J. Am. Chem. Soc. **1981**, *103*, 2967-2971

Phase Separation in Metal Solutions and Expanded Fluid Metals

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Received November 13, 1980

Abstract: A most striking feature of concentrated metal–ammonia solutions (excluding cesium) is their separation into two liquid phases below a certain critical temperature (T_c; ca. −42 °C for sodium–ammonia). Pitzer, over 20 years ago, suggested that this phenomenon in metal–ammonia solutions is the analogue within the liquid-ammonia matrix of the liquid–vapor separation that accompanies the cooling of a nonideal alkali metal vapor. In this communication we reexamine Pitzer's hypothesis in the light of the considerable advances made recently both in the theoretical and experimental study of supercritical fluid alkali metals, doped semiconductors, metal–ammonia, and metal–methylamine solutions. For the entire spectrum of gaseous- and matrix-bound systems, there exists a fundamental link between this type of *thermodynamic* condensation phenomenon and the major constitutional changes that must occur in the *electronic* properties of a system as it moves through a metal–nonmetal (M–NM) transition. Critical electron densities (n_c) at the metallic onset for all systems are well described by the simple experimental relation $n_c^{1/3}a^*_H = 0.26 \pm 0.05$, where a^*_H is a characteristic radius associated with the electron state wave function in the low-electron-density (nonmetallic) regime. This relation is therefore applicable to both gaseous- and matrix-bound systems, and its apparent universality (Edwards, P. P.; Sienko, M. J. *Phys. Rev. B*: *Condens. Matter* **1978**, *17*, 2575) now extends over almost 9 orders of magnitude in n_c and approximately 600 Å in a^*_H. Our recent studies of lithium–methylamine solutions are used to highlight the matrix dependence of both phenomena in metal solutions; the liquid–liquid phase separation in this system occurs around 13 mol % metal, compared to approximately 4 mol % metal in sodium–ammonia solutions. In both solvent systems this critical composition also marks the onset of M–NM transitions for $T > T_c$. We report calculations based on the adiabatic cavity model of Jortner for the solvated electron which lead us to suggest that the observed differences in critical compositions for meta–ammonia and lithium–methylamine solutions may simply arise from the differences in the radial extension of the isolated, solvated electron wave function.

In the absence of catalysts, alkali, alkaline earth, and some lanthanoid metals dissolve freely in anhydrous liquid ammonia to produce highly conducting solutions.[1,2] In the dilute range, solutions are blue and conduction is electrolytic; in the concentrated range they are bronze and metallic, and at an intermediate composition the system undergoes a metal to nonmetal (M–NM) transition.[1–4] Samples prepared with metal compositions in this transition region exhibit a most surprising, and easily observed, property. If, for example, a solution containing 3.7 mol % sodium is cooled below 232 K, a liquid–liquid phase separation occurs. The solution physically separates into two distinct layers—a low-density metallic phase which floats out on top of a more dense, less concentrated dark blue phase.[5,6]

The first experimental observation of this striking phenomenon in sodium–ammonia solutions was made by Kraus in 1907.[5] In 1958, Pitzer,[7] in a remarkable contribution which appears to have been the first theoretical consideration of this phenomenon, likened the liquid–liquid phase separation in alkali metal–ammonia solutions to the vapor–liquid condensation that accompanies the cooling of a nonideal alkali-metal vapor in the gas phase. This idea of a "matrix-bound" analogue of the critical liquid–vapor separation in pure metals preceded almost all of the experimental investigations into dense, metallic vapors[9–11] and was also in advance of the realization of the possible, fundamental connection between this type of critical phenomenon and the M–NM transition.[8] Here we attempt to rectify the situation somewhat and inspect Pitzer's suggestion in the light of major advances in recent years in both experimental and theoretical aspects of the subject.

Liquid–Vapor Phase Separation in Expanded Fluid Alkali Metals. In the fluid alkali metals, a transition between the localized and itinerant-electron regimes can be continuously studied by an expansion of the metallic liquid up to supercritical conditions. In spite of the extreme experimental conditions of elevated temperatures and pressures, a detailed picture of the electrical, magnetic, and structural properties of expanded fluid alkali metals is now emerging.[9–11]

In the current discussions of critical phenomena in these pure metals, the general consensus is that the liquid–vapor phase transition at the critical density (ρ_c) and temperature (T_c) is coincident with a M–NM transition in these disordered systems.[9–16] Stated simply, the precise nature of the electronic interactions between atoms changes dramatically at the M–NM transition, e.g., from van der Waals' type interaction to metallic cohesion. These *gross* changes in electronic properties at the transition are sufficient noticeably to influence the *thermodynamic* features of the system, and the conditions therefore appear highly conducive for a thermodynamic phase transition to accompany the electronic transition at the critical density for metalization.[13–17]

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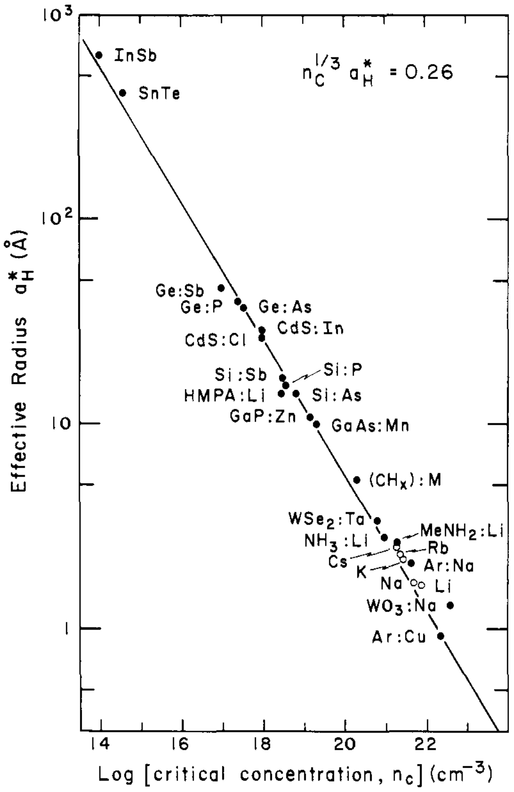

Figure 1. Logarithmic plot of effective radius, a^*_H, of the localized-electron state vs. critical concentration for metalization, n_c, in various systems.

Concerning this threshold density for metallic condensation, Mott[18] first introduced the idea of an abrupt (first-order) *electronic* transition from a metal to a nonmetal at a critical concentration (n_c) of centers given by the simple criterion (eq 1), where a_H is

$$n_c^{1/3} a_H = C \qquad (1)$$

an effective Bohr radius for the isolated (localized-electron) center, usually taken as

$$a_H = K^2/m^* e^2 \qquad (2)$$

K is a background dielectric constant, m^* is the effective mass of an electron in the conduction band of the host matrix, and C is a constant, typically of the order 0.25.

This simple criterion has been applied with considerable success to donor (impurity) centers in the group 4 semiconductors (Si, Ge) where K is reasonably taken as an *appropriate* dielectric constant for the host material.[19] From an extensive analysis of experimental data for a wide variety of (disordered) semiconductor materials, we have recently found[20] that a particular (scaled) form of the Mott criterion (eq 3) exhibits an apparent universality in

$$n_c^{1/3} a^*_H = 0.26 \pm 0.05 \qquad (3)$$

that the relation predicts the critical concentration for the onset of (electronic) metallic character for matrix-bound systems spanning a range of ca. 10^9 in critical densities and approximately 600 Å in Bohr radii, *provided* a^*_H is now defined as an effective radius associated with a *realistic* wave function (not necessarily that given by eq 1) for the localized-electron state in the low-electron-density limit. Figure 1 shows the experimental data.[21] We point out that for the majority of systems, effective Bohr radii are determined directly from experimental parameters which characterize the localized electron state.

These "matrix-bound" impurity atom data serve to emphasize the very important role played by the host matrix in the phenomenon of the M-NM transition:[20] primarily through the determination of the precise form of the radial distribution function for the (localized) state and hence, via eq 3, to the threshold densities for metalization (Figure 1). This is clearly visible even when one considers the M-NM transition for sodium in slightly different situations. For example, sodium-argon (matrix-isolated) mixtures[22] at 4.2 K have $\rho_c = 0.14$ g/cm^3, compared to pure sodium metal at its critical point with $\rho_c = 0.206$ g/cm^3.[13,14,23] The deformation of the (atomic) electron cloud of sodium in the rare-gas matrix leads[24] to a slight increase in the effective Bohr radius of the "atom" (easily measured by using electron spin resonance[25] and optical spectroscopy)[26] and, consequently (via eq 3), to a slightly lower critical density for metalization than in the pure metal.[22] A similar effect has been suggested[27] for supercritical mercury and the two component mercury-xenon system in order to explain the lower value of the critical density for the M-NM transition in the low-temperature, two-component system.[28]

Similarly, as Mott pointed out in his major work on the transition to the metallic state,[3,8] if we are dealing with an array of "gaseous" atoms, then the background dielectric constant is of course unity and a^*_H now represents a characteristic radius for the isolated gas-phase atom. The phrase "metal-doped vacuum" has been utilized previously[29] for these pure metals, and this provides the direct semiconductor analogy. In the present instance, simple estimates of the effective Bohr radius of the gaseous alkali atoms are possible both from a consideration[30] of well-known atomic properties (ionization potential, electron affinity, etc.) and from radii corresponding to the principal maxima in the radial distribution functions $r^2\psi_i^2(r)$, using relativistic wave functions.[31,32] As shown elsewhere,[33] the radii corresponding to these maxima represent a good measure of the "size" of each atom.

On this basis, Hensel[9] and more recently Freyland[30] and Cusack[34] have shown that the Mott criterion, as expressed in the scaled form[20] suggested earlier (eq 3), is indeed capable of predicting the critical concentration for the onset of metallic character in the electronic properties (conductivity etc.) for several of the fluid alkali metals. *We stress that this onset of metallization occurs at the same metal density as the liquid-vapor critical point.*

We include experimental data for the entire alkali metal series in Table I. We note once again, even for the pure alkali metals, the fundamental importance of the "size" of an isolated atom in dictating the threshold density both for the M-NM transition in these systems and the concomitant liquid-vapor critical point.

Thus, the conclusion[16] that for the pure alkali metals, the liquid-vapor phase transition is a direct manifestation of the electronic constitution change at the M-NM transition seems secure.

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Table I. The Mott Criterion for Metal Solutions and Expanded Fluid Metals

system	ρ_c, g cm^{-3}	n_c, cm^{-3}	a^*_H, Å	$n_c^{1/3} \cdot a^*_H$
I. Supercritical Fluid Metals				
Li	0.11^a	9.43×10^{21}	1.59^d	0.34
Na	0.21^b	5.48×10^{21}	1.71^d	0.30
K	0.19^c	2.89×10^{21}	2.16^d	0.31
Rb	0.34^c	2.40×10^{21}	2.29^d	0.31
Cs	0.42^c	1.9×10^{21}	2.52^d	0.32
II. Metal Solutions[e]				
Li-NH_3 (209 K)	$\sim 0.65^g$	$9.94 \times 10^{20\,f,g}$	2.76 (mon)[h]	0.28
			2.83 (pol)[i]	0.28
Na-NH_3 (231 K)	0.653	$9.03 \times 10^{20\,f}$	2.68 (mon)[h]	0.26
			2.88 (pol)[j]	0.28
Li-$MeNH_2$ (ca. 200 K)	$\sim 0.64^k$	$1.85 \times 10^{21\,k}$	2.59 (mon)[l]	0.32
			2.60 (pol)[m]	0.32

[a] References 13b and 15. Normal (bulk) densities from "Handbook of Chemistry and Physics", 60th ed., 1979-1980. [b] References 13b and 23. [c] Values attributed to Bhise, V. S., Bonilla, C. F., and Cezairliyan, A., Eds. Proceedings of the 7th Symposium on Thermochemical Properties, ASME: Maryland, 1977 cited in ref 30. [d] Reference 31. [e] Parameters derived at the critical consolute temperature for each metal-solvent system. [f] From ref 36, p 9. [g] Assuming $\rho = 0.65$ g cm^{-3} at 213 K, from: Lo, V. R. E. *Z. Anorg. Allg. Chem.* 1960, *344*, 230. [h] Monomer (interstitial ion); low-frequency dielectric constant from ref 52; $m/m^* \approx 1$. [i] Polaron calculation; dielectric constant data as in footnote *h*; R = 2.88 Å at 203 K giving $\mu = 0.3557$, $\alpha = 0.3745$; $h\nu(\text{calcd}) - h\nu(\text{obsd}) \lesssim 2.5 \times 10^{-3}$ eV.[52] [j] Polaron calculation; dielectric constant data as in footnote *h*; R = 3.04 Å at 233 K; $\mu = 0.3479$, $\alpha = 0.3730$; $h\nu(\text{obsd}) - h\nu(\text{calcd}) \lesssim 1.5 \times 10^{-3}$ eV.[52] [k] 13 MPM, based on ref 44a. Density data from: Yamamoto, M.; Nakamura, Y.; Shimoji, M. *Trans. Faraday Soc.* 1971, *67*, 2292. [l] Low-frequency dielectric constant from ref 49; high-frequency dielectric constant at 200 K interpolated from measured values;[50] $m/m \approx 1$. [m] Polaron calculation, dielectric constant data as in footnote *l*; R = 2.50 Å at 200 K; $h\nu(\text{calcd}) - h\nu(\text{obsd}) \lesssim 2 \times 10^{-2}$ eV. Compare this cavity radius to that measured at 266 K for Li-$MeNH_2$ solutions, R = 3.34 Å (Yamamoto et al. *Trans. Faraday Soc.* 1971, *67*, 2292); gives $dR_0/dt \approx 1 \times 10^{-2}$ Å/deg for Li-$MeNH_2$ compared to $dR_0/dt \approx 5.8 \times 10^{-3}$ Å/deg for Na-NH_3.[52]

Liquid-Liquid Phase Separation in Metal-Ammonia and Lithium-Methylamine Solutions. But what of metal solutions? The early experimental studies of Kraus[5] showed that solutions of sodium in liquid ammonia separate into two liquid phases with an upper critical temperature of -41.6 °C. Since that time, precise studies of the phase coexistence curves for a variety of alkali and alkaline earth metals in liquid ammonia have been carried out and these are delineated and discussed elsewhere.[2,4,6]

In 1965, Krumhansl[16] gave an authoritative survey[35] of the electronic and thermodynamic nature of dense, metallic vapors. This provocative article once again preceded the major experimental advances in the study of expanded fluid alkali metals. Consequently, Krumhansl chose metal-ammonia solutions as a model system and discussed the observed liquid-liquid phase separation and the M-NM transition in these solutions in terms of a matrix-bound congener of the *anticipated* situation in dense vapors. In this scheme, as in Pitzer's early contribution,[7] the ammonia is simply regarded as a liquid dielectric medium and the alkali metal takes on the role of a donor or impurity state in this host matrix. Thus, in sodium-ammonia solutions below -41.6 °C, we have a phase separation into an insulating vapor (corresponding to matrix-bound, localized excess electrons) and a metallic (matrix-bound), liquid metal.

At Colloque Weyl I, Sienko[6] elaborated upon the simple semiconductor analogy and suggested a possible link between the M-NM transition and phase separation in metal-ammonia solutions. Thus, the binding energy and effective radius for the donor (alkali) atom in liquid ammonia were treated in terms of a hydrogenic picture for an interstitial alkali atom in the host dielectric. Utilizing the simplest form[8,18] of the Mott criterion (eq 1), Sienko showed[6] that the critical metal composition for liquid-liquid phase separation in metal-ammonia solutions does indeed appear to be identical with the concentrations predicted for the M-NM transition.[35]

That the condensation phenomenon in sodium-ammonia solutions occurs[5,6,35,36] for temperatures below a critical temperature of ca. 231 K and at a critical density ca. 9×10^{20} atoms cm^{-3} compared to T_c = 2573 K and 5.48×10^{21} atoms cm^{-3} in the pure metal[23] arises quite naturally within the content of the semiconductor analogy.[6,7,16] In this, the effect of the host dielectric properties on the electronic properties of the lattice of impurity centers in the dilute regime is primarily[7,37] to reduce all energies (including the cohesive energy) by (approximately) a value of K^{-2} and increase all distances by (again, approximately) the factor K. An extension of these ideas is found in perhaps the first consideration of the M-NM transition in sodium-ammonia solutions—Herzfeld, in 1927, considered[38] that K goes to infinity *at* the metallic onset, the resultant force on the (isolated) electron vanishes and the system acquires metallic status!

We have recently[20] stressed the underlying importance of this type of "matrix-induced" scaling, or renormalization, of the Bohr radius and critical interaction distances when considering the critical Mott densities for (electronic) metallization (Figure 1). If this idea of a suitably renormalized concentration grid applies both to the electronic (there is already good evidence[20,21] for this) *and* thermodynamic phase transitions in metal solutions, then we anticipate a marked solvent dependence in both the onset of metallic character *and* the critical concentration for liquid-liquid phase separation.

Recently, in an effort to understand better the influence of the host solvent on the electronic nature of the M-NM transition, we have initiated investigations into the magnetic and magnetic resonance properties of solutions of lithium in anhydrous methylamine.[40-44] A preliminary study[40,41] of the temperature dependence of the electron spin-lattice relaxation time (T_{1e}) indicated that the *sign* of (dT_{1e}/dT) is a sensitive marker for determining whether the excess electron is localized (nonmetallic) or itinerant (metallic). For lithium-methylamine solutions the sign reversal in (dT_{1e}/dT) occurred in the range 13.4-15.6 mol % lithium.[42,44a] Kinks in some of the T_{1e} vs T curves together with coincidences in the low-temperature T_{1e} values suggested that a liquid-liquid phase separation occurs in the lithium-methylamine system.[44b] This was supported by two visual sightings. On the basis of the analysis of the T_{1e} behavior and DTA results, a tentative phase diagram has been proposed for the lithium-methylamine system.[44b] It is shown in comparison with the lithium-ammonia phase diagram in Figure 2. (Further studies based on conductivity and ultrasound measurements are still in progress.)

The most significant difference between the two systems is the concentration at which the miscibility gap appears. In Li-NH_3 it lies around 4.4 mol % Li and 210 K, whereas in the $LiMeNH_2$ system the phase separation occurs with a consolute point approximately 12-13 mol % Li and 200 K. As in the earlier discussion[6,7] of metal-ammonia solutions, we (initially) regard the lithium atom as an electron donor in the liquid methylamine

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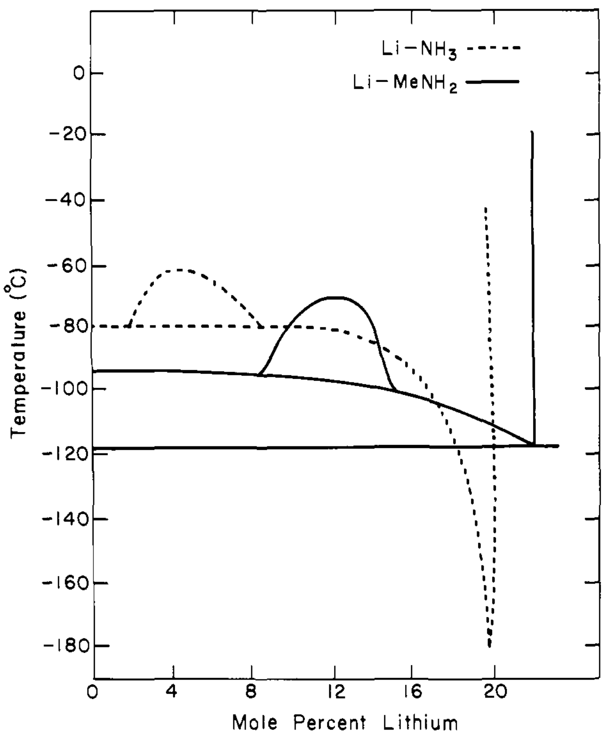

Figure 2. Comparison of phase relations in the systems lithium–ammonia and lithium–methylamine.

dielectric and compare the critical concentration for phase separation with the Mott criterion for the M–NM transition, on the basis of the derived alkali-metal monomer radius.

As outline earlier, a fundamental parameter in this type of discussion is a realistic, effective radius for the isolated electron wave function.[20] The interstitial metal ion description of the alkali monomer[6,46,47] represents a reasonable, *first-order* description of an excess electron trapped in the field of a positive point charge in a continuous dielectric medium. Perhaps a more realistic description of the localized electron wave function in dilute ammonia and methylamine solutions is the polaron model.[45–48] For our purposes, the original formulation of Jortner[45] is still perhaps the most transparent in relating the *major* characteristics of solvent properties (high- and low-frequency dielectric constants, cavity size) to the optical absorption spectrum and, ultimately, to the spatial extent of the solvated electron eigenfunction in dilute solutions. Certainly, considerably more elaborate treatments are possible,[48] but we feel that the adiabatic polarized cavity model of Jortner is sufficiently realistic, and rigorous, for a discussion of the comparative features of the (localized) excess-electron wave function in ammonia and methylamine.

Both the interstitial ion and polaron results will be quoted here (Table I), since it is well established[47] that both treatments have a certain common ground in solvents of high dielectric constant.

For the interstitial ion picture, the effective dielectric constant can be calculated by using Simpson's relation[6]

$$K_{\text{eff}}^{-1} = K_{\text{st}}^{-1} + {}^{5}\!/_{16}(K_{\text{op}}^{-1} - K_{\text{st}}^{-1})$$

where K_{st}, the low-frequency dielectric constant of methylamine,[49] is 17.9 and K_{op}, the high-frequency dielectric constant, is estimated from the square of the refractive index[50] to be 1.8818 at 200 K. Then with $K_{\text{eff}} = 4.89$ and the free-electron mass for m^*, we calculate the hydrogenic (donor) radius from $a^*_{\text{H}}/\text{Å} = K_{\text{eff}}(m/m^*)\ 0.529$ to be 2.59 Å for lithium–methylamine solutions and an associated critical density for metallization of (1–6) × 10^{21} cm^{-3} on the basis of the scaled form of the Mott criterion.

Electronic energy levels and eigenfunctions according to the simplified polarized-cavity model of Jortner[45] were calculated for the excess electron in methylamine (200 K) by using well-established procedures. Briefly, the binding energy potential of the electron is given by[45–48]

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

where H(x) is a step function and $\beta = K_{\text{op}}^{-1} - K_{\text{st}}^{-1}$. R is some characteristic cavity radius. The corresponding energies (E_{i}) of the 1s and 2p states are given by[45,47] the sum of an electronic energy term, W_{i}, and a contribution from the electronic polarization energy, S_{i}^{e}

$$E_{\text{i}} = W_{\text{i}} + S_{\text{i}}^{\text{e}}$$

A simple variational approach, utilizing one-parameter wave functions [μ(1s) and α(2p)] of hydrogen-like form, serves to evaluate the energies $W_{1\text{s}}$ and $W_{2\text{p}}$ by their minimization with respect to μ and α. $S_{1\text{s}}^{\text{e}}$ and $S_{2\text{p}}^{\text{e}}$ can then be estimated for these (fixed) values of μ and α, and the energy of the 1s → 2p transition of the electron within the potential well is then given by $h\nu = E_{2\text{p}} - E_{1\text{s}}$. This transition energy can then be compared directly with the near-infrared absorption band.[51–53]

The eigen energies were calculated by using the accurate values for the dielectric constants of liquid ammonia[49,52] and methylamine,[49,50] at 209 K (for Li-NH$_3$), 231 K (Na-NH$_3$), and 200 K (Li-MeNH$_2$). In all cases calculated, optical transition energies, based on the cavity radii and variational parameters (μ and α) given in Table I, were within 5 × 10^{-3} eV of the experimental values.[51–53]

The Bohr radius for the 1s level is approximately represented[45] by $a^*_{\text{H}} = 1/\mu$, and we take this as a reasonable estimate of the characteristic radius for the eigenfunction of the localized, excess electron in dilute ammonia and methylamine solutions.

Both the polaron and interstitial ion estimates of a^*_{H} (Table I) for the two solvents suggest a greater confinement of the excess electron in methylamine compared to ammonia. This is indeed in line with both optical[51] and excess-volume studies[54,55] of lithium–methylamine solutions. The fact that the optical absorption spectrum for Li–MeNH$_2$ (single broad asymmetric maximum at 7350 cm^{-1}) is very much like that of Li–NH$_3$ (single broad asymmetric maximum at 6700 cm^{-1}) argues that the electron trap is probably quite similar in the two solvents. Concerning the critical density for the onset of metallic character in this system, the concentration range 5 to 14 MPM (mole % metal) is characterized by a rapid increase in electrical conductivity,[56] and in the same region the relaxation properties of both electron and nuclear spins change dramatically (for a review, see ref 43). Clearly, then, the electronic properties of lithium–methylamine solutions for $T > 200$ K reveal a M–NM transition for the concentration range given[56] by eq 3. Similarly, as in metal–ammonia solutions,[6,35,36] this electronic transition *above* the consolute temperature appears to be closely related to the miscibility gap occurring below the consolute temperature ($T < 200$ K).

On these considerations, we suggest that the origin of the differences in critical compositions for metal–ammonia and lithium–methylamine solutions may possibly arise quite simply from the difference in the degree of confinement, or spatial extension, of the localized-electron wave function in the two solvents.

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Thompson[2] has advocated a slightly different approach in which electrons are effectively localized in the metal anion. However, the recent optical studies of thin films of lithium with methylamine by Dye and co-workers[57] show no absorptions which can be attributed to Li$^-$.

Summary

In the previous sections we have discussed the relationship between the vapor–liquid condensation that accompanies the cooling of an alkali-metal gas, and the liquid–liquid phase separation in metal–ammonia and lithium–methylamine solutions. Table I is a collation of critical (consolute) densities in lithium- and sodium–ammonia solutions and lithium–methylamine solutions together with the observed critical densities of the pure alkali metals and the corresponding estimates of the Mott criterion for all systems under investigation.

These condensation phenomena observed in both the gaseous and matrix-bound systems appear to be closely related. Furthermore, they are significantly correlated in that, in all cases, critical (metal) densities at the metallic onset are in good agreement with the Mott criterion (eq 3, Table I). The slightly different constants found for the two solvent systems may possibly be related[21] to differences in the nature of the (host) conduction band; but any further considerations must await more detailed experimental and theoretical studies of the localized, excess electron in lithium–methylamine solutions. However, there is evidence[30] to suggest that the slightly lower constant of ca. 0.26 found for metal–ammonia solutions and the wide variety of highly doped semiconductors,[20] as compared with the value of ca. 0.30–0.34 found for the expanded fluid alkali metals (Table I), may be related to the proximity of an unoccupied (host) conduction band in the matrix-bound systems.

In summary, we suggest that the observed condensation phenomena for both gaseous and matrix-bound alkali metals are indeed a direct manifestation of the major electronic constitution change at the M–NM transition.[16,17] Thus, the critical Mott density in these systems signals the onset of an electronic transition *without* a thermodynamic phase transition for temperatures above a certain critical temperature, T_c. This critical density is also that at which a thermodynamic phase change accompanies the electronic transition below T_c.

It is also apparent that Pitzer's suggestion[7] that phase separation in metal–ammonia solutions is the analogue within the liquid-ammonia medium of the liquid–vapor separation of the pure metal does indeed represent a particularly apt description of the phenomenon. In this context, we have attempted to stress the fundamental importance[20] of the localized-electron entity in dictating the composition for the electronic/thermodynamic transition.

We are still, however, no nearer any reasonable explanation for the *absence* of phase separation in cesium–ammonia solutions.[2] Expanded fluid cesium does indeed show a two-phase regime[9–11] with a critical point[23] at a density of 0.42 g cm^{-3} and a temperature of 2023 K. In addition, electrical, transport, and magnetic properties indicate that the M–NM transition is closely correlated with both the Mott density and the liquid–gas critical point.[11,30] Cesium is miscible in all proportions in liquid ammonia near room temperature, and measurements of electrical and magnetic properties reveal a M–NM transition in the range 4–5 MPM. However, there is *no* evidence[61] for liquid–liquid phase separation in this system. This is even more intriguing in view of recent magnetic susceptibility studies[30,58] of metallic and nonmetallic expanded fluid cesium which reveal notable similarities with the corresponding magnetic behavior in metal–ammonia solutions in the approach to the metallic state.[59,60]

Acknowledgment. This research was sponsored by the National Science Foundation under Grant No. DMR-78-12238 and was supported in part by the Air Force Office of Scientific Research and the Materials Science Center at Cornell University. P.P.E. wishes also to acknowledge the support of the Science Research Council.

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Chemical Reaction Paths. 7.[1] Pathways for S_N2 and S_N3 Substitution at Sn(IV)

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Abstract: Reaction pathways involving four-, five- and six-coordinated Sn(IV) are derived from an examination of 186 crystal structures found from a search of the Cambridge Crystallographic Data Centre Database. For the reaction $Y + SnR_3X \rightleftharpoons [YSnR_3X] \rightleftharpoons YSnR_3 + X$, the structure correlation method provides a convincing mapping of the S_N2 pathway with inversion of configuration. The S_N2 pathway with retention of configuration is not so well-defined, but some of its features are revealed. For the reaction $2Y + SnR_2X_2 \rightleftharpoons [Y_2SnR_2X_2] \rightleftharpoons Y_2SnR_2 + X_2$, there is a well-defined pathway involving a symmetrical double addition and elimination process. We call this type of termolecular reaction an S_N3 reaction and show that it can be distinguished from alternative reaction types with the same stoichiometry. Structures involving seven- and eight-coordinated Sn(IV) are briefly mentioned. The somewhat meager data for Ge(IV) and Pb(IV) are discussed in the Appendix.

While tetraorganotin compounds RR′R″SnR‴ are optically stable, triorganotin halides are not.[3] This has been explained by the tendency of the triorganotin compounds in the presence of nucleophiles to expand their coordination number to form stereochemically nonrigid five- or six-coordinated intermediates or

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