plane (Figure 7). At minimum, this data can be accounted for by the imidazole orientation. Notably, the data of Table II indicate that HRP-CN exhibits a resonance pattern similar to CcP in that pyrroles II and IV (methyl pair 8 and 3) exhibit larger shifts than pyrroles I and III (methyl pair 5 and 1). These data imply that the heme orientation in HRP, relative to a fixed proximal histidine-iron bond, is similar to that in CcP.[47] We conclude that HRP also will exhibit a hemin orientation reversed by 180° about the α-γ meso axis when compared to metmyoglobin.

Whether, and to what extent, peripheral hemin-protein contact may influence the methyl shift pattern in low-spin heme proteins remains to be evaluated. There is evidence from the data of Table II, in fact, that heme-protein peripheral contacts constitute at least a minor part of the rhombic perturbation in these CcP forms. We deduce this by comparing the 3,8-shifts in both CcP and HRP as shown in Figure 7. At 35 °C the most downfield resonances are HRP (8) and CcP (3). The more upfield pair are HRP(3) and CcP(8). A reasonable source for this reversal of trans pyrrole methyl shifts between CcP and HRP lies in different heme-protein peripheral contacts at the trans pyrroles (II,IV). Crystal structure data has only been reported for CcP,[6,16] and it indicates that Trp-51, a critical residue to the proposed peroxidase catalysis mechanism[16,36] lies above pyrrole II. Primary sequence studies of HRP[42,43] indicate a high degree of homology in the B helix of CcP, which forms the distal side of the heme pocket. However, in place of Trp-51, the HRP sequence places a phenylalanine. In view of the greater charge-donating ability of tryptophan compared to phenylalanine, the inversion of the 3,8-methyl resonance ordering that is observed here can be understood by assuming significant peripheral contact between the position-51 residue and the hemin. Donation of charge density to pyrrole II from the tryptophan enhances the Por $\rightarrow$ Fe π donation by pyrrole II, thereby shifting the 3-CH_3 further downfield and, hence, inverting the methyl ordering in CcP relative to HRP. In support of this possibility we note that the mean 3,8-methyl resonance position in CcP (28.2 ppm at 35 °C) is much larger than the mean 3,8-shift in HRP (27.3 ppm at 35 °C). This shift pattern indicates that the porphyrin 3e π-orbital which includes pyrroles II and IV contains relatively greater unpaired spin density in CcP than does the same orbital in HRP.

Summary

Hemin methyl, vinyl, and propionic acid methylene protons have been assigned for CcP-CN and CcP-N_3 by reconstitution with specifically deuterated hemins. The results indicate the pattern of unpaired spin delocalization about the porphyrin and lead to the prediction that the heme orientation in HRP-CN will be similar to that in CcP-CN. By analysis of the assigned resonances for CcP and the crystal structure, the proximal histidine rotational orientation alone is shown to be capable of explaining the rhombic perturbation. However, evidence is also presented which suggests that peripheral heme-protein contacts may contribute to the perturbation.

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Registry No. Cytochrome c peroxidase, 9029-53-2; [1,5-$^2H_6$]hemin, 84848-82-8; [1,3-$^2H_6$]hemin, 84848-81-7; [2,4-$^2H_4$]hemin, 84848-80-6; [4-$^2H_3$]hemin, 84848-79-3; [2,4-$^2H_2$]hemin, 82113-45-9; [6,7β-$^2H_4$]hemin, 84848-78-2.

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Multinuclear NMR Study of the Solvated Electron in Lithium-Methylamine Solutions

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Abstract: We report a multinuclear NMR study of lithium-methylamine solutions. NMR Knight shift data for solvent (^{1}H, ^{13}C, ^{14}N) and metal (^{6}Li, ^{7}Li) nuclei are reported for concentrations from 2 mol % lithium to saturation at ca. 200 K. The NMR results have been used in conjunction with recent magnetic susceptibility measurements on the title system to provide a precise description of the unpaired-electron spin-density distribution in both the solvated electron, $e^-{}_s$, and lithium monomer species, $Li^+{}_se^-{}_s$. For both species, the vast majority of the unpaired-electron spin density resides in the nitrogen fragment of the solvent molecule. As with metal-ammonia solutions, we also find a small, negative spin density in the ^{1}H 1s orbital. The occupancy of the ^{6}Li and ^{7}Li 2s orbital in the electron-cation aggregate species $Li^+{}_se^-{}_s$ corresponds to approximately 0.5% of the lithium free-atom value for a 7 mol % metal solution. We conclude that the excess-electron species in lithium-methylamine solutions resides in a ground-state orbital which is composed of a simple 1s-like orbital for the electron within a solvent cavity, in combination with a set of Rydberg-like orbitals derived from the 3s orbitals of the host solvent matrix.

Introduction

Metal-ammonia solutions have been the subject of considerable attention from both chemists and physicists for almost two centuries.[1-3] In this system, comprehensive optical, conductivity, and magnetic data (among other properties) now exist over something like five orders of magnitude in concentration.[3] With this background it is natural, as Dye has suggested,[4] that in any general description of metal solutions we invariably return to the metal-ammonia system for guidance. However, the study of metal

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Table I. Representative Knight Shift Data[a] for the Nuclei ^1H, ^6Li, ^7Li, ^{13}C, and ^{14}N in Lithium-Methylamine Solutions[b]

	isotope					
MPM	$^1H(CH_3)$	$^1H(NH_2)$	^6Li	^7Li	^{13}C	^{14}N
2	−2.26	−4.69	+12.53	+12.47	+150.88	
	(7)	(18)	(11)	(25)	(280)	
7	−4.53	−7.69	+17.03	+16.62	+158.36	
	(4)	(7)	(3)	(4)	(190)	
17	−7.60[c]	−11.76[c]	+15.15	+15.08	+318.27[c]	+1002.8[c]
	(8)	(18)	(1)	(1)	(100)	(270)
27[d]	−5.77[e]	−10.26[e]		+19.35		
	(54)	(75)		(14)		

[a] Knight shifts defined as eq 2; $\Delta\nu_{1/2}$ given in parentheses (Hz). [b] Data at 203 K except where indicated. [c] 218 K. [d] Nominal composition; saturated solution containing 5 mol % excess lithium. [e] Proton resonance shows additional splitting.

solutions in other nonaqueous solvents over the last two decades has resulted in major advances,[1-4] particularly in the study of distinguishable and identifiable paramagnetic and diamagnetic species existing in dilute solution. In the concentrated regime, the study of different solvent systems allows one to assess the important role of the host solvent on the metal-nonmetal (M-NM) transition and the associated phenomenon of phase separation in metal solutions.[5-7] Metal-methylamine solutions have been studied with both objectives in mind. Rubidium- and cesium-methylamine solutions provided the first unambiguous magnetic evidence for the (atomic) stoichiometry of the monomeric $M^+{}_se^-{}_s$ species in dilute solutions.[8,9] Similarly, lithium-methylamine solutions have recently attracted considerable attention in the context of the M-NM transition.[5,10,11] In this paper we report the preliminary results of a multinuclear NMR study of lithium-methylamine solutions. Our main interest here is to provide a precise description of the unpaired-electron spin-density distribution in both the solvated electron and the electron-cation encounter species, $Li^+{}_se^-{}_s$, in dilute solutions. Future studies will concentrate on changes in the integrity of the electron spin-density distribution as the M-NM transition is approached at higher metal concentrations.

Experimental Section

Solutions of lithium in methylamine were prepared using established high-vacuum techniques.[11,12] A variety of cleaning procedures were employed for the Pyrex preparation cells. These included $HF-HNO_3$ mixtures, concentrated HNO_3, etc. All glassware was generally soaked for several days in these cleaning agents, rinsed thoroughly at least 10 times with distilled water, and oven-dried. The cleaning agent Decon-90 was also used instead of the acid mixtures. Sample tubes were then attached to the vacuum line and the entire preparation cell was degassed at 1000 °C, first under low vacuum (10^{-2} torr) and subsequently under high vacuum (ca. 3×10^{-5} torr) until no further outgassing was noticeable; this procedure generally took 2–3 h.

Lithium metal (99.99%, Alfa Products, Lancaster Synthesis Ltd., U.K. Distributors) was cut and mechanically cleaned in an argon-atmosphere glove box. This inert-atmosphere facility typically operates below 10 ppm oxygen, as monitored continuously by an Anacon (76) oxygen meter. The metal was cut and shaped from the center of a new piece of lithium rod, weighed on a high-precision electric balance (Mettler AC 100), and introduced directly into an NMR sample cell equipped with a greaseless, high-vacuum tap (J. Young, Acton, London). The cell was removed from the glove box and attached to the high-vacuum line. The argon atmosphere above the lithium metal was pumped off until the sample cell stabilized at a working vacuum of ca. 10^{-5} to 10^{-6} torr. Methylamine (99.99%) (British Oxygen Co.) was distilled into the main vacuum manifold from a round-bottomed flask containing clean, freshly cut lithium metal. The dried gas was then condensed onto a known weight of lithium in the sample cell in stoichiometric amount. Subsequent analysis of the methylamine by mass spectrometry indicated water and ammonia impurity levels below 0.1% wt values. The sample cell containing the required proportions of lithium and methylamine was frozen to 77 K, sealed off from the vacuum system with a hand torch, and stored in liquid nitrogen. Prior to spectroscopic measurements, the samples were thoroughly homogenized using a cardice-acetone bath (−78 °C).

NMR spectra were recorded on a Jeol FX-90Q pulsed FT spectrometer operating at the following frequencies: ^6Li, 13.14 MHz; ^7Li, 34.80 MHz; ^{13}C, 22.50 MHz; ^{14}N, 6.42 MHz; ^1H, 89.56 MHz. The magnetic field was stabilized by the signal from a separate D_2O sample built into the probe, and referencing was done by substitution to give a reproducibility of measurement of ±0.2 ppm. The reference standards were pure methylamine (for ^1H, ^{13}C, and ^{14}N) and a solution of $LiNO_3$ in methylamine (^6Li, ^7Li).

Each NMR spectrum was monitored continuously until no further change in chemical shift position could be detected. This established that complete equilibration of the sample had been attained. To ensure reproducibility, each NMR spectrum was recorded several times under equilibrium conditions. Knight shifts were found to be entirely reproducible over a considerable period of time, indicating that the degree of decomposition of the samples was slight.

Results

The Larmor frequency, ν_X, of a particular nucleus X is given by[13,14]

$$\nu_X = \frac{\gamma_X}{2\pi}B_0\{1 - \sigma_X\} \qquad (1)$$

where B_0 is the external magnetic field, γ_X is the nuclear gyromagnetic ratio, and σ_X is the shielding or screening constant of the nucleus. Variations in the electronic distribution around the nucleus X lead to chemical shifts in the NMR frequency. This NMR Knight shift, κ, is here defined[13,14] as

$$\kappa/\text{ppm} = \left\{\frac{\nu_X - \nu_{ref}}{\nu_{ref}}\right\} \times 10^6 \qquad (2)$$

where ν_{ref} is the reference frequency for the operating standard.

Table I is a compilation of a representative section of our Knight-shift data for the nuclei ^1H, ^6Li, ^7Li, ^{13}C, and ^{14}N; also included are NMR peak widths at half-height ($\Delta\nu_{1/2}$). At the outset we draw attention to the extremely large variations in both κ and $\Delta\nu_1/_2$ for the metal and solvent nuclei. These range from κ = 1002.8 ppm and $\Delta\nu_{1/2}$ = 270 Hz for ^{14}N (I = 1) to κ = −4.53 ppm and $\Delta\nu_{1/2}$ = 4 Hz for the CH_3 proton resonance. In par-

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Table II. Structure of the Solvated Electron, e^-_s, and Aggregate Species, $Li_s^+e^-_s$, in Lithium–Methylamine Solutions[a]

property	isotope					
	$^1H(CH_3)$	$^1H(NH_2)$	^6Li	^7Li	^{13}C	^{14}N
$\kappa(X)$/ppm	-4.53	-7.69	$+17.03$	$+16.62$	$+158.36$	$+1002.8$
$\{n\|\Psi_{(0)}\|_X^2\}$/e cm^{-3}	-3.25×10^{22}	-5.22×10^{22}			$+11.37 \times 10^{23}$	$+2.35 \times 10^{24}$
$[nA_{iso}(X)]$/G	-7.7	-13.0			67.6	40.1
$\langle\|\Psi_{(0)}\|_{Li}^2\rangle_{av}$/e cm^{-3}			8.61×10^{21}	8.41×10^{21}		
$A_{iso}(Li)$/G			0.30	0.77		
% atomic (2s) character			0.55	0.54		

[a] Data shown for a 7 MPM solution for all nuclei except ^{14}N (17 MPM). Molar spin susceptibility values used in calculations: $\chi_m^{sp} = 143 \times 10^{-6}$ per mol of Li at 203 K (7 MPM); $\chi_m^{sp} = 134 \times 10^{-6}$ at 203 K (17 MPM); $\chi_m^{sp} = 150 \times 10^{-6}$ at 218 K (17 MPM).

ticular, ^6Li ($I = 1$) and ^7Li ($I = {}^3/_2$) nuclei give rise to extremely narrow signals; e.g., $\Delta\nu_{1/2} = 1$ Hz for a 17 mol % metal (MPM) sample.

Discussion

The unequal population of the electron spin states in an applied magnetic field results in an effective local field at the nucleus via the Fermi-contact interaction between the resonating nucleus and the s electrons.[13-16] This local field modifies the applies magnetic field and is manifest as a Knight shift (κ) of the NMR.[17] The Knight shift permits a direct estimate of the electron spin-density distribution at both the lithium and solvent nuclei.[18-21]

A. Lithium ($^{6,7}Li$) Knight Shifts. Knight shifts for both ^6Li and ^7Li nuclear resonances are shifted to high frequency of the reference sample, $LiNO_3$ in methylamine. The lithium Knight shift arises primarily via the isotropic Fermi contact interaction between the unpaired electron and the lithium nucleus in cation–electron encounter species ($Li^+_se^-_s$) known variously[4,9,22] as ion-pair or centrosymmetric, monomeric entities (see also ref 3). No distinction is made here between the various models. Anisotropic (dipolar and pseudodipolar) interactions will not be considered here since they are expected to average to zero in a time short compared with the inverse of the Knight shift (expressed in frequency radians per second) and therefore will not contribute to the observed shift. The metal Knight shifts may be used to calculate the total (average) electron-spin density, $\langle|\Psi_{(0)}|_{Li}^2\rangle_{av}$

$$\kappa(\text{Li}) = \left(\frac{8\pi}{3}\right)(\chi_m^{sp}/L_0)\langle|\Psi_{(0)}|_{Li}^2\rangle_{av}\gamma \qquad (3)$$

where χ_m^{sp} is the molar spin susceptibility, L_0 is the Avogadro number, and γ is the fraction of unpaired electrons ion-paired to lithium cations. We obtain estimates of χ_m^{sp} from recent magnetic susceptibility measurements on the title system.[11a] As is well known, the observed static magnetic susceptibility (χ_{stat}) is a measure of the sum of the diamagnetism and paramagnetism of all the species present. A common problem with these types of measurement is the difficulty in obtaining accurate values for the diamagnetic correction of both the container and the diamagnetism associated with the (closed-shell) atomic cores. This problem was overcome recently by Stacy, Johnson, and Sienko,[11b] whereby bucket correction and core diamagnetism were made on a metastable sample in situ by allowing the sample to decompose. Therefore, reported values of magnetic susceptibility are due only to the unpaired electrons. These recent data also suggest that fluid lithium–methylamine solutions *do not* display the extensive spin-pairing phenomena encountered in dilute lithium–ammonia solutions. Indeed, Stacy[11a] has found that the magnetic data are in good agreement with the values expected for a system moving from simple Curie-like behavior in dilute solutions (characteristic of noninteracting electrons) to Pauli-like behavior in the concentrated regime. Similarly, Nakamura et al.[32] had previously shown that magnetic susceptibility data for lithium–methylamine solutions at room temperature are in good agreement with calculated molar electron susceptibilities based on a simple electron-gas picture. Consequently, we take these static susceptibility data[11a] as reasonable estimates of the paramagnetic susceptibility, in order to extract information concerning the unpaired-electron wave function.

Table III. Unpaired Electron Spin Densities in Lithium–Ammonia, –Methylamine, and –Ethylamine Solutions

property	$Li\text{-}NH_3$	$Li\text{-}CH_3NH_2$	Li-$CH_3CH_2NH_2$
$\{n\|\Psi_{(0)}\|_H^2\}$	-7.2×10^{22}	-5.52×10^{22} ($-NH_2$ protons)	$\leqslant -3.4 \times 10^{21}$
$\{n\|\Psi_{(0)}\|_N^2\}$	$+6.44 \times 10^{24}$	$+2.35 \times 10^{24}$	$+5.85 \times 10^{23}$
$\langle\|\Psi_{(0)}\|_{Li}^2\rangle_{av}$	$+6.8 \times 10^{21}$	8.4×10^{21}	$\leqslant 5.5 \times 10^{20}$
% Li atomic (2s) character	0.43	0.54	$\leqslant 0.035$
% H atomic (1s) character	3.4	2.6	$\leqslant 0.16$

Assuming a single ion-pairing equilibrium, then, γ (eq 3) may be calculated from the known equilibrium constant for the association process[23]

$$Li^+_s + e^-_s \rightleftharpoons Li^+_se^-_s$$

in lithium–methylamine solutions at −78 °C.

Average electron spin densities, $\langle|\Psi_{(0)}|_{Li}^2\rangle_{av}$, at both ^6Li and ^7Li nuclei were calculated from the available magnetic susceptibility[11a] and equilibrium constant data[23] for the title system at 200 K. The derived estimates of $\langle|\Psi_{(0)}|_{Li}^2\rangle_{av}$ are listed in Table II, together with the corresponding percentage occupation of the lithium 2s orbital. The latter was estimated using the experimental values[24,25] of the electron density at the lithium nucleus in the corresponding free (gaseous) lithium atom, $|\Psi_{(0)}|_{Li}^2$.

Our results again highlight a recurrent problem in using both NMR and ESR to extract detailed information about the unpaired-electron wave function at alkali metal sites in ion-pair species.[26] Unpaired-electron densities at the lithium nucleus in most nonaqueous solvents are extremely small compared to free-atom values. For "atomic" character values of between 1 and 5%, one could argue that the bare cation, M^+, rather than the free atom, might be a more realistic marker for comparison purposes. It is generally accepted that, if this were the case, the extension of the outer s orbital would be substantially reduced relative to that of the free atom. The effect of this neglect, then,

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is to reduce the actual unpaired spin densities at the lithium nucleus; i.e., the atomic character values for the three solvents cited in Tables II and III may well represent *upper* limits. However, as Sharp and Symons[26] have pointed out, it would be very difficult to allow quantitatively for this contraction of the outer s level because of the uncertainties associated with the precise role of the solvent in these electron–cation encounter species. For this reason we follow accepted procedure and utilize free-atom values for comparison purposes; the problem remains.

Note that the observed metal Knight shifts in lithium–methylamine solutions are considerably larger than those observed in lithium–ammonia solutions;[20,21,27] a 2 MPM solution of lithium in ammonia, for example, has a ^{7}Li Knight shift of 10 ppm at 300 K relative to a solution of $LiNO_3$ in ammonia,[20] whereas the corresponding value for a lithium–methylamine solution is 32 ppm at 294 K with respect to $LiNO_3$ in methylamine. This arises because the lithium Knight shift is dependent upon both $\langle|\Psi_{(0)}|_{Li}{}^2\rangle_{av}$ and also χ_m^{sp} (eq 3). The values of $\langle|\Psi_{(0)}|_{Li}{}^2\rangle_{av}$ are of the same order of magnitude in both solvent systems (Table III), but the extremely large paramagnetism[11a,12] associated with fluid lithium–methylamine solutions (first noted by Fowles et al.[28]) leads to the abnormally high lithium Knight shifts. The electron spin density at both ^{6,7}Li nuclei is very small, corresponding to approximately 0.5% 2s atomic character for a 7 MPM solution. This is comparable with that observed in dilute lithium–ammonia solutions[20,21] (ca. 0.43% atomic character), but an order of magnitude larger than the corresponding value (~0.035%) in lithium–ethylamine solutions.[29]

However, we stress that the observed Knight shifts represent the summation of *all* interactions averaged over all participating electron–cation encounter species in solution. As in metal–ammonia solutions, we cannot unequivocably rule out the possibility that the observed shifts arise from a very small concentration of "atomic-like" entities[4,30,31] having a much larger electron density at the metal nucleus.

B. Proton, Nitrogen and Carbon Knight Shifts. For solvent nuclei, X = ^{1}H(NH_2 and CH_3 constituents), ^{13}C, and ^{14}N, ϕ, the Knight shift of the nuclear resonance arising from the polarization of electron spins with a Fermi contact density $|\Psi_{(0)}|_X{}^2$ at *each* particular nucleus is given by[19] by[19]

$$\kappa(X) = \left(\frac{8\pi}{3}\right)(\chi_m^{sp}/L_0)\{n|\Psi_{(0)}|_X{}^2\}\frac{x_M}{(1 - x_M)} \tag{4}$$

where x_M is the mole fraction of (x_M = MPM/100) and n is the "effective" number of solvent nuclei encompassed within the orbital of the unpaired electron. For a detailed review of the basic theory and effective approximations currently adopted, see ref 5. Using our NMR results together with recent magnetic susceptibility data,[11,32] we evaluate $\{n|\Psi_{(0)}|_X{}^2\}$, the *total* unpaired electron-spin density at the various nuclei under consideration. The magnetic and spectroscopic data are given in Table II. The corresponding values for the total isotropic hyperfine coupling constant $[nA_{iso}]$ are obtained via the equation

$$[nA_{iso}(X)] = \left(\frac{8\pi}{3}\right)\left(\frac{\mu_I}{I}\right)\mu_N\{n|\Psi_{(0)}|_X{}^2\} \tag{5}$$

where μ_I is the magnetic moment (in units of the nuclear magneton μ_N) and I is the spin of nucleus X. Table III gives experimental values of $\{n|\Psi_{(0)}|_X{}^2\}$ and $\langle|\Psi_{(0)}|_{Li}{}^2\rangle_{av}$ for solutions of lithium in ammonia, methylamine, and ethylamine.[29]

(i) Proton Knight Shifts. In all three solvents, isotropic coupling constants to protons are small and negative. This suggests that the major contribution to the hyperfine field is core polarization, similar to that observed in organic radicals[33] and d-band metals.[14] The effect is minor, but so surprisingly constant from one solvent to another that it surely represents an important, characteristic feature of the solvated electron in polar liquids. Ab initio calculations[34,35] have now produced the sign of the electron density at the proton in aquated electrons, but a simple descriptive model for the general phenomenon in metal solutions is still elusive.[22] However, Symons[22] has suggested the combination of the 1s (cavity) level for the excess electron and the 1s hydrogen orbital of the solvent molecule can give rise to a negative, isotropic coupling to the protons, and a positive isotropic coupling to the nitrogen nuclei (Table II). The two types of substituent proton in methylamine provide an interesting addition to the results for metal–ammonia solutions. We find that the electron densities at both proton sites, NH_2 and CH_3, are negative. The spin density at the NH_2 protons is (numerically) always larger (i.e., more negative) than that observed for their CH_3 counterparts. Presumably this arises because CH_3NH_2 molecules are orientated at the edge of a cavity such than an "ammonia-like" trap is produced.[36] Negative electron spin densities at alkyl protons have also been observed in sodium–HMPA solutions.[37]

(ii) Nitrogen Knight Shift. Unpaired-electron spin densities at the nitrogen-14 nucleus were determined from the ^{14}N Knight shift data (Table II). The very large ^{14}N Knight shifts (e.g., κ = 1002.8 ppm for a 17 MPM solution) indicate a substantial degree of unpaired electron density at the nitrogen nucleus. However, when the abnormally large paramagnetism of the lithium–methylamine solution is taken into account, the total electron density on nitrogen, $\{n|\Psi_{(0)}|_N{}^2\}$, is approximately *half* the value found in lithium- and sodium–ammonia solutions. Nevertheless, this still represents a substantial isotropic coupling to nitrogen giving $[nA_{iso}(^{14}N)]$ = 40 G for lithium–methylamine solutions, compared with $[nA_{iso}(^{14}N)] \simeq$ 110 G for sodium–ammonia solutions.[21,22] Recall that this total isotropic coupling to nitrogen represents unpaired-electron spin density at *all* the constituent nuclei encompassed within the unpaired-electron wave function, viz., summations over weakly interacting second and third solvation shells, and strongly interacting primary shells,

$$[nA_{iso}(X)] = \underset{\substack{\text{over all}\\ \text{shells}}}{\sum_{i=1}^{j}} \quad \underset{\substack{\text{over all interactions}\\ \text{within a shell}}}{\sum_{k=1}^{l}} \quad n_{i,k}(A'_{i,k}) \tag{6}$$

where $n_{i,k}$ is the number of interacting magnetic nuclei (X) within a solvation shell (i = 1, primary; i = 2, secondary, etc.) and $A'_{i,k}$ is the isotropic coupling constant characteristic of each *individual* electron–nuclear contact interaction. No further progress can be made until some reasonable estimate is made of the distribution function for $n_{i,k}$ and $A_{i,k}$.[31]

We represent hyperfine interactions within a particular solvation shell in terms of average, or effective, values of n and A. Each solvation shell may then be represented as a number, n_i, of solvent nuclei all judged to be interacting *equally* with the unpaired electron, and eq 6 reduces to

$$[nA_{iso}(X)] = \underset{\substack{\text{over}\\ \text{all}\\ \text{shells}}}{\sum_{i=1}^{j}} n_i(A'_i) \tag{7}$$

Symons[22] has estimated a ^{14}N *isotropic* coupling constant of ca. 12 G for *each* of the six primary solvent molecules in metal–ammonia solutions, viz.

$$n_1 = 6;\ A'_1 = 12\ \text{G}$$

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and

$$n_2 = 12;\ A'_2 = 3\ \text{G}$$

for the second solvation shell. This leads to $[nA_{\text{iso}}(^{14}\text{N})] = 108$ G, as the total isotropic coupling to ^{14}N in metal–ammonia solutions. On the basis of our ^{14}N NMR data for lithium–methylamine solutions (Table II), a corresponding picture for the structure of e^-_s would lead to $[nA_{\text{iso}}(^{14}\text{N})] \simeq 40$ G. A *possible* representation of the first coordination shell would then be $n_1 \lesssim 4$, $A_1 \lesssim 10$ G, and this is certainly consistent with recent data for (MgO) surface trapped electrons in methylamine (see below). This suggests a high degree of charge localization of the electron wave function within the solvent cavity and on the surrounding primary solvation shell. This is indeed consistent with the available magnetic,[7,11] optical,[36,38] and volumetric studies[10b,39] on lithium–methylamine solutions which suggest a more confined wave function for e^-_s than in the metal–ammonia systems.

Additional supportive evidence comes from recent ESR studies of the interaction of surface-trapped electrons on MgO with adsorbed ammonia or amines.[40,41] Smith et al.[41] report detailed spectroscopic properties for these species which are very similar to those of e^-_s in the corresponding metal solutions. Indeed, these centers are now viewed[22,41] as solvated electrons trapped on the oxide surface. Resolved ^{14}N and ^{15}N hyperfine interactions with the surrounding solvent molecules in the primary solvation shell also permit a detailed determination of isotropic coupling constants. For ammonia, the total isotropic coupling is[41] ca. 33 G per molecule, for methylamine approximately 18 G per molecule, and for ethylamine 15 G per molecule. This ordering of coupling constants is in agreement with the NMR Knight shift data for $\{n|\Psi_{(0)}|_N^2\}$ for the three solvents (Table III).

Our results then suggest that the orbital containing the excess electron in ammonia and methylamine solutions has a substantial (and positive) electron density at both the ^{14}N and ^{13}C nuclei (in CH_3NH_2), but a node at, or close to, the proton. This was the basis of the early suggestion by Pitzer,[42] recently utilized by Symons,[22] that a natural choice for this type of excited-state orbital is a linear combination of suitably modified 3s-like orbitals on nitrogen, in fact, the first Rydberg level of ammonia. A precise estimate of the hyperfine coupling expected for unit occupancy of the 3s orbital of the Rydberg state is at present unknown. However, recent ESR studies of ($Li{-}NH_3$) molecular units isolated in rare-gas matrices suggest that unit occupancy of the 3s orbital on a single (complexed) ammonia molecule produces an isotropic coupling to nitrogen of ca. 30–33 G. This is indeed similar to the observed coupling constant for surface-trapped electrons in the MgO/ammonia system.[40,41] We conclude that the excess electron in both ammonia and methylamine resides in a combination of both a cavity-like (1s) orbital and a Rydberg-like orbital constructed from 3s orbitals on the solvent.

Concluding Remarks

The main features of our multinuclear NMR study of lithium–methylamine solutions can be summarized as follows.

(i) For the monomer, or ion-pair species of stoichiometry ($Li^+{}_s, e^-{}_s$), we find a low value for the unpaired-electron spin density at both the ^{6}Li and ^{7}Li nuclei; this amounts to something like 0.5% occupation of the (free atom) lithium 2s orbital in the aggregate species. Both current descriptions[3,9,30] of the encounter species ($Li^+{}_s, e^-{}_s$) in this sytem can predict such a small delocalization of the unpaired electron onto the metal cation.

(ii) For samples in the composition range 2 to 27 MPM, a small, *negative* isotropic coupling is observed to both the amine (NH_2), and methyl (CH_3) protons.

(iii) In contrast to (ii), a large, *positive* isotropic coupling is observed to both the ^{14}N and ^{13}C nuclei.

Results ii and iii once again highlight certain perplexing features of the solvated-electron wave function. Our results show clearly that when excess electron density enters the accessible orbitals on the methylamine molecule, a large unpaired-electron spin density appears at both the ^{13}C and ^{14}N nuclei. However, the results also require that this ground-state orbital has a node at (or close to) protons of both the NH_2 and CH_3 groups.

We favor the following picture for the excess electron in methylamine, ammonia, and related solvents. We take the ground-state orbital of the solvated electron in these polar solvents to be composed of a simple 1s-like level for the electron within the cavity, in combination with a set of appropriate Rydberg, or Wannier-type orbitals derived from the host solvent.[44–46] For ammonia and methylamine, an assembly of suitably modified 3s orbitals on nitrogen look like ideal contenders.[22] In fact, recent ab initio calculations[45] on the low-lying electronic states of ammonia do indeed reveal Rydberg-like 3s and higher excited states for this molecule. Such a description has its links in current descriptions of impurity or donor states in semiconductor materials.[18,44,47] For example, in phosphorus-doped silicon, the Rydberg orbitals are closely related to Wannier functions constructed predominantly from Bloch (free-electron) states of the first unoccupied band of the host,[48] the silicon conduction band. Such Bloch functions were, until recently, considered only in the context of *crystalline* materials. However, Rice and Jortner[49] first conjectured, and then demonstrated conclusively,[50] that these localized Wannier states could exist even in a structurally disordered medium. The fundamental requirement was that the conduction band of the host medium be free-electron-like. Similarly, Catterall and Edwards[44] have reported the experimental observation of Wannier-type impurity states in rapidly quenched (vitreous) metal–HMPA solutions.

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