localized excess electron. As a possible indirect test, the relations in eq 42 and 47 suggest a connection between the effective cavity radii determined by magnetic resonance spectroscopy methods[26] and values of the root-mean-squared deviation-in-position which can be determined by optical spectroscopy methods similar to those used for solvated electrons in fluid media.[26] That such a connection may exist is already suggested by certain of the available magnetic resonance results in glasses[6] and optical absorption results in fluids.[26] Should the connection be found to hold generally, it would provide some independent support—probably not unequivocal, however—for the conclusions reached here. The radii which have been described then will have been shown to be a

property of the configurational distribution of the excess electron and not a direct property of its environment.

Despite the foregoing limitations, an illustration of how $D(Y)$ (i.e., $|\bar{X}_{eff}|$) and Y (i.e., $|\langle \bar{X} \rangle|$) are related for two assumed choices of $\rho_{00}(\xi)$ is given in Figure 2. The value of $\langle \xi^2 \rangle$ has been taken to be approximately the value of the mean-squared dispersion-in-position of solvated electrons in water.[26] The artifactitious cavity radii that result can be seen to compare favorably with the reported cavity radii for excess electrons in aqueous glasses.

Finally, we note that the effect of averaging the point-dipole–dipole interaction energy has been considered in the past,[3,27] but the results obtained here appear to be new.

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Electron Spin-Echo Studies of Relaxation Times in Lithium–Methylamine Solutions

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The electron spin relaxation times T_1 and T_2 of lithium-6– and lithium-7–methylamine solutions have been measured by electron spin-echo techniques over the temperature range 200–260 K. T_1 and T_2 are not equal in the concentration range studied (0.1–5.0 MPM); their values differ most at low concentrations and low temperatures. No significant lithium isotope effect is observed. The accepted relaxation mechanism for dilute metal–ammonia solutions (motional modulation of the electron–^{14}N hyperfine interaction) cannot alone account for the observed relaxation times in lithium–methylamine solutions.

Introduction

Electrons in metal–ammonia solutions have been extensively studied by electron spin resonance techniques.[1-12] Continuous wave ESR and electron spin-echo studies have given important information regarding electron–solvent, electron–metal cation, and electron–electron interactions and their lifetimes in these solutions. Such data are extremely useful for evaluating models for the structure and electron transport mechanism in these solutions, particularly at the metal–nonmetal transition.

Early electron spin resonance experiments[4,7,8] revealed that the transverse (T_2) and longitudinal (T_1) electron relaxation times are equal for Li–, Na–, and Ca–ammonia solutions at all concentrations and temperatures. The relaxation times for dilute lithium and sodium solutions are relatively long (3 μs) and are concentration independent up to concentrations of 0.2 mole percent metal (MPM). Above this concentration, the relaxation times decrease as the nonmetal–metal transition (4 MPM) is approached. Interestingly, T_1 and T_2 relaxation times for potassium–ammonia solutions were found to be slightly different below 0.5 MPM.[5,7,8] This difference was verified by several researchers and is apparently independent of microwave frequency and temperature.[8] More recent work[12] has suggested that T_1 and T_2 are slightly different in very dilute (<0.04 MPM) Na–, Rb– and Cs–ammonia solutions as well.

The most widely accepted theory for interpretation of dilute metal–ammonia ESR data involves motional narrowing of the electron–nitrogen hyperfine interaction.[4,6-9,11-14] Equations developed for relaxation via this mechanism give the following relaxation times[6-8,11]

$$T_1^{-1} = \frac{128\pi^2}{27\hbar^2}(g_e g_n \beta_e \beta_n)^2 I_n(I_n + 1)\frac{1}{N}\{N|\Psi(0)|_n^2\}^2 \left[\frac{\tau_c}{1 + (\omega_s - \omega_n)^2\tau^2_c} \right] \quad (1)$$

$$T_2^{-1} = \frac{64\pi^2}{27\hbar^2}(g_e g_n \beta_e \beta_n)^2 I_n(I_n + 1)\frac{1}{N}\{N|\Psi(0)|_n^2\}^2 \times \left[\tau_c + \frac{\tau_c}{1 + (\omega_s - \omega_n)^2\tau^2_c} \right] \quad (2)$$

where g_e and g_n are the electronic and nuclear g factors, β_e and β_n are the Bohr and nuclear magnetons, I_n is the nuclear spin, N is the number of interacting nuclei, $|\Psi(0)|_n^2$ is the electron density at the nucleus, τ_c is the correlation time for a given electron–nuclear interaction, and ω_s and ω_n are the electron and nuclear Larmor frequencies, respectively. Typical values of the Larmor frequencies at 3300 G are $\omega_s \sim 6 \times 10^{10}$ rad s^{-1} and $\omega_n \sim 8 \times 10^7$ rad s^{-1} and thus the nuclear Larmor frequency can be safely neglected in the above equations. It must be noted that eq 1 and 2 are oversimplified since they were derived from a simplistic exponential correlation function, and it has been shown that the dependence on $\omega_s\tau_c$ is more complex when $\omega_s\tau_c \sim 1$.[15]

For very short correlation times, $\omega_s\tau_c \ll 1$ and T_1 equals T_2 for the nitrogen hyperfine mechanism. τ_c is often taken to be the Debye rotational time

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$$\tau_R = \eta V_0/kTN_A \qquad (3)$$

where η is the bulk viscosity, V_0 is the molar volume, k is the Boltzmann constant, and N_A is the Avogadro number. However, rotational motion cannot modulate isotropic Fermi contact interactions and thus τ_R is not an appropriate correlation time. Such interactions can be modulated by relative translation of the electron and solvent molecules and hence are described more accurately by the diffusional correlation time

$$\tau_d = d^2/6D = d^2\left(\frac{6\pi a \eta}{kT}\right)$$

where d is the nearest-neighbor distance and D is the self-diffusion coefficient.[9] The temperature dependences of τ_R and τ_d are approximately the same ($\eta/\rho T$ and η/T, respectively). O'Reilly[9] has calculated τ_d for ammonia to be 1.6×10^{-12} s at 300 K. Thus, $\omega_s \tau_d \sim 0.09$ and the approximation leading to equal relaxation times is apparently valid. Calculations of relaxation times for this mechanism using electron densities at the nitrogen nucleus derived from nitrogen Knight shift data are in very good agreement with experimental results.[4,7] This mechanism does not, however, explain the differences between T_1 and T_2 in very dilute metal–ammonia solutions for which the correlation times are presumably very short. Harris and Lagowski[12,16] have recently proposed a spin–site exchange mechanism in addition to the nitrogen hyperfine interaction in order to explain the different relaxation times.

Lithium–methylamine solutions have also been examined by electron spin resonance.[3,11,17-19] However, only continuous wave T_2 measurements have been made on relatively concentrated samples (>5 MPM), though it must be noted that the non-metal–metal transition in methylamine solutions occurs at considerably higher concentrations than in ammonia solutions. As for ammonia solutions, the results of Li–methylamine measurements in the dilute regime have been interpreted in terms of motional modulation of the nitrogen hyperfine interaction with the assumption that $\omega_s \tau_c \ll 1$ and the relaxation times are equal.

It is expected that the diffusional correlation time for methylamine will be longer than that for ammonia, and thus $\omega_s \tau_c$ may not be negligible. Direct measurements of T_1 and T_2 relaxation times using electron spin-echo techniques were undertaken in this work in order to investigate whether the assumptions that $\omega_s \tau_c \ll 1$ and $T_1 = T_2$ are valid.

Experimental Section

Lithium–methylamine solutions were prepared from 99.94% isotope enriched ^{7}Li and 98.68% isotope enriched ^{6}Li (Oak Ridge National Laboratory) and 98% methylamine (Matheson Co.) containing 0% ammonia, 0.8% (maximum) and 0.6% (maximum) di- and trimethylamine, respectively, water 0.8% (maximum), all in wt % values.

The lithium metal was cut and weighed in an evacuable Dri-Lab (Vacuum Atmospheres) under a helium atmosphere containing less than 1 ppm of oxygen or nitrogen, and then transferred in 3-mm i.d. Spectrosil tubing to a vacuum line.

Methylamine was purified by a procedure similar to that outlined in ref 17. The methylamine was introduced into a vacuum line which was outgassed at 10^{-6} torr for several days previously. A portion of the gas was allowed to blow off into the fume hood through a manometer. Methylamine (60 mL) was then condensed onto freshly cut lithium in a round-bottom flask at 77 K. The methylamine was warmed to 195 K and kept at this temperature for at least 48 h before samples were prepared to ensure that all water was removed. Immediately prior to sample preparation, the methylamine storage bulb was frozen at 77 K and evacuated

for 30 min to remove any hydrogen evolved during storage. The methylamine was then double distilled and condensed onto a known weight of lithium in a 3-mm i.d. sample tube at 77 K. The ESR tube was sealed off from the vacuum line and stored in liquid nitrogen. Immediately prior to measurement, samples were homogenized at 195 K.

Electron spin-echo techniques were used to measure the longitudinal and transverse relaxation times of dilute lithium–methylamine solutions. The pulsed ESR measurments were made at X-band frequencies on one of the author's spectrometers (J. H. Freed).[20] The pulse lengths were typically 25–60 ns. 90–τ–180–τ– pulse sequences were employed to measure the phase memory time, which for the system under study is approximately equal to T_2.[20] T_1 relaxation times were measured with 90–τ–90–T–90–τ– pulse sequences. Relaxation times could be measured for systems with phase memory times as short as 100 ns. Lithium-6 and lithium-7 samples of concentration 0.1, 0.5, 1.0, and 5.0 MPM were studied in the temperature range 200–260 K by spin-echo techniques.

Continuous-wave (CW) ESR measurements were made on a Varian E-12 spectrometer.

For both spin-echo and continuous-wave ESR, temperatures were maintained to within ±1 K with a carefully calibrated Varian nitrogen-flow variable-temperature controller.

Results

The results are shown in Figure 1. For all concentrations studied, T_1 and T_2 are not equal. The relaxation times differ by an order of magnitude in the most dilute samples (0.1 MPM) examined. The relaxation times begin to converge with increasing concentration and temperature. T_1 and T_2 are essentially equal in 5 MPM samples at 260 K.

No lithium isotope effect is observed for any of the concentrations studied. The slight difference between ^{6}Li and ^{7}Li transverse relaxation times at 1.0 MPM is most likley due to slightly different concentrations. Therefore, lithium hyperfine interactions are probably not important relaxation mechanisms in these solutions.

Continuous-wave ESR studies of 0.1 and 1.0 MPM samples gave narrow, Lorentzian line shapes. Transverse relaxation times derived from the Lorentzian relation $T_2^{-1} = {}^3/_2\gamma_e \Delta H_{pp}$ are denoted by open symbols in Figure 1, a and c. The excellent agreement with spin-echo data indicates that the resonances are not broadened by inhomogeneous fields or unresolved hyperfine interactions.

Discussion

Evidence for the dominance of the electron–nitrogen hyperfine relaxation mechanism in dilute metal–ammonia solutions is substantial. Knight shift studies show a very large unpaired electron density at the nitrogen nuclei (the Fermi contact term $|\Psi(0)|^2 = 6.44 \times 10^{24}$ e cm^{-3}) and much smaller densities at the hydrogen and metal nuclei.[13,20] Changing the magnetic moment and nuclear spin of the nitrogen nuclei via nitrogen-15 substitution changes the relaxation times in a manner predicted by this mechanism.[4] There is also evidence that the electron–nitrogen mechanism is dominant in higher-order amines. Continuous-wave ESR of lithium–ethylamine and lithium–butylamine solutions actually shows resolved hyperfine coupling attributed to four equivalent nitrogen nuclei.[22,23] In view of this evidence, it seems reasonable to postulate that the nitrogen-hyperfine interaction is also a dominant relaxation mechanism in dilute lithium–methylamine solutions. This postulate is supported by recent Knight shift data for lithium–methylamine solutions,[24] which indicate a large unpaired electron density at the nitrogen nuclei ($|\Psi(0)|^2 =$

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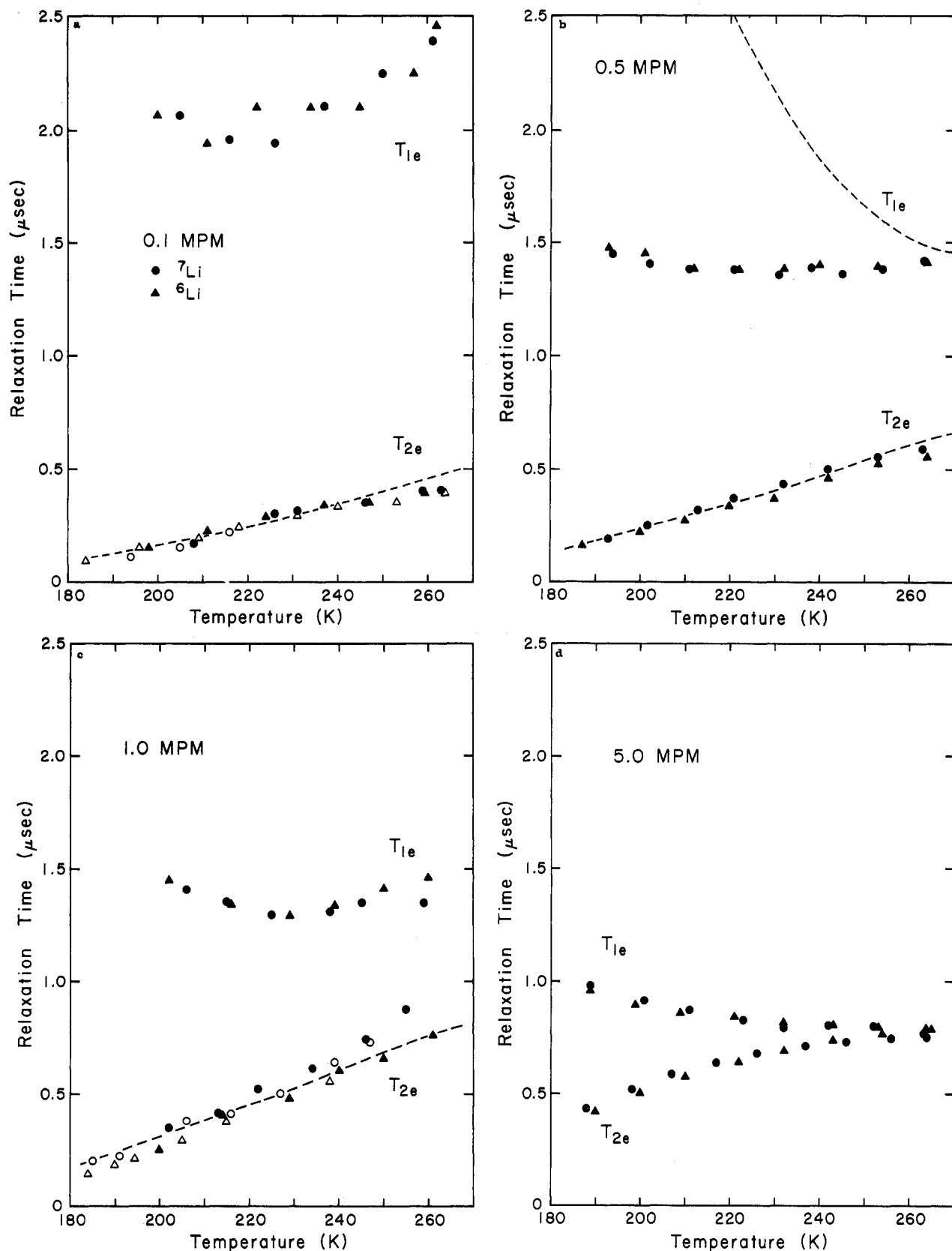
Figure 1. T_1 and T_2 relaxation times for (a) 0.1 MPM, (b) 0.5 MPM, (c) 1.0 MPM, and (d) 5.0 MPM lithium–methylamine solutions. Circles and triangles represent ^{7}Li and ^{6}Li solutions, respectively. Hollow symbols denote T_2 values measured by continuous-wave ESR.

2.35 × 10^{24} e cm^{-3} for a 17 MPM sample), a smaller but substantial density at the carbon nuclei (1.13 × 10^{23} e cm^{-3}), and much smaller densities at the lithium and hydrogen nuclei.

For the motionally modulated nitrogen hyperfine interaction, the relaxation times T_1 and T_2 begin to diverge as $\omega_s \tau_c$ approaches unity. Both spin-echo and CW experiments in this work were

performed at a frequency of 9.2 GHz, and thus ω_s is essentially constant and equal to 5.8 × 10^{10} rad s^{-1}. Therefore, a correlation time longer than 6 × 10^{-12} s is expected to give an observable difference between T_1 and T_2. A log–log plot of the relative relaxation times due to this mechanism as a function of τ_c is shown in Figure 2. These relaxation times were calculated with eq 1
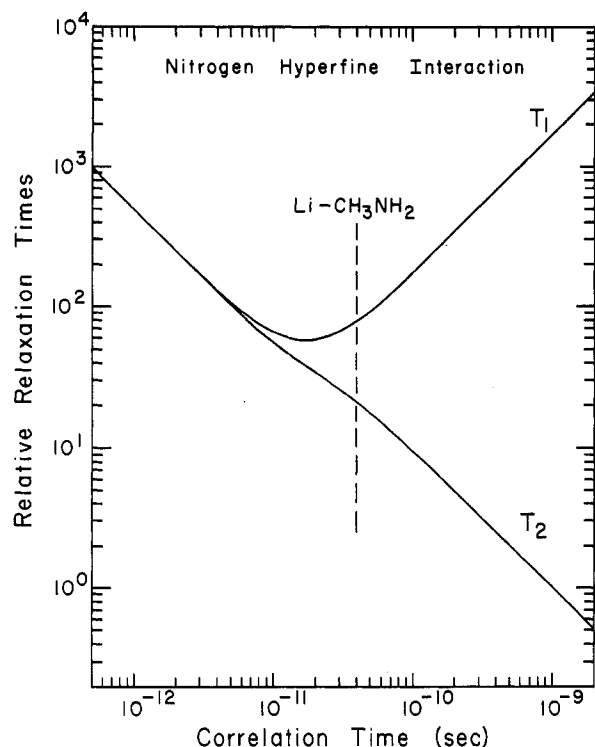
Figure 2. A log–log plot of the relative T_1 and T_2 relaxation times due to the nitrogen hyperfine mechanism as a function of τ_c. The minimum in the T_1 curve occurs where $\omega_s\tau_c = 1$. For ammonia solutions, $\tau_c \sim 1 \times 10^{-12}$ s.

and 2, which are valid for $\tau_c \ll T_2$, which is the case for lithium–methylamine solutions (see below).

If the nitrogen hyperfine interaction is assumed to be the only dominant mechanism for both T_1 and T_2 relaxation, then a correlation time can be calculated from the ratio T_1/T_2 (derived from eq 1 and 2):

$$T_1/T_2 = 1 + \tfrac{1}{2}(\omega_s\tau_c)^2$$

Correlation times calculated from values of T_1 and T_2 at 240 K are in the range $(3–8) \times 10^{-11}$ s for 1.0–0.1 MPM solutions. If, indeed, the motionally modulated nitrogen hyperfine mechanism is correct, the correlation times should scale roughly as η/T for each concentration as the temperature is varied. Calculated T_2 curves using scaled correlation times (assuming a temperature-independent hyperfine coupling) are in very good agreement with experimental data for 0.1, 0.5, and 1.0 MPM samples. T_1 data, however, exhibit more complex temperature and concentration behavior. The 1.0 and 0.1 MPM samples show a slight minimum in the temperature dependence of T_1. Normally, T_1 minima occur in the motionally narrowed regime when the inverse of the correlation time is equal to the Larmor frequency ($\omega_s\tau_c = 1$). If we assume the appropriate correlation time at the minima, the T_1 data cannot be approximated by scaling the correlation time with motional parameters by using eq 1. In addition, correlation times approximately equal to the inverse of the Larmor frequency (i.e., 1.7×10^{-11} s) yield a T_1/T_2 ratio which is much smaller than the observed ratio at the minima. However, the T_1 dependence on $\omega_s\tau_c$ for translational diffusion mechanisms (involving a more sophisticated correlation function) can be quite different than would be expected from eq 1.[15] The T_1/T_2 ratio arising from a model of relaxation through scalar interactions modulated by diffusion is indeed found to yield a flatter dependence upon τ_c that is more in accord with the observations in this work.

In light of the fact that T_1 behavior cannot be accounted for by eq 1, some preliminary conclusions can be drawn. It is possible that eq 1 and 2 (derived from a simplistic exponential correlation function) do not accurately represent the methylamine system. Alternatively, if these equations are applicable, then the data presented in this work indicate that T_1 and T_2 cannot share the

TABLE I: Comparison of Calculated Nitrogen Hyperfine Correlation Times for 0.1, 0.5, and 1.0 MPM Lithium–Methylamine Solutions

concn, MPM	$\tau_{c,min}$,[a] s	τ_c,[b] s		
		$N = 4$	$N = 5$	$N = 6$
0.1	5.3×10^{-11}	2.2×10^{-11}	3.0×10^{-11}	3.9×10^{-11}
0.5	3.0×10^{-11}	1.3×10^{-11}	1.8×10^{-11}	2.4×10^{-11}
1.0	2.1×10^{-11}	0.8×10^{-11}	1.0×10^{-11}	1.3×10^{-11}

[a] Correlation times calculated from T_1/T_2 at 260 K. [b] Calculated from Knight shift data and estimated N.

nitrogen hyperfine mechanism as the only relaxation mechanism. We shall discuss, in the present work, just the latter possibility, i.e., we shall consider the consequences of eq 1 and 2. Thus, with these equations and the data presented here, several possibilities exist:

(1) T_2 relaxation is due to motionally modulated nitrogen hyperfine interaction and T_1 relaxation proceeds via the nitrogen interaction and at least one other mechanism which contributes significantly to T_1

$$\frac{1}{T_1} = \frac{1}{T_{1,nitrogen}} + \frac{1}{T_{1,other}}$$

(2) T_1 relaxation is due only to the nitrogen hyperfine interaction in the region where $\omega_s\tau_c \sim 1$, and T_2 is shortened from the nitrogen hyperfine T_2 by an additional mechanism.

(3) T_1 and T_2 are both influenced by the nitrogen hyperfine mechanism and some other mechanism.

(4) The nitrogen hyperfine interaction does not contribute significantly to either T_1 or T_2 relaxation.

Possibility (4) is unlikely in light of the significant contribution the nitrogen interaction makes toward relaxation in ammonia and other amine solutions.

Possibility (2) is unlikely because T_1 data do not scale with rotational and diffusional motion even in the region where $\omega_s\tau_c \sim 1$. Furthermore, although 0.1 and 1.0 MPM samples show a slight minimum in the temperature dependences of T_1, this minimum is not evident in the temperature dependence of T_1 for the intermediate concentration, 0.5 MPM. Presumbaly the correlation times increase with decreasing concentration.[9] It is therefore highly improbable that a single mechanism could give rise to the temperature dependence and concentration dependence of the observed T_1 data.

The merits of possibility (3) cannot be determined until nitrogen isotopic substitution experiments are done (vide infra). However, the fact that T_2 relaxation times for 0.1, 0.5, and 1.0 MPM samples scale so well with T/η suggests that T_2 is motionally modulated and lends support to possibility (1).

Assuming, then, for the time being, that T_2 relaxation proceeds via the nitrogen hyperfine mechanism and that T_1 relaxation involves at least one other mechanism, one can calculate minimum values of τ_c for which the observed difference between T_1 and T_2 is actually smaller than the difference due to the nitrogen hyperfine interaction. The minimum values are calculated from T_1/T_2 at high temperatures (260 K) since τ_c is shortest at high temperatures. These values are shown in Table I, labeled $\tau_{c,min}$. Scaling these τ_c values with η/T and calculating T_2 values by fitting one temperature point gives very good agreement with experimental data. These calculated T_2 curves are shown by dashed lines in Figure 1a–c. Hypothetical $T_{1,nitrogen}$ values were calculated with the same correlation times. The values are plotted for the 0.5 MPM samples in Figure 1b and are also represented by a dashed line.

Assuming that T_2 relaxation is due solely to the nitrogen interaction, one can calculate correlation times directly from eq 2, provided $\{N|\Psi(0)|_n^2\}$ and the number of interacting nuclei, N, are known. Unfortunately, nitrogen Knight shift data[24] and magnetic susceptibility data[25] giving rise to $\{N|\Psi(0)|_n^2\}$ are only available for concentrated (17 MPM) lithium–methylamine solutions. For

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TABLE II: Nitrogen Hyperfine Coupling Constants, Unpaired Electron Spin Densities, Dielectric Constants, Debye Rotational Times, and Correlation Times for Electron–Nitrogen Interactions in Dilute Lithium–Ammonia, –Methylamine, and –Ethylamine Solutions

system	$N\|\Psi(0)\|^2$, e cm^{-3}	A_n(total), G	N	ϵ_0 (at 263 K)	τ_R(260 K), s	τ_c, s
Li–NH$_3$	$6.44 \times 10^{24\,a}$	110	$6-11^{b,c}$	20.2	8×10^{-12}	$\sim 1 \times 10^{-12\,d}$
Li–CH$_3$NH$_2$	$2.35 \times 10^{24\,e}$	40	$4-6^f$	11.4	1.6×10^{-11}	$\sim 3 \times 10^{-11\,i}$
Li–CH$_3$CH$_2$NH$_2$	$5.85 \times 10^{23\,f}$	10	$4-5^f$	6.3^g	3.3×10^{-11}	$>6 \times 10^{-9\,h}$

[a]Reference 13. [b]Reference 26. [c]Reference 27. [d]References 7 and 9. [e]Reference 24. [f]Reference 23. [g]Value for 298 K. [h]Calculated from $A_n\tau_c$ > 1 for resolved hyperfine interaction. [i]This work, assuming T_2 relaxation due to nitrogen hyperfine interaction.

ammonia solutions, electron densities on the nitrogen nuclei are slightly concentration dependent at 240 K,[13] though the exact nature of the concentration dependence is not well established. Thus the actual electron density at the nitroen nucleus in dilute methylamine solutions could be somewhat more (or less) than that measured at high concentrations. The number of interacting nitrogens is most likely intermediate between the number in ammonia solutions (7–11)[26,27] and that in lithium ethylamine solutions (4–5).[23] Results of τ_c calculations using the available Knight shift and susceptibility data, $N = 4-6$, and T_2 data at 260 K are given in Table I. These values are slightly lower than $\tau_{c,min}$ values calculated from T_1/T_2 ratios at 260 K. However, the agreement is quite good considering the approximate $\{N\|\Psi(0)\|_n^2\}$ values used.

It is also possible to estimate a maximum correlation time for the nitrogen hyperfine mechanism. As T_2 relaxation times from pulse and continuous-wave ESR measurements are essentially equal, there can be no substantial hyperfine broadening of the continuous-wave line width. The condition for resolution of hyperfine structure in the continuous-wave spectrum is $\tau_c A > 1$, where A is the hyperfine coupling constant. Since no broadening is observed, $\tau_c A < 1$ for this system. The nitrogen hyperfine coupling constant is derived from Knight shift data[24] and is calculated to be 40 G for 17 MPM Li–methylamine solutions. This corresponds to a frequency of 7×10^8 rad s^{-1} for a g value of 2. Therefore, $\tau_c < 1 \times 10^{-9}$ s for the nitrogen interaction in methylamine solutions. The calculated correlation times (assuming the nitrogen interaction is dominant for T_2 relaxation) are well under this limit.

The physical properties, Knight shift data, and calculated nitrogen hyperfine correlation times for methylamine solutions fit in well with data for ammonia and ethylamine solutions. Table II compares the total electron densities at the nitrogen nuclei, $\{N\|\Psi(0)\|_n^2\}$, the total electron–nitrogen hyperfine coupling (A_N, G), the number of nitrogen nuclei with which the electron interacts strongly (N), the static dielectric constants of the pure solvents (ϵ_0), the Debye rotational times for the pure solvents, and the estimated correlation times for the nitrogen hyperfine interactions in dilute solutions. It is interesting to note that, as the dielectric

constant decreases and the electron is bound more tightly (the cavity potential well is deeper),[28] the electron density at the nitrogen atoms decreases. It is also interesting to note that the Debye rotational times change by a factor of four from ammonia to ethylamine while the actual nitrogen hyperfine correlation times change by four orders of magnitude. This highlights the macroscopic, simplistic nature of the Debye rotational time and the inappropriate use of this parameter as a correlation time for this mechanism.

To determine whether the assumptions concerning the importance of the nitrogen hyperfine interaction in T_1 and T_2 relaxation are correct, nitrogen-15 isotopic substitution ESR studies are necessary. If, indeed, T_2 relaxation is dominated by the nitrogen hyperfine, Knight shift and magnetic susceptibility data for dilute methylamine solutions are necessary in order to make a more accurate calculation of the correlation times in dilute solutions. These experiments are under way.

In more concentrated solutions, it appears that another mechanism may be become important. The T_2 temperature dependence of 5 MPM samples does not correlate with T/η (except at the lowest temperatures). Preliminary studies show that T_2 actually decreases with increasing temperature for samples of concentration >10 MPM. This agrees well with previous continuous-wave T_2 studies on solutions of intermediate concentration (6–15 MPM)[18] and has been attributed to the onset of a spin–orbit relaxation mechanism. Even at 10 MPM concentratons, T_1 and T_2 are not equal at low temperatures, though they converge at lower temperatures than in 5 MPM samples. T_1 and T_2 are probably equal at concentrations higher than the nonmetal–metal transition (15 MPM). Further studies are needed in this concentration range to determine the exact nature of the relaxation mechanisms in this intermediate regime.

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