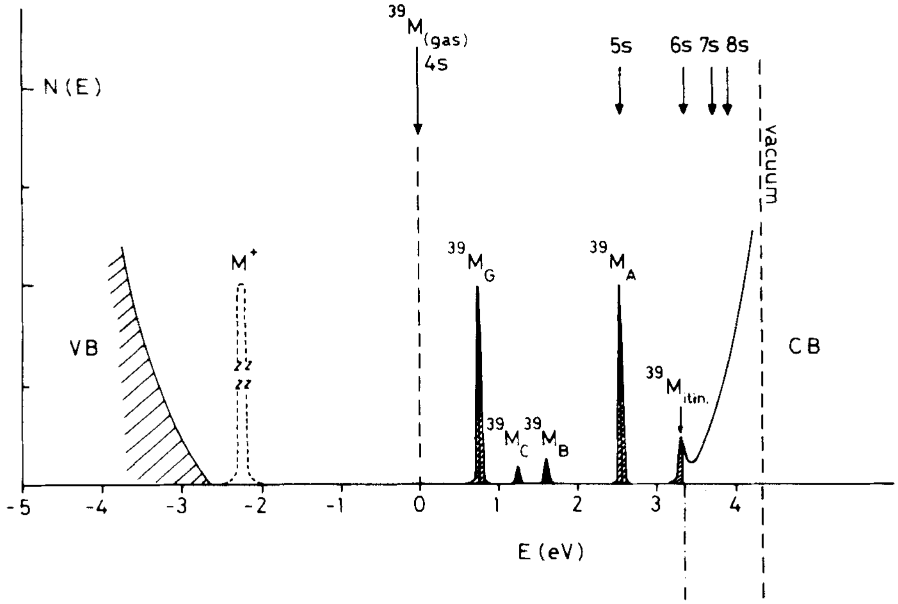

FIGURE 9 A representative picture of the electronic density of states for rapidly quenched K-HMPA solutions (77K). Each particular monomeric state is classified in terms of its percentage occupancy of the potassium 4s-orbital; labelling alphabetically from the lowest atomic state ($^{39}M_A$, ca. 1 %) to the highest ($^{39}M_G$, ca. 80 %). Energies are defined relative to the ground and excited states of the gas phase potassium atom (arrows indicate the appropriate positions of the ground (4s) and excited states, 5s–8s, Ref. 52).

with $< 1\%$ metal ns-orbital occupation. The latter has also been described[54c] in terms of a Wannier–Mott impurity state, similar to those found in the doped Group IV semiconductors[55] (P: Si, etc.). In these vitreous solids, then, the *entire* spectrum of possible monomeric states appear to exist, and it has been possible[52] to arrive at a representative picture of the electronic density-of-states (Figure 9). The discrete nature of these states in this disordered material most probably arises from fractionally distinct trapping sites associated with various local (solvent) configurations around the donor (alkali) atoms.

ii) Diamagnetic states: Alkali metal anions

Perhaps the most striking characteristic of metal-amine and ether solutions which sets them apart from metal-ammonia solutions is the metal dependent absorption band which occurs at higher energies then the infra-red band associated with e_s^-.[6,21,43,49] This shifts progressively to higher energies for

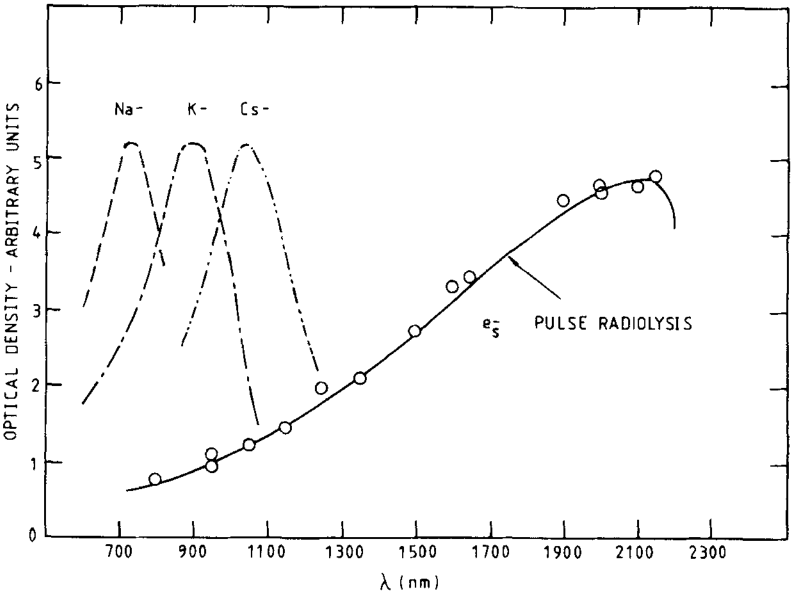

FIGURE 10 Optical absorption spectra observed in metal-tetrahydrofuran solutions. Adapted from Ref. 49.

solution of Cs, Rb, K and Na in a given solvent (Figure 10). The metal-, temperature-, and solvent dependence of this band[6] prompted Matalon, Golden and Ottolenghi[56] to suggest that the species responsible were alkali metal anions, and that the transitions were similar to the charge-transfer-to-solvent (CTTS) bands of I^-. The term alkali metal anion refers to a spherically symmetric species with two electrons in the outer *s*-like orbital centered on the metal.

The evidence for M^- in metal solutions has accumulated steadily over the last decade.[43,57] In addition, the existence of alkali metal anions in the gas-phase has been recognised for some time.[58] However, for a variety of reasons, the possibility of genuine M^- species in metal solutions evoked very little excitement among chemists in general.[6] However, in 1974, Dye and co-workers[59] isolated and characterized a crystalline salt of the sodium anion. When a saturated solution of sodium metal in ethylamine in the presence of a cation-complexing agent (for example—bicyclic diamino ether, or "crypt") is cooled, gold coloured crystals form whose structure corresponds to a sodium cation trapped in the crypt and a sodium anion outside (Figure 11). More recent studies have also revealed the existence of alkali metal anions in thin solid films formed by evaporation of metal-ammonia solutions containing cation-complexing agents.[60]

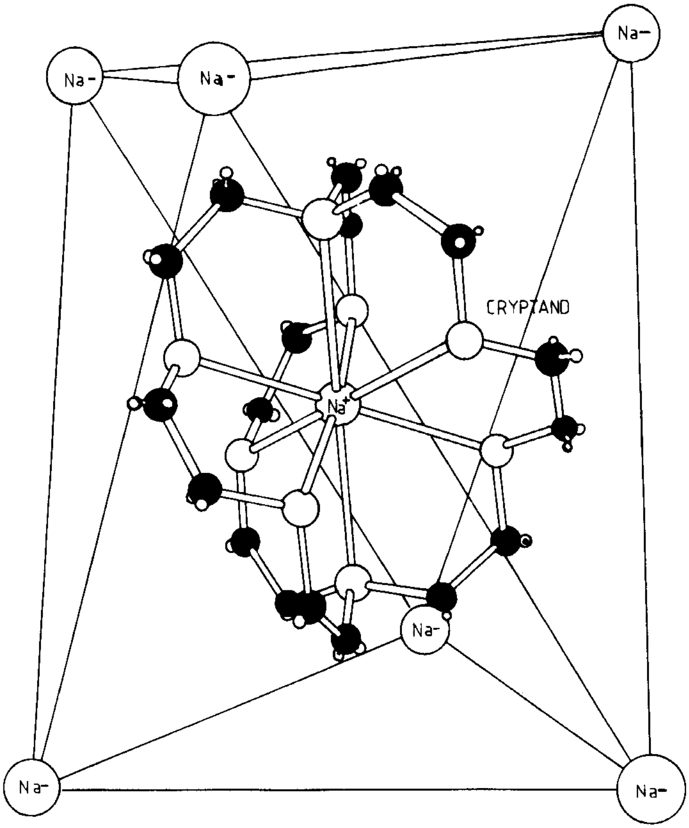

FIGURE 11 The structure of crystals of the sodium salt of the sodium anion. It can be resolved into alternating layers of sodium anions and the complexes formed by a cryptand and sodium cation. Adapted from Ref. 59.

The n.m.r. spectra of Na^-, Rb^- and Cs^- have now been reported.[61] The chemical shift of Na^-, large and diamagnetic, is the same as that calculated for the gaseous anion and is essentially independent of solvent. The apparent absence of a large paramagnetic shift of Na^- upon solvation and the independence of solvent, have been cited[43] in support of a model in which solvent is excluded from the region occupied by the sodium 2p electrons. However, recent studies[62] of the photodetachment of electrons from K^- and Rb^- in HMPA glasses at low temperatures reveal a significant degree of solvation in the alkali anion species. The overall conclusion must be that the alkali anion in these systems is a distinct, centro-symmetric species with the two valence electrons residing in an expanded ns orbital on the metal.[62]

The existence of metal anions in these systems is not confined to elements of Group I of the Periodic Table. Lagowski and co-workers[63] have recently presented spectroscopic evidence for the existence of the auride ion (Au^-) in liquid NH_3 solutions, whilst Dye[43] has recently given an extensive assessment of the stability of crystalline salts of a variety of metal anions.

3 CONCENTRATED SOLUTIONS AND THE METAL NON METAL TRANSITION

Over the composition range 10^{-3} to 10 MPM in Li–NH_3 solutions the electrical conductivity increases by approximately four-orders-of-magnitude,[1,5,64,65] and in the neighbourhood of the saturation point (ca. 22 MPM), it reaches a limiting value of approximately 5×10^3 ohm^{-1} cm^{-1}. In the intermediate composition range 1 to 7 MPM, a Metal to non-Metal (M–NM) transition occurs, and changes in the electronic, thermodynamic and mechanical properties of the system are equally impressive.[1,5,66] A detailed discussion of the concentration dependence of various properties in M–NH_3 solutions has been given by Thompson,[5] and the reader is referred to this work for an excellent assessment of the situation in that solvent. However, here we will be concerned with the general features of the transition both in M–NH_3 and Li–$MeNH_2$ solutions. The latter system has recently received considerable attention;[67] the shift in emphasis from NH_3 to other solvents represents an effort to expand our "understanding" of the M–NM transition in metal solutions. Until recently, the cardinal problem has always been one of low solubility of metal. Only NH_3, CH_3NH_2[68] and HMPA[69] as pure solvents apparently dissolve alkali metals in sufficient quantity to effect a transition to the metallic state. However, the use of cation-complexing cyclic (crown) polyethers or cryptates to enhance metal solubilities[41,43] opens up the possibility of studies on other solvent systems.[5]

However, even at the present time there exists a growing catalogue of thermodynamic,[68a,70,71] electrical[68b] and magnetic data[72,73,74] for the Li–$MeNH_2$ system which enable comparisons[67] to be made with the situation in M–NH_3 solutions.

A Metal-ammonia and lithium-methylamine solutions

The overall changes[67] in magnetic and transport properties by M–NH_3 and Li–$MeNH_2$ solutions across the M–NM transition are shown in Figure 12.

i) *Electrical conductivity* Concentrated M–NH_3 solutions (> 7 MPM) are liquid metals with a conductivity at saturation (ca. 22 MPM) exceeding that of liquid Hg.[1,5] However, both the concentration, and temperature de-

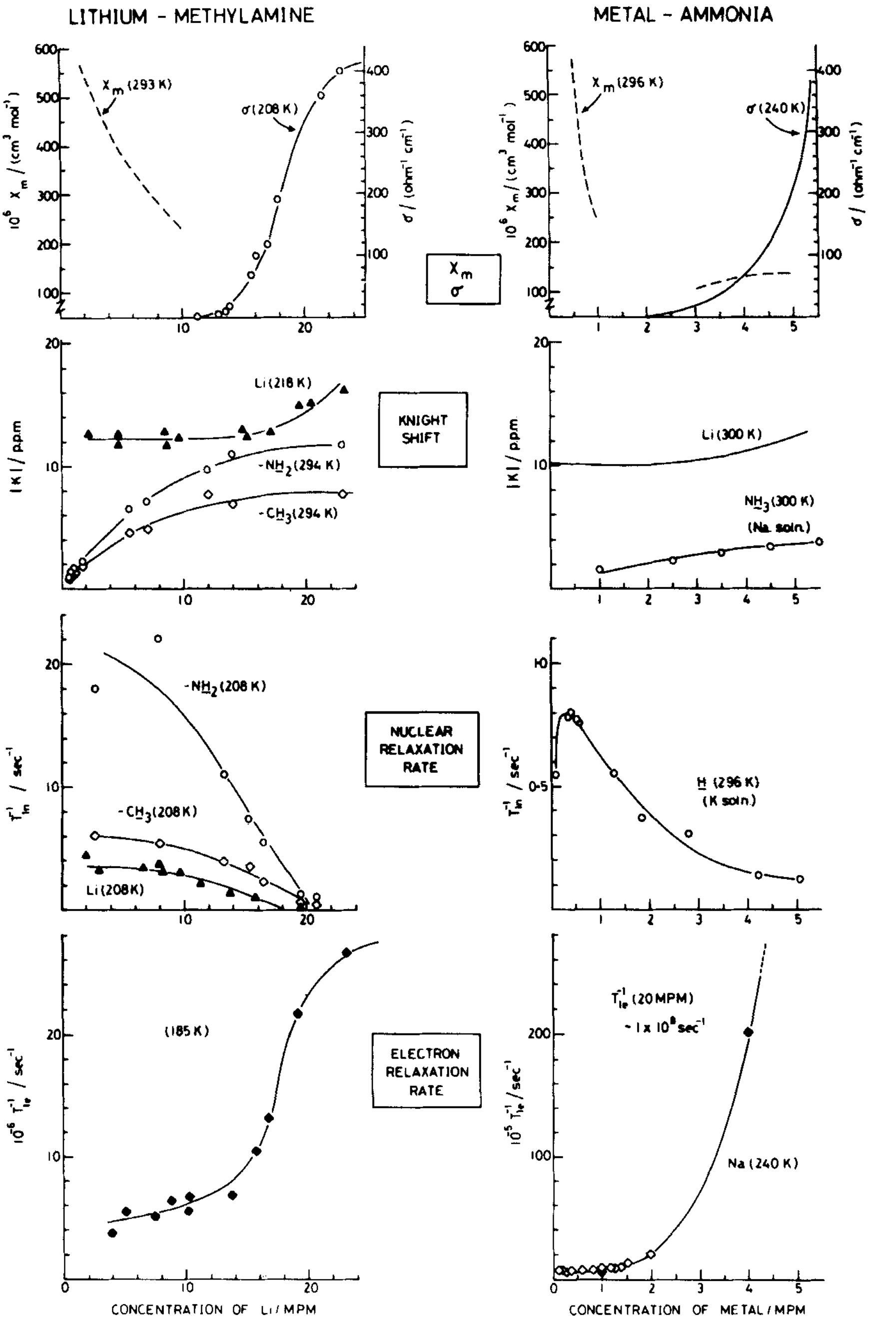

FIGURE 12 The electronic properties of lithium-methylamine and metal-ammonia solutions. Detailed references to the experimental data included here are given in Ref. 67, from which this figure is taken. Note the change in concentration scales between the two systems.

pendences are completely different from normal liquid metals.[5] The conductivity increases with concentration approximately as the cube[1] (simple theory predicts a concentration weaker than linear), and the conductivity *increases* with temperature, again at variance with the predictions ($\delta \alpha T^{-1}$) of a nearly-free-electron (NFE) model. A detailed exposition of the various models proposed to explain this behaviour in NH_3 solutions is given in the book by Thompson.[5]

In contrast, saturated Li–$MeNH_2$ solutions have a conductivity[68b] of ca. 400 ohm^{-1} cm^{-1}, a factor of approximately 40 below the corresponding value for saturated Li–NH_3 solutions. This saturation value lies close to the minimum electrical conductivity[31,38,66] for metallic states

$$[\delta_{\text{crit}} \simeq 100\text{–}300 \text{ ohm}^{-1} \text{ cm}^{-1}].$$

Therefore this system can be classified in terms of the strong scattering regime[72,73] of metallic behaviour. Once again, the temperature coefficient of the conductivity in Li–$MeNH_2$ solutions is *positive* for the entire concentration range studied (ca. 2–27 MPM), with a maximum occurring around 11 MPM.[68b]

In both solvent systems the electrical resistivity appears to be sensitive to *scattering both from* solvated ions *and* unbound solvent dipoles.[5,75] However, a recent investigation[76] of conduction electron spin resonance (c.e.s.r.) in concentrated Li–$MeNH_2$ solutions reveals that, in contrast, the electron *spin*-scattering (relaxation) appears to be sensitive *only* to the resistive scattering from the solvated-ion complex.[5] This gives rise to negative temperature coefficient for the relaxation rate in concentrated solutions, as observed in c.e.s.r. of normal (bulk) metals.[67]

Another significant difference between the two solvent systems is the concentration at which the M–NM transition occurs.[67,68b,77] In Li–NH_3 solutions it lies around 4 MPM,[64,65] whilst in the Li–$MeNH_2$ system transition occurs between 13 and 16 MPM. A possible explanation[67,77] for these differences in critical compositions is the degree, or extent, of "confinement" of the localised electron wavefunction within the cavity in the solvent. This would lead to reduced overlap interactions in $MeNH_2$ solutions, where there is evidence from optical,[78] and excess-volume[70,79] studies for a more spatially confined wave function for the excess electron than in NH_3 solutions. An alternative viewpoint[5] suggests that the electron delocalization process may well proceed via different mechanisms for the two systems. However, our recent studies[77] do reveal phase separation in Li–$MeNH_2$ solutions, somewhat similar to the Li–NH_3 case in that the miscibility gap in both systems appears at the critical concentration for metallization,[80] *i.e.* approx. 4 MPM for Li–NH_3; approx. 14 MPM for Li–$MeNH_2$. This aspect is dealt with in more detail in Section 3c. Moreover, there is some evidence[67] (see below) for a considerably reduced spin-pairing interaction in Li–$MeNH_2$ solution, possibly arising from reduced electron-electron overlap interactions in the dilute region.

ii) *Electron spin-pairing and the onset of metallic character* Molar electron susceptibilities in Li–$MeNH_2$ solutions have so far only been derived from measurements using the Guoy method. For the concentration range where the data for both fluid systems overlap, spin-pairing in Li–$MeNH_2$ solutions appears to be much less than that occurring in M–NH_3 solutions.[67] Precise paramagnetic susceptibility data for Li–$MeNH_2$ solutions are required. However, both e.s.r.[73] and (lithium) Knight shift data[74] also suggest a considerably enhanced paramagnetism compared to sodium-ammonia solutions. In both ammonia and methylamine solutions spin-pairing processes occur at considerably lower metal concentration than the M–NM transition (Figure 2). For comparable electron densities (recall the data given in Figure 12 are in terms of MPM), the degree of spin-pairing and the magnitude of the electrical conductibility differ dramatically. For an electron density of approximately 5×10^{20} cm^{-3} (ca. 4 MPM for Na/NH_3; ca. 3.4 MPM for Li–$MeNH_2$) $\delta \sim 10^{-1}$ ohm^{-1} cm^{-1} for Li/$MeNH_2$ compared to $\delta \sim 6 \times 10^2$ ohm^{-1} cm^{-1} for Na–NH_3 (see also Ref. 5).

In sodium-ammonia solutions, the paramagnetic susceptibility exhibits a minimum around 1 MPM and then increases with concentration in the range 3 to 10 MPM. (Figure 2) Most importantly, the spin-pairing interaction appears *complete* for the concentration range immediately preceding the M–NM transition. Once the metallic state is attained (ca. 7 MPM), the paramagnetic susceptibility once again rapidly approaches the value expected for a lattice of independent electrons.[1,5]

Mott[31,38c] has recently drawn attention to the somewhat similar behaviour of expanded fluid caesium[81] in the region of the M–NM transition. As the density is decreased from the metallic regime, there is a marked increase in the susceptibility, possibly arising from a correlation (Brinkmann–Rice) enhancement.[31,38] Even closer to the transition region, the susceptibility again decreases, and this has been attributed to Cs_2 formation. It is interesting to note that there is no evidence of this type of correlation enhancement for metal solutions, although the transition from a metallic state to a localised electron regime existing predominantly as spin-paired entities (as in Cs) is well recognised.[31]

iii) *Knight shifts of the n.m.r.* In dilute metal-ammonia solutions, the Knight shift[82] at the metal nucleus (K(M)) is particularly small, indicating a low s-electron density at the nucleus. For both solvent systems the Knight shift at the metal nucleus decreases near the concentration at which electron localization occurs (ca. 4 MPM for Na/NH_3, and 14 MPM for $Li/MeNH_2$). A most surprising feature is the near constancy of K(M) over a wide concentration range below the localization onset. In this region, the Hall coefficient[5] (amongst several other properties) changes quite markedly, and the conductibility drops approximately two-orders-of-magnitude.[67] A similar situation exists in expanded fluid mercury,[83] for which March[84] notes "... that these results do not have a ready explanation in terms of available theories of the disordered state", (see also Cusack).[85]

iv) *Nuclear and electron spin relaxation* Spin-lattice relaxation is a general term representing the process of thermal equilibration between a system of spins and the thermal reservoir provided by the "lattice",—i.e., the various modes of thermal motion exhibited by the assembly of atoms. The spin-lattice relaxation mechanisms are characterised by a time constant, T_1, the spin-lattice relaxation time.

The relaxation properties of both electron and nuclear spins change quite dramatically in the region of a M–NM transition.[67,72,86] *Electron* spin relaxation rates T_{1e}^{-1} decrease markedly with the onset of electron localisation, whilst the converse is true for *nuclear* spin relaxation rates T_{1n}^{-1} (Figure 12). A recent article[67] addresses the problem of describing the continuous changes in T_{1e}^{-1} and T_{1n}^{-1} across the M–NM transition.

Changes in the nuclear relaxation properties in $Li/MeNH_2$ solutions appear to be reasonably well described[67,72] by the compositional dependence of the electron-nuclear reside time,[86] τ_{NMR}, at a particular metal site. At high lithium concentrations, in the metallic state, the electron-nuclear reside time is very short (ca. 10^{-15} s. at 20 MPM) and nuclear relaxation (which is usually dominated via the electron-nuclear Fermi contact interaction) is therefore relatively inefficient. Moving across the M–NM transition, the electron-nuclear residue time increases by almost two orders of magnitude as electron localisation sets in (ca. 5×10^{-14} s at 5 MPM), and there is a corresponding increase in the efficiency of the nuclear relaxation process.

For itinerant electron states the Korringa process, involving the coupling of nuclear spins to the spins of s-like conduction electrons, is usually the dominant relaxation mechanism.[86] The Korringa magnetic relaxation rate $(T_{1n}^{-1})_{\mathrm{Korr}}$ can be expressed in terms of the Knight shift via.

$$(T_{1n}^{-1})_{\mathrm{Korr}} = \frac{4\pi\gamma n^2 K T \kappa^2}{\gamma_e^2} \tag{7}$$

where γ_n and γ_e are, respectively, the nuclear and electron gyromagnetic ratios, and T is the temperature.

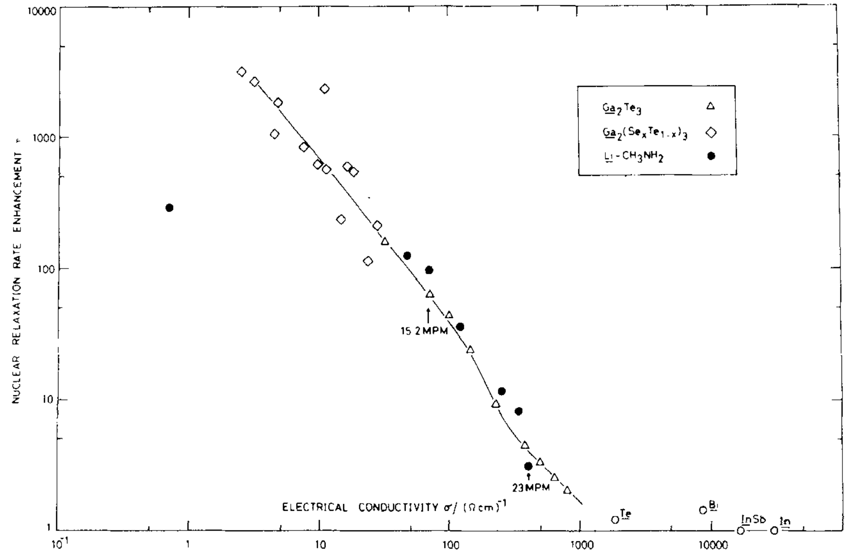

FIGURE 13 Nuclear relaxation-rate enhancement across the Metal-non-Metal transition. A plot of the Korringa enhancement parameter (η) versus electrical conductivity for the liquid alloy systems Ga_2Te_3 and $Ga_2(Se_xTe_{1-x})_3$ and lithium-methylamine solutions. Relaxation rate enhancement refers to the underlined species, and the two arrows denote data points for lithium-methylamine solutions of concentrations 15.2 and 23 mole percent metal. Taken from Ref. 67.

Warren[86a] has previously shown that an enhancement in T_{1n}^{-1} over the predicted Korringa value (Eq. 7) is indicative of electron localisation, and one may define a Korringa enhancement parameter

$$\eta = \frac{T_{1n}^{-1}}{(T_{1n}^{-1})_{\mathrm{Korr}}} \simeq \frac{T_{NMR}}{N(E_F)} \tag{8}$$

where $N(E_F)$ is the density of states per atom for a single direction of electron spin at the Fermi energy, E_F.

Thus η provides a relatively direct measure of the extent of electron localization on a particular nuclear site.[86] The data assembled in Figure 13 show how this enhancement parameter is correlated with conductivity data for Li-$MeNH_2$ solutions and various liquid metals and semiconductors.[67] Once again, there are striking similarities with liquid alloy systems. Recent ^{133}Cs results[87] for liquid Cs–Au alloys similarly reveal a rapid drop in the ^{133}Cs Knight shift, accompanied by a sharp peak in the nuclear relaxation rate when electrons localise as a "change-transfer insulator" Cs^+Au^- for concentrations of excess Cs below about 7%.

An analogous treatment for *electron* spin relaxation in metal solutions has recently been developed.[67] In this instance, an enhancement in T_{1e}, the electron spin-lattice relaxation *time*, arises quite naturally[72] when one considers the increasing importance of electron-electron and electron-phonon interactions in the approach to the M–NM transition (Figure 12).

The marked differences in relaxation behaviour for nuclei and electrons in the two electronic regimes may permit the identification of *co-existing* localised *and* itinerant electron states within a disordered material, as observed recently[52] in rapidly quenched metal-HMPA solutions (see also reference 88).

v) *Changes in transport and magnetic resonance properties at a M–NM transition* The experimental basis for detecting a transition from the localised- to itinerant-electron regime involves monitoring the changes in various electronic properties which reflect the extent of electron delocalisation. Indeed in all models[66] for the transition, the precise conditions under which delocalisation/localisation of the electronic wave function occur are of fundamental importance in suggesting the nature of the transition itself. In this context, it is important to highlight the differences between the onset of both *spin*, and *electron* (charge transport) delocalisation in the approach to the transition, and the M–NH_3 system is well suited for an investigation along these lines.[72]

In particular, it has been recognised for some time[89] that magnetic resonance properties (and in particular ESR) detect what appears to be the onset of delocalisation effects at lower concentrations than those inferred from transport property measurements. In particular, magnetic resonance measurements are sensitive not only to complete delocalization (i.e. free ionization of carriers as, say, it appears in the classical approach[66,90] for the transition) but also to partial delocalization effects which might involve the extension of the (localised) electron wave function over several sites. This latter process usually occurs *without* the formation of free carriers and *without* the concomitant changes in transport properties. Variations in the intersite exchange energy, arising possibly from the formation and breakup of microscopic cluster states, need only be of the order of magnitude of the magnetic Zeeman or hyperfine energies (both typically in the range 10^{-4} eV) for noticable changes to be detected in, say, T_{1e}. In contrast, transport properties require, as a prerequisite for the detection of metallic character, the complete breakup of an electron-hole pair, a process typically involving changes in the range 10^{-1} to 10 eV.

This type of behaviour is illustrated in Figure 14. For sodium-ammonia solutions, magnetic resonance, transport and thermodynamic properties all suggest *complete* delocalization of the electronic wave function at metal

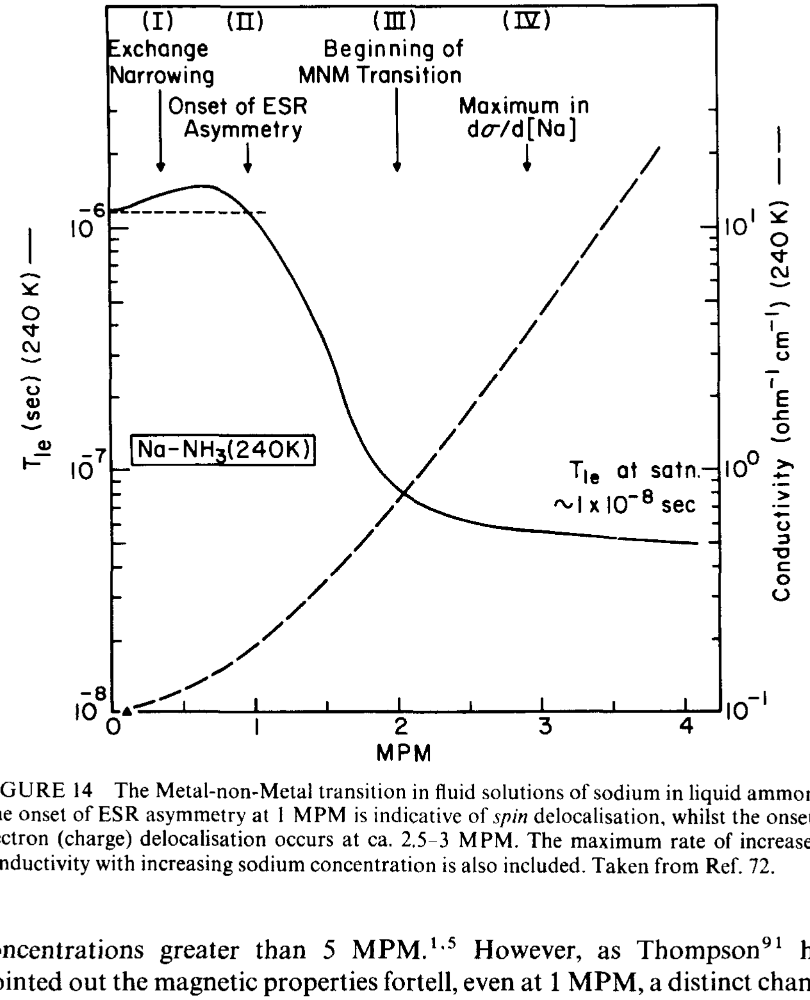

FIGURE 14 The Metal-non-Metal transition in fluid solutions of sodium in liquid ammonia. The onset of ESR asymmetry at 1 MPM is indicative of *spin* delocalisation, whilst the onset of electron (charge) delocalisation occurs at ca. 2.5–3 MPM. The maximum rate of increase of conductivity with increasing sodium concentration is also included. Taken from Ref. 72.

concentrations greater than 5 MPM.[1,5] However, as Thompson[91] has pointed out the magnetic properties fortell, even at 1 MPM, a distinct change in the electronic wave function on the cavities. Figure 14 shows the compositional dependence of T_{1e} and electrical conductivity in sodium-ammonia solutions.[72]

Around 1 MPM, the onset of spin-delocalisation is monitored via an asymmetry in the e.s.r. and a decrease in T_{1e}. However, in this concentration range in which we see noticeable changes in the e.s.r. behaviour, the electrical conductivity is still relatively low (approximately 10^{-1} ohm^{-1} cm^{-1}, or less). According to Cohen and Thompson[1] the beginning of the M–NM transition (as gauged by conductivity studies) occurs at approximately 2.5 MPM, whilst the maximum rate of increase of conductivity with increasing sodium concentration occurs around 3 MPM. (Figure 14).

These fundamental differences in requirements for detecting changes in the electronic wavefunction must obviously be borne in mind when comparing magnetic and transport data. They may, in part, account for the disparities often found when comparing critical densities from different physical techniques.[92]

B Models for the metal-non-metal (M-NM) transition

Two primary models have been proposed concerning the nature of the M–NM transition in metal-ammonia solutions.[5]

i) *A Mott transition in a disordered system?* The first has its basis in the classic Mott transition,[90] involving the effects of long-range screening. Both Sienko[80] and also Kyser and Thompson[93] pointed out some time ago that M–NH_3 solutions satisfied Mott's criterion for a M–NM transition.[90]

$$n_c^{1/3} a_H^* \simeq 0.26 \tag{9}$$

near 4 MPM, when the particular features of the dielectric screening of NH_3 were taken into account. Here n_c is the critical metal concentration and a_H^* is the Bohr radius of the isolated solvated electron. In later studies, attention was focused on a Mott transition within a Hubbard band originating from (short-range) electron-correlation effects.[94] Both approaches have since been modified to include the effects of a random structure, leading to a pseudo-gap, and the possibility of Anderson (disorder-induced) localisation.[31,38,95]

However, an important feature to emerge from our earlier discussion (Section 2A(ii)) is that in the concentration range immediately preceding the transition region, the majority of localised electrons are in spin-paired states. These molecular "bipolarons",[31,66] are probably best described in terms of two electrons in separate cavities, possibly associated with a metal cation. Mott's ideas concerning a pseudogap in these systems involves two bands:[31,38c] one for an extra *electron* on this molecular bipolaron ("H_2^-" band), and one for a *hole* in a bipolaron ("H_2^+ band) (Figure 15).

When these two bands overlap, $N(E_F)$ becomes finite and a M–NM transition may occur. Specifically, a pseudogap is formed when the criterion[38b,66,94]

$$g = \frac{N(E_F)}{N_{\mathrm{f.e}}(E_F)} < g^* \simeq \frac{1}{3} \tag{10}$$

is satisfied. $N(E_F)/N_{\mathrm{f.e}}(E_F)$ is the ratio of the density of states and the free-electron density of states. Although the transition may be viewed in terms of "band-crossing" type, the Hubbard U parameter ($\langle e^2/r_{ij}\rangle$, two electrons on the same site) is obviously still important in determining the pseudogap.[31,38c]

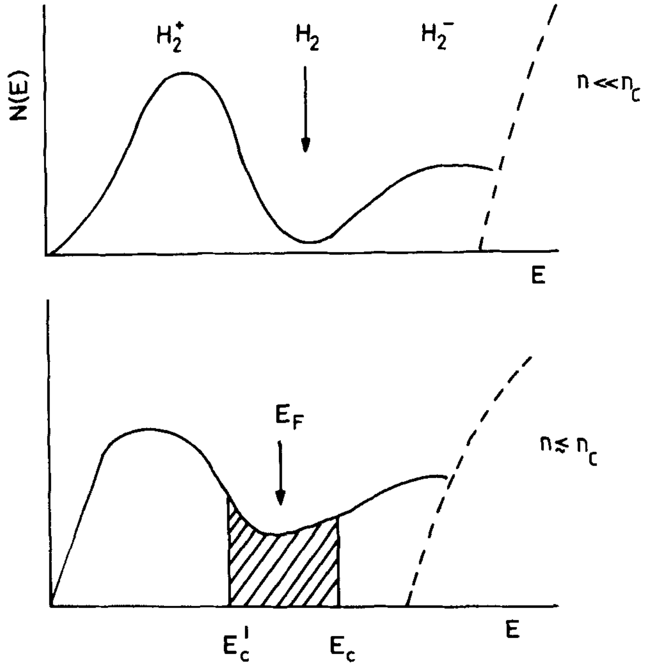

FIGURE 15 Schematic representation of the Metal-non-Metal transition in fluid metal-ammonia solutions in terms of two overlapping bands: $n \ll n_c$ the dilute regime; $n \lesssim n_c$ in the region of the Metal-non-Metal transition. E_F is the Fermi energy of the system, and E_c and E_c^1 are limits to the mobility edge in this disordered material.

For a crystalline array, when any two bands cross, it is predicted that there should be a discontinuous change in the number of carriers, an electron-hole gas being formed.[31,66] As a consequence, the free energy of any system showing a M–NM transition will be as in Figure 16.[90b,108] At low temperatures, the transition region will be unstable against separation into two phases.[31] However, disorder (and elevated temperatures) can remove the discontinuity, leading to an activation for conduction which goes *continuously* to zero at the transition.[95] This appears to be the case in P doped Si.[96]

In M–NH_3 (and Li–$MeNH_2$), however, disorder does *not* appear to turn the "Mott" transition into an Anderson transition.[38c] A striking indication of this is the observation of a liquid-liquid phase separation in these systems for temperatures below 200 K[80] (see also Section 3C). Mott has recently suggested[31] that the electrostatic repulsion between ions in concentrated M–NH_3 dictates strong short-range order, and the remaining disorder is not sufficient, as it is for the band crossing transition in fluid mercury, to get rid of the discontinuity in the free energy versus composition curve (Figure 16).

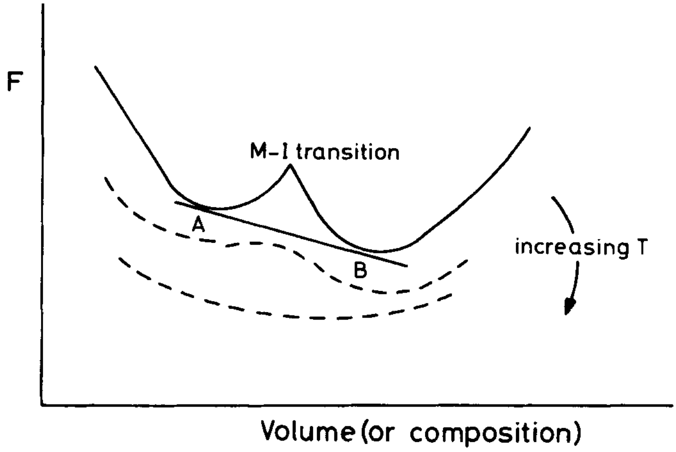

FIGURE 16 Suggested form of the free energy (F) of an alloy system plotted against composition (or volume) in the neighbourhood of a Metal to non-Metal transition. When there exists a discontinuity in the number of free carriers in the system, the free energy-volume/composition curve must necessarily show a kink and give rise to a two-phase region in the system.

ii) *Inhomogeneous picture for the transition* The fundamental basis of Mott's ideas on the M–NM transition in M–NH_3 is that the system is essentially homogeneous, and slightly disordered, for temperatures sufficiently removed from the consolute temperature for phase separation. Jortner and Cohen proposed an alternative view[97,98] in that the metallic propagation regime is separated from a non-metallic regime by a microscopically inhomogeneous regime in which the concentration fluctuates locally about either of two well defined values (2.3 and 9 MPM). A percolation problem was then posed, and the approach utilised to account for numerous transport properties.[97,98] However, the fundamental question is whether we have any *direct* experimental evidence for a microscopic structure in which the local concentration fluctuates between these two well-defined boundaries. Damay and Chieux[99] have recently carried out small angle neutron scattering (SANS) studies on Na and Li solutions in liquid ND_3 at concentrations near 4 MPM from the liquid-liquid critical temperature up to room temperature. The complete data could be entirely attributed to concentration fluctuations as predicted on purely thermodynamical ground for systems close to a critical point. The correlation lengths (ξ) for fluctuations which are large near T_c decrease as a function of temperature following a power law of the type

$$\xi = \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu} \tag{11}$$

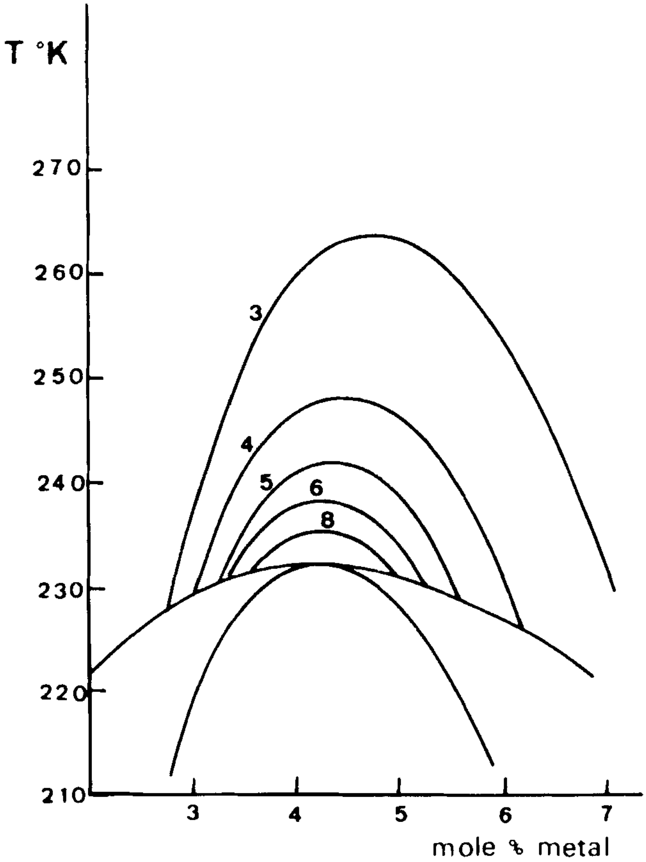

FIGURE 17 The liquid-liquid phase separation and iso ξ line in fluid Na-ND$_3$ solutions. Iso ξ lines are given on a reduced scale, ξ/ξ_0, with $\xi_0 = 5.07$ Å. Taken from Ref. 99.

where $\nu = 0.5$ for $T > T_c + 4°C$. Figure 17 summarises their findings. The plot is on a reduced scale ξ/ξ_0, with lines of constant ξ value shown, and $\xi_0 = 5.07$ Å for Na-ND$_3$.

All the SANS data for M-NH$_3$ solutions in the intermediate concentration range indicate that the Jortner-Cohen approach[97,98] is unrealistic except, possibly, for temperature and concentration ranges in the region of phase separation. The effect of the critical concentration fluctuations themselves on the transport properties appears to be confined to a small concentration/temperature region bounded by the iso ξ line $\xi/\xi_0 = 7$ (T range; 235-230 K: MPM range; 3-6 MPM for Na-ND$_3$, $T_c \sim 230$ K) rather than the more extensive region postulated by Jortner and Cohen[98] ($T < 310$ K, for 2-8 MPM). The reader is also referred to the general discussion by March[84] on the effects of critical fluctuations on electrical transport. As Damay and Chieux[99] point out the Cohen/Jortner model in essence corresponds more to what one would expect for a segregating glass, rather than a liquid. Indeed, in one system—*frozen* solution of metals in HMPA, —there is direct experimental evidence for microscopic inhomogeneity involving coexisting regions of localized and itinerant electrons.[52,67]

iii) *Herzfeld theory of metallization* Before leaving our general summary of the principal models for the transition, it is interesting to comment briefly on what is probably the earliest model[100] for the concentration dependent conductivity of sodium in ammonia. In 1927, K. F. Herzfeld[101] published a paper in which he proposed a simple criterion for determining when an element or system will exhibit true metallic characteristics. On classical grounds Herzfeld argued that the characteristic frequency of bound electrons, representing a measure of the force holding the electron in the free atom, is diminished at high electron densities to the value

$$\nu = \nu_0\left(1 - \frac{R}{V}\right)^{1/2} \tag{12}$$

where ν_0 is the characteristic frequency in the isolated (low electron-concentration) species, R is the molar refractivity and V is the molar volume.

If $R/V = 1$, the resultant force on the localised electron vanishes, the electron is set free and the system acquires metallic status. The previous statements may be recast in slight different form using the Lorenz–Lorentz equation, where

$$R = \frac{(n^2 - 1)}{(n^2 + 2)} V \tag{13}$$

and n is the index of refraction.

When the condition $(R/V) \sim 1$ is fulfilled, the refractive index/dielectric constant goes to infinity, and we have a M–NM transition. The Herzfeld criterion when applied to M–NH_3 solutions does indeed predict that the solvated electrons are set free by mutual action of neighbouring electrons at metal concentrations above ca. 4–5 MPM.[101,102] Measurements of the dielectric constant of Na–NH_3 solutions have been made at 1.2, 5.4 and 10 GHz.[103,104] The results[103] at 10 GHz (shown in Figure 18) exhibit an increase in the dielectric constant to nearly 100 before a rapid decrease to large negative values characteristic of Drude behaviour for metals. The Na–NH_3 results have recently been discussed by Castner[105] in an overall review of the dielectric anomaly and the M–NM transition.

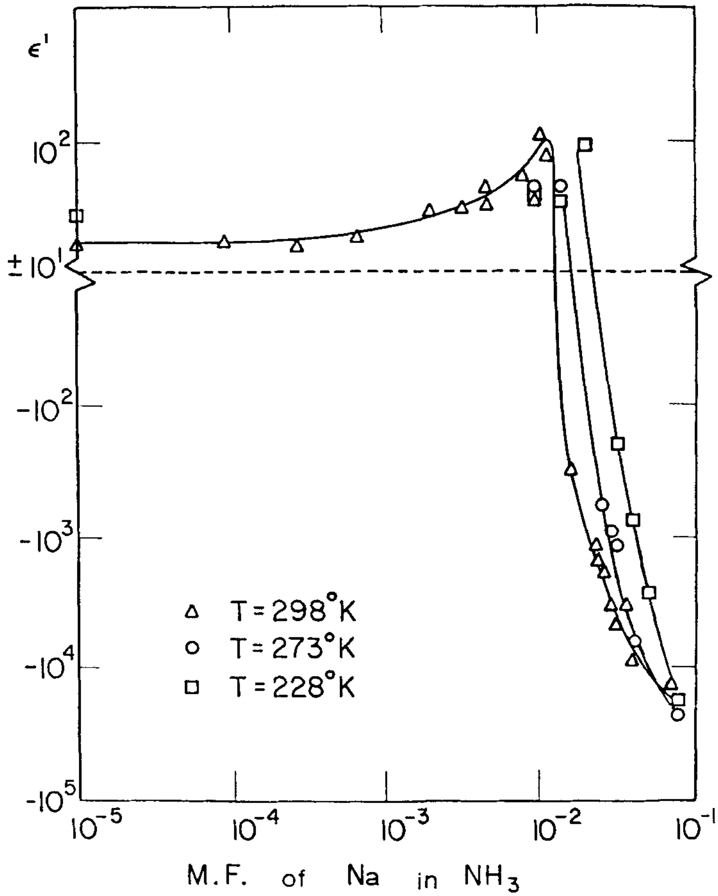

FIGURE 18 The real part of the microwave frequency (10 GHz) dielectric constant versus sodium concentration (expressed in terms of mole fraction; moles metal/(moles metal + moles solvent). Note the break in the ordinate around the Metal-non-Metal transition. Taken from Ref. 103.

C Phase separation and the M-NM transition in metal-ammonia and lithium methylamine solutions

If a solution containing approximately 4 mole percent sodium in ammonia is cooled below−42° C (231 K) a liquid-liquid phase separation occurs. The solution separates into two distinct layers—a light, bronze metallic phase which floats out on top of a dense, less concentrated dark blue phase. The first experimental observation of this striking phenomenon in Na–NH$_3$ solutions was made by Kraus in 1907,[106] and more recent studies have mapped out the phase co-existence curves for a variety of alkali and alkaline earth metals (see, for example. Figure 5.3 of Ref. 5).

In 1958, K. S. Pitzer[37] in a remarkable contribution which appears to have been the first theoretical consideration of this phenomenon, likened the liquid-liquid phase separation in M–NH_3 solutions to the vapour–liquid condensation that accompanies the cooling of a non-ideal alkali metal vapour in the gas phase. Thus in Na–NH_3 solutions below 231 K we would have a phase separation into an "insulating vapour" (corresponding to "matrix-bound" excess electrons) and a metallic (matrix-bound), liquid metal. This idea of a "matrix-bound" analogue of the critical liquid-vapour separation in pure metals preceded almost all of the experimental investigations into dense, metallic vapours,[107] and was also in advance of the possible, fundamental connection between this type of critical phenomenon and the M–NM transition, as pointed out by Mott[90b] and Krumhansl[108] in the early 1960's. We have recently[77] attempted to rectify the situation somewhat, and have inspected Pitzer's early suggestion in the light of recent studies of supercritical alkali metals,[107,109] and also Li–$MeHN_2$ solutions which exhibit a miscibility gap at a different metal composition than M–NH_3 solutions.[110]

For the entire spectrum of gaseous, and matrix-bound systems, there appears[77] to be a fundamental link between this type of thermodynamic condensation phenomena, and the gross constitutional changes that must occur in the electronic properties of a system as it moves through a M–NM transition.[108] Our recent studies of [77,110] Li–$MeNH_2$ solutions highlight the matrix-dependence of both phenomena in metal solutions. The liquid-liquid phase separation in this system occurs around 15 MPM compared to approximately 4 MPM is Na–NH_3 solutions (Figure 19). In both solvent systems, this critical composition also marks the onset of a M–NM transition for $T > T_c$. In all cases (Table 1) critical (metal) densities at the metallic onset/critical consolute composition are in good agreement[77] with a scaled (variational) form of the Mott criterion, $n_c^{1/3} a_H^* = 0.26 \pm 0.05$, which exhibits[111] an apparent universality over almost 10^{10} in n_c, and ca. 600 Å in a_H^*.

It appears[77] that the critical Mott density in both the supercritical alkali metals, and metal solutions signals the onset of an electronic transition without a thermodynamic phase transition for temperatures above the critical temperature. This critical density is also that at which a thermodynamic phase change accompanies the electronic transition below T_c (Figure 16).

D Expanded metal compounds

The lithium-ammonia phase diagram shows a deep pseudoeutectic (Fig. 19) at approximately 20 MPM and 88.8 K which signals the appearance of a compound, tetramminelithium (o) of stoichiometry $Li(NH_3)_4$. A great deal

TABLE I

The Mott criterion for metal solutions and expanded fluid metals[a]

System	n_c (cm^{-3})	a_H^* (Å)	$n_c^{1/3}a_H^*$
I. Supercritical alkali metals			
Li	9.43×10^{21}	1.59[b]	0.34
Na	5.48×10^{21}	1.71	0.30
K	2.89×10^{21}	2.16	0.31
Rb	2.40×10^{21}	2.29	0.31
Cs	1.9×10^{21}	2.52	0.32
II. Metal solutions			
Li-NH_3 (209 K)	9.94×10^{20}	2.83[a]	0.28
Na-NH_3 (231 K)	9.03×10^{20}	2.88	0.28
Li-$MeNH_2$ (ca. 200 K)	1.85×10^{21}	2.60	0.32

[a] Full details given in Ref. 77.

[b] Derived from radii corresponding to the principal maxima in the radial distribution functions $r^2\psi_2^2$ (r), using relativistic wave functions.

[c] Derived from the adiabatic cavity model for the solvated electron (see Section 2.A).

of evidence has now been amassed which shows that a true compound, rather than a simple eutectic solid, does indeed exist at low temperatures (see Ref. 76, and references therein). Recent studies of metal-ammonia compounds suggest that they may crystallise in unusual structural arrangements.[112] For example, the compound $Ca(ND_3)_6$ may possess a novel ND_3 geometry in which the ammonia molecules are nearly planar. Whatever the pecularities of the local structure in these complexes, the most appealing overall description[76,80] of the solid compound is that of an "expanded metal". In this the NH_3 simply takes the role of a space-filling diluent, effectively increasing the Li–Li separation relative to the pure metal. This dilution effect highlights one of the great attractions of these materials; namely that via pertinent choice of solvent these low electron-density materials could be tailored in such a fashion as to move them toward the M–NM transition.

We have recently measured[76] c.e.s.r. in the compound $Li(CH_3NH_2)_4$, which bears all the traits of a highly expanded metal lying extremely close to the M–NM transition. Specifically,[67,76] both the nuclear- and electron-spin characteristics of the compound, although nominally metallic, cannot be described in terms of the conventional theories for c.e.s.r. and n.m.r. in pure metals.

The use of cyclic (crown) polyethers or cryptates to enhance metal solubilities (Section 2B(ii)) also opens up many possibilities for studying expanded-metal compounds in the low-dielectric solvents.

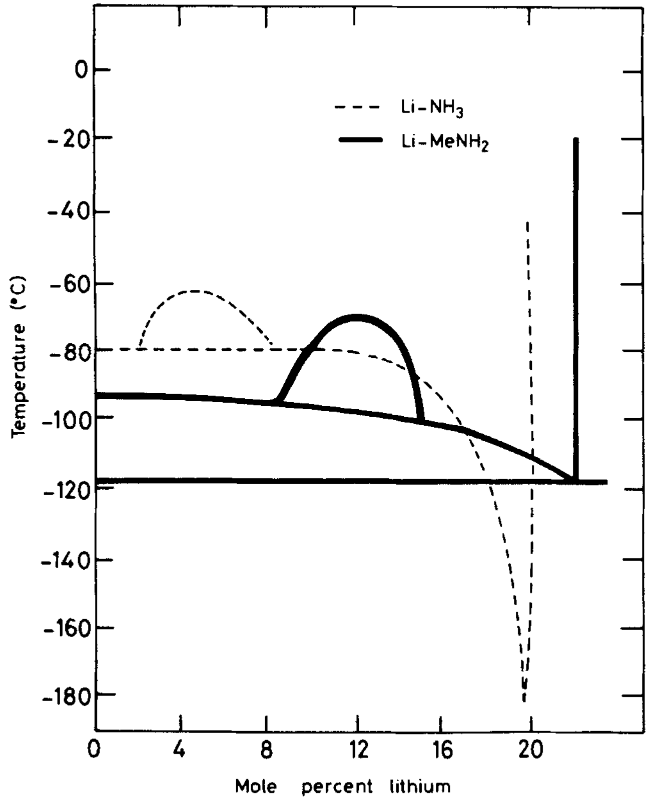

FIGURE 19 The phase diagram for solutions of lithium in ammonia and methylamine (P. P. Edwards and M. J. Sienko, *J. Am. Chem. Soc.*, in press).

CONCLUDING REMARKS

Although we generally attribute the discovery of metal-ammonia solutions to Weyl in 1863, it is possible that they were actually first prepared, in slightly different form, some 50 years earlier. An entry by Sir Humphry Davy for November 14th (or thereabouts) 1808 in his experimental notebook is one of many referring to numerous experiments conducted on the mutual action of potassium and ammonia with each other:

"When 8 grains of potassium are heated in ammoniacal gas—it assumed a beautiful metallic appearance and gradually became of a fine blue colour. . . . ."

Almost 200 years later, their systems still attract considerable attention from both experimentalists and theorists alike. In this article I have attempted to give a brief overview of the status of our present understanding of the electronic properties of metal solutions.

If one were to summarize the present status of our knowledge of these intriguing systems, it might be that most of the properties of excess electrons in solution can be interpreted in terms of models which are quite easily understandable, but quantitatively evaluated only with considerable effort. In this review I have attempted to illustrate both facets. Moreover, the preceding comment must also surely be an observation on the physics and chemistry of disordered materials in general!

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