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^{205}Tl, ^{14}N, and ^{1}H NMR Studies of Thallium Salt Solutions in Liquid Methylamine

K. R. Metz,[*†] **J. F. Hinton, and T. L. Goforth**[‡]

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701 *(Received: October 29, 1984)*

^{205}Tl, ^{14}N, and ^{1}H NMR techniques were used to investigate thallium(I) salt solutions in liquid methylamine from 1 mM to 7.2 M. Essentially complete association was observed between Tl^+ and NO_3^- or HCO_2^- at 1 mM. Thermodynamic parameters for the ion association of Tl^+ and ClO_4^- were found to be $\Delta H_A = +10.3 \pm 4$ kcal mol^{-1} and $\Delta S_A = +50 \pm 15$ eu. Due to its lower dielectric constant, more extensive ion association occurs in liquid methylamine than in liquid ammonia. Ion pairs in liquid methylamine appear to be of the solvent-shared or solvent-separated type, as opposed to contact ion pairs previously found to exist in liquid ammonia. Relative anion and solvent donicities, as determined from ^{205}Tl chemical shifts, were strongly temperature dependent. At high concentrations, no evidence for a structural rearrangement of the solvated $TlNO_3$ species was found. However, the anomalous behavior of the ^{205}Tl chemical shift observed at $TlNO_3$ concentrations below 0.5 M may result from such rearrangements. Two methylamine molecules were determined to be the minimum number necessary to "saturate" the associated ionic species at very high concentrations.

Introduction

Due to its importance in the development of both experimental and theoretical chemistry, the nature of the solution state has been the subject of many research investigations. Historically, major advances in the understanding of ion–ion and ion–solvent interactions resulted from studies of the electrical properties of ionic solutions. Conductance techniques, in particular, occupied a central role in the investigation of ionic solutions at low concentrations. However, the results obtained from traditional conductance experiments are averaged over all of the conducting species in solution and often fail to provide sufficiently detailed information.

With the application of spectroscopic techniques, it became possible to examine individual solute species or types of interactions. NMR spectroscopy, one of the most powerful of these techniques, unfortunately suffers from poor inherent sensitivity for all but a few nuclides, a property which severely limited its value for studies of solution chemistry prior to the Fourier transform "revolution" of the early 1970s. When Fourier transform NMR is employed in combination with an inherently sensitive nuclide, it is now possible to study solute concentrations ranging from below 1 mM to the neat solute itself.

Recently, solutions of thallium salts in liquid ammonia have been investigated by using ^{1}H, ^{14}N, and ^{205}Tl NMR methods.[1,2] The excellent NMR receptivity, high natural abundance, and relatively fast relaxation rate of ^{205}Tl enable its observation in quite dilute samples, while the extraordinary solubilities of thallium salts in liquid ammonia allow studies of concentrations approaching 10 M. We report here the results of a parallel investigation of thallium salts in liquid methylamine. The solubilities of many salts in this solvent resemble those in liquid ammonia,[3,4] enabling studies of solutions at high concentrations. In spite of its structural similarity to liquid ammonia, however, liquid methylamine possesses greater donicity[5,6] and a significantly lower dielectric constant.[7,8] This investigation was conducted in order to examine the effects of these differences on solvation and ion association in these two solvents.

Experimental Section

Thallium(I) nitrate was Fisher purified grade which was recrystallized several times from conductivity water. The salt melted sharply at 206 °C after drying under vacuum for 16 h at 110 °C. Thallium(I) perchlorate was synthesized from thallium(I) carbonate and perchloric acid, purified by repeated recrystallization from conductivity water, and dried under vacuum for 12 h at 100 °C. Thallium(I) formate was prepared from thallium(I) carbonate and formic acid, followed by multiple recrystallization from methanol and vacuum drying. The melting range was found to be 98–100 °C, in agreement with literature values.[9,10] Infrared spectra showed no evidence of residual carbonate in the perchlorate and formate salts.[11,12]

Solutions of thallium(I) salts in liquid methylamine were prepared under anhydrous conditions using vacuum line techniques. Immediately prior to use, each 5-mm (o.d.) medium-wall NMR tube (Wilmad 503-PS) was flamed with a hand torch for 15 min under continuous evacuation and then cooled. A thallium salt was weighed into the tube under a dry nitrogen atmosphere, and the tube was reattached to the vacuum line. Liquid methylamine (Matheson anhydrous) which had been dried over metallic sodium and degassed was distilled from the sodium through an efficient trap and condensed directly into the NMR tube. The sample was then frozen with liquid air, sealed under vacuum, and warmed to 45 °C for at least 15 min prior to use. No sample tubes burst under these conditions.

The molar concentration of each sample was calculated from the amount of thallium salt and the solution volume as determined from the height of the solution in the tube. For concentrations below 0.025 M, where weighing errors were significant, the quantity of the salt was determined by slowly vaporizing the amine and diluting the solid residue with water to a known volume, forming a solution containing 15–35 ppm Tl(I). The actual concentration was then measured against known standards by flame-emission spectroscopy at 377.57 nm using a Varian Techtron Model 1200 spectrophotometer.

Calculation of the methylamine:salt mole ratio required knowledge of the amount of methylamine in each solution. This was determined by subtracting the weight of thallium salt from the total solution weight as measured by the decrease in tube weight following removal of the solution. In the worst case, less than 1% of the total methylamine was present as vapor inside the sample tube, so corrections for solvent vaporization were not applied.

All proton chemical shifts were determined with respect to Me_4Si by a Varian EM-360 spectrometer. Pulsed Fourier transform ^{205}Tl and ^{14}N NMR spectra were measured at 2.114 T with a modified Bruker HFX-90 spectrometer which included

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[†] Present address: Department of Radiology, The Pennsylvania State University College of Medicine, The M. S. Hershey Medical Center, Hershey, PA 17033.

[‡] Present address: Department of Physics, Oklahoma State University, Stillwater, OK 74078.

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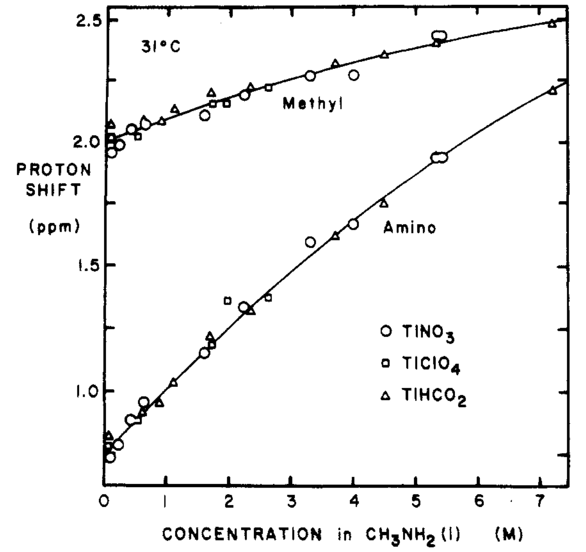

Figure 1. Liquid methylamine proton chemical shifts as a function of thallium salt concentration at 31 °C.

a Nicolet NMR-80 computer system, Schomandl frequency synthesizer, and ENI 3100L rf power amplifier. Sample temperature was controlled by a Bruker B-ST 100/700 temperature control unit.

All resonance frequencies reported here are referenced to the protons of Me_4Si at 90 MHz. The basic NMR frequencies were 51.9154 MHz for ^{205}Tl and 6.49 MHz for ^{14}N. ^{205}Tl chemical shifts are referenced to the infinite-dilution resonance frequency of aqueous $^{205}Tl(I)$ at 25 °C. ^{14}N shifts are referenced to the $^{14}NO_3^-$ resonance line in a saturated, nonacidified, aqueous solution of NH_4NO_3. All chemical shifts are corrected for the concentration dependence of the solvent proton resonance used for field-frequency locking. Shifts to high frequency have been assigned positive values.

^{14}N line widths at half-height were determined by use of spinning samples. The magnetic field homogeneity was optimized just prior to line width measurements and did not degrade noticeably during data acquisition. The quality of the field was shown to be suitable for line width studies, since widths measured for ^{14}N lines in the spectrum of aqueous NH_4NO_3 proved smaller than literature values[13,14] by several hertz.[2] The total ^{14}N line broadening induced by magnetic field inhomogeneities is not believed to exceed about 1 Hz.

Results and Discussion

Of the three thallium(I) salts investigated, the formate proved most soluble, followed by the nitrate and perchlorate. Thallium(I) formate concentrations in excess of 7 M were achieved at room temperature, while even the perchlorate was soluble to the extent of about 3 M. Figure 1 shows the dependence of the methylamine solvent proton chemical shift on thallium(I) salt concentration. Spectra from all solutions exhibited only two peaks at 60 MHz, demonstrating that microscopic solvent exchange rates were rapid on this time scale. As the solute concentration increases, the relative amount of solvent bound to Tl(I) increases, resulting in the observed shifts to high frequency (low field). Since Tl(I) presumably coordinates with the nitrogen lone electron pair in methylamine, the amino proton shift is more sensitive to the salt concentration than is the methyl proton shift. In contrast to the proton shift in liquid ammonia,[1] no anion dependence is observed. This suggests that the anion is probably less closely associated with the cation in liquid methylamine than in liquid ammonia over this concentration range.

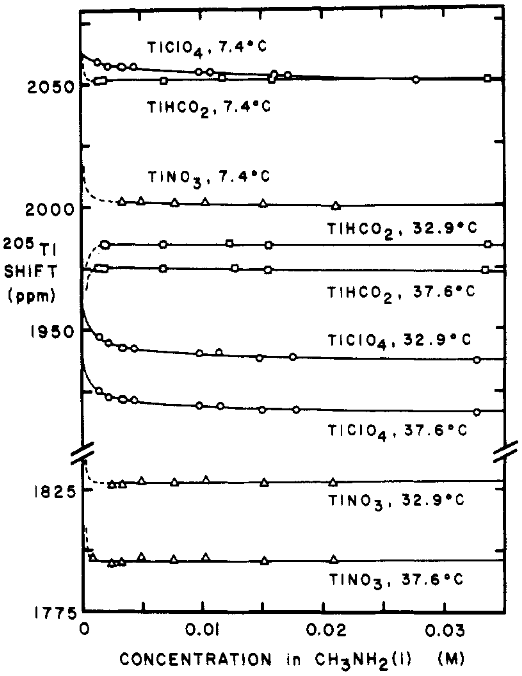

Figure 2. Dependence of the ^{205}Tl NMR chemical shift on thallium salt concentration in liquid methylamine at three representative temperatures.

TABLE I: Ion Association Parameters for Thallium(I) Salts in Liquid Methylamine

temp, °C	dielectric constant[a]	δ_f, ppm	δ_{ip}, ppm ClO_4^-	NO_3^-	HCO_2^-	$10^{-2}K_A$, M^{-1} [b]
7.4	10.4	2063 ± 2	2040 ± 4	2002	2051	7 ± 3
13.9	10.0	2037 ± 2	2018 ± 4	1961	2033	13 ± 7
24.7	9.4	1994 ± 3	1970 ± 3	1886	2004	21 ± 7
32.9	8.9	1961 ± 4	1930 ± 3	1828	1985	33 ± 8
37.6	8.7	1941 ± 4	1911 ± 2	1796	1975	48 ± 20

[a] Dielectric constant calculated from a linear plot of ln D against temperature by using data from ref 8. [b] $Tl^+ClO_4^-$.

^{205}Tl chemical shifts were determined for solutions of all three salts, and results for low concentrations at several temperatures are shown in Figure 2. The shifts for formate and nitrate solutions are quite different and essentially independent of concentration down to about 1 mM over the entire temperature range. This behavior would be consistent with very strong ion association in one solution and either complete association or dissociation in the other. Fortunately, the plots for thallium(I) perchlorate solutions exhibit sufficient curvature to demonstrate unambiguously that the shift at infinite dilution does not correspond to the experimental shifts of either the formate or nitrate solutions. Therefore, both of these salts must be highly associated over the concentration range of Figure 2.

By means of a fitting procedure, it proved possible to estimate the infinite-dilution free ion shift (δ_f), the shift of the ion pair (δ_{ip}), and the ion-pair association constant (K_A) for thallium(I) perchlorate in liquid methylamine. Briefly, the method employs initial estimates of δ_f and δ_{ip} to calculate a preliminary value of K_A from each experimental data point. The mean of these K_A values is then used to generate a theoretical chemical shift at each experimental concentration. In an iterative procedure which minimizes the deviations between theoretical and experimental shifts, the best-fit values of δ_f, δ_{ip}, and K_A are obtained. This method, which has been described in detail previously,[15] was used to generate the solid curves drawn through the perchlorate data of Figure 2.

Numerical results of the analysis are presented in Table I. The experimental chemical shifts of the most dilute nitrate and formate solutions are also tabulated as estimates of δ_{ip} for these salts. Literature values for the K_A of thallium(I) perchlorate in liquid methylamine are not available for comparison. However, the

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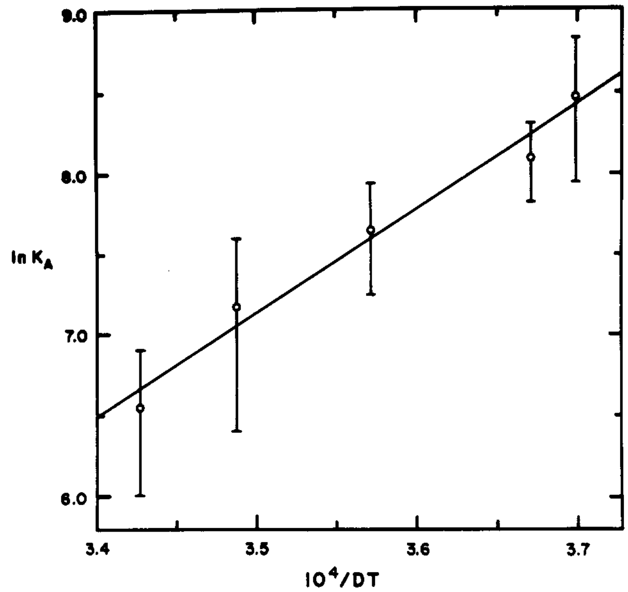

Figure 3. Plot of ln K_A against $(DT)^{-1}$ for thallium(I) perchlorate in liquid methylamine.

values in Table I are in general agreement with results for thallium salts in related solvents. For example, thallium(I) perchlorate exhibits $K_A = 1750 \pm 200$ in pyridine at 24 °C.[15] In *n*-butylamine at 24 °C, the K_A values for thallium(I) nitrate and dimethylthallium(I) nitrate are 1670 ± 500 and 3190 ± 300, respectively.[15] Thallium(I) nitrate possesses $K_A = 1200 \pm 200$ in liquid ammonia at 25 °C,[1] while Figure 2 shows that K_A for this salt is too large to measure in liquid methylamine. In contrast, the K_A for thallium(I) perchlorate in liquid ammonia is too small to measure by NMR methods. The increase in thallium salt association constant in liquid methylamine as compared with that in liquid ammonia is attributable to the significantly lower dielectric constant of the former.[8] A similar trend in K_A has recently been observed for the association of cesium salts and crown complexes in these solvents.[16-18]

Using the criteria of Fuoss and Accascinia,[19] Khazaeli et al.[16] have pointed out that triple ion formation is potentially significant in liquid methylamine, particularly at salt concentrations greater than about 0.5 mM. Indeed, these investigators observed specific manifestations of multiple ion species in plots of ^{133}Cs chemical shift vs. concentration in liquid methylamine. We have not included triple ion formation in the model leading to the results of Table I primarily because good fits to the experimental data were achieved without this assumption. In addition, the uncertainty in the data was sufficiently large that the effect of a few percent triple ions on the results would be negligible. Finally, the addition of triple ions to the model greatly complicates the analysis and requires various simplifying assumptions in order to obtain numerical results.[16]

Theoretical expressions for K_A based on the sphere-in-a-continuum model have been derived independently by Eigen,[20] Denison and Ramsey,[21] and Fuoss.[22] All of these equations predict that ln K_A should be inversely proportional to both temperature and solvent dielectric constant D. Figure 3 shows a plot of ln K_A against $(DT)^{-1}$ using the thallium(I) perchlorate data of Table I. This plot is indeed linear and demonstrates that the nearly 20% decrease in solvent dielectric constant over this range is responsible for the observed K_A increase in spite of the opposing effect of increasing temperature.

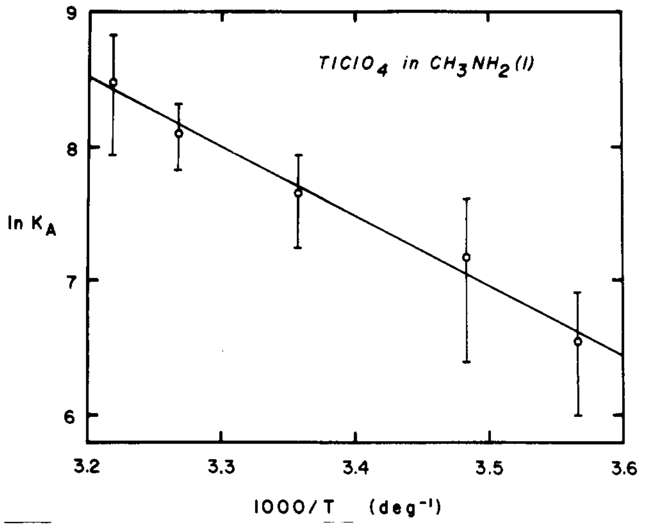

Figure 4. van't Hoff plot for thallium(I) perchlorate in liquid methylamine using the data of Table I.

TABLE II: Infinite-Dilution ^{205}Tl$^+$ Chemical Shifts in Various Solvents at 2.114 T and 25 °C[a]

solvent	donor number[b]	frequency, MHz	δ_f, ppm
pyrrole	13.1	51.895 57	−382.8
water	18.0	51.915 45	0.0
N,*N*-dimethylformamide	26.6	51.9230	145
N-methylformamide	24	51.923 83	161.3
N-ethylformamide		51.931 33	305.8
dimethyl sulfoxide	29.8	51.934 13	359.7
hexamethylphosphoramide	38.8	51.941 46	500.7
N,*N*-diethylacetamide		51.943 00	530.4
pyridine	33.1	51.956 13	783.2
liquid ammonia		52.009 61	1813.0
n-butylamine	ca. 56	52.015 30	1922.5
liquid methylamine		52.018 93[c]	1992.4[c]

[a] References 1 and 15. [b] References 15 and 27. [c] This work.

Thermodynamic parameters for ion association in thallium(I) perchlorate solutions were determined from a linear least-squares fit to a plot of ln K_A against T^{-1} (Figure 4). Calculated values are $\Delta H_A = +10.3 \pm 4$ kcal mol^{-1} and $\Delta S_A = +50 \pm 15$ eu. Both the association enthalpy and entropy agree in sign and, roughly, in magnitude with corresponding values of +6.5 kcal mol^{-1} and +36 eu determined previously for thallium(I) nitrate in liquid ammonia.[1] Positive ΔH_A and ΔS_A values have also been measured recently for ion association of cesium iodide and tetraphenylborate in liquid methylamine.[16] In view of the high donicity of this solvent,[3,4] the replacement of one or more solvent molecules by a perchlorate anion might be expected to show endothermic character. The release of methylamine from the solvation spheres of the cation and, possibly, the anion during ion pairing results in a large net entropy increase despite the greater constraints placed upon the ions themselves. It is this favorable entropy change which drives the equilibrium toward associated species at room temperature.

As suggested by Ramsey,[23,24] nuclear magnetic shielding can be understood primarily in terms of diamagnetic and paramagnetic contributions, although additional perturbations may occur in special cases. The ^{205}Tl chemical shift is known to depend almost exclusively on paramagnetic effects, which accounts for the extreme dependence of the shift of this nuclide on its local environment.[25] Furthermore, the dominance of the paramagnetic

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TABLE III: Best-Fit Parameters Resulting from a Linear Least-Squares Analysis of the Chemical Shift vs. Temperature Data of Figure 5

	liquid ammonia[a]		liquid methylamine[b]			
parameter	δ_f	$\delta_{ip}(NO_3^-)$	δ_f	$\delta_{ip}(HCO_2^-)$	$\delta_{ip}(ClO_4^-)$	$\delta_{ip}(NO_3^-)$
intercept, ppm	3253	3557	3190	2769	3249	3920
slope, ppm/K	−4.829	−6.100	−4.015	−2.562	−4.300	−6.832

[a] Reference 1. [b] This work.

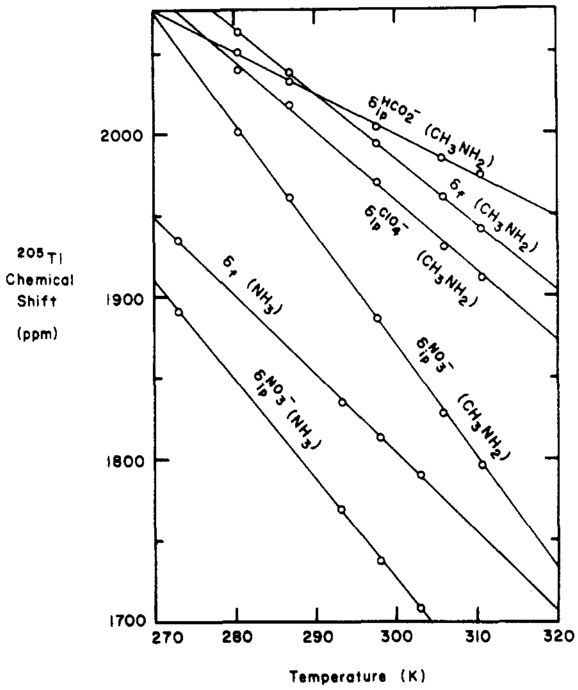

Figure 5. Dependence of free-ion and ion-pair ^{205}Tl chemical shifts on temperature for various anions in liquid ammonia and liquid methylamine. Data for liquid ammonia solutions are from ref 1.

shielding contribution induces ^{205}Tl shifts to high frequency with increasing electronic overlap between the nuclide and neighboring species. Table II lists infinite-dilution resonance frequencies for ^{205}Tl(I) in a range of solvents having widely differing donicities. Not only is the ^{205}Tl chemical shift range extraordinarily large but a strong correlation exists between the shift and the donor number[27,28] of the solvent. At 25 °C, liquid methylamine appears to donate electron density to Tl(I) more efficiently than any other solvent investigated to date.

As the temperature and thermal activity of the solvent and ions decrease, the electronic interactions between them increase. For a nuclide such as ^{205}Tl, this produces high-frequency shifts at lower temperatures (Figure 5). The change in chemical shift with temperature is found to be linear for δ_f and δ_{ip} in all cases. This linear dependence was previously observed for thallium(I) nitrate in liquid ammonia,[1] as reproduced in Figure 5, and has more recently been reported for dialkylthallium(I) solutions[26] and for solutions of cesium salts in liquid amines.[16] No quantitative explanation for the observed linearity is yet available. However, the δ_{ip} plots of Figure 5 qualitatively argue that the nature of the ion pair remains unchanged over the temperature range investigated. A transition from ion pairs to higher order ion aggregates, for example, would be expected to cause significant curvature in the plot.

Over the temperature range studied, the ^{205}Tl resonance signal in methylamine solutions containing formate generally occurs at higher frequencies than signals from solutions containing the other anions. This suggests that, in liquid methylamine at these temperatures, formate possesses the greatest donicity, followed by perchlorate and nitrate, respectively. According to Figure 2, $TlClO_4$ signals appear to high frequencies of the signals from $TlHCO_2$ solutions at 7.4 °C, in apparent contradiction to the relative anion donicities. However, the formate salt is highly associated at this temperature while the perchlorate K_A is approximately 700 M^{-1}. Therefore, the experimental shifts of Figure 2 result mainly from associated species of $TlHCO_2$ but largely free Tl(I) ions in $TlClO_4$ solutions at 7.4 °C. Figure 5 demonstrates that the relative order of donicity is quite temperature dependent, and just below 278 K, for example, the order becomes $ClO_4^- > HCO_2^- > NO_3^-$. Values for the slopes and intercepts of the plots in Figure 5 are given in Table III and show that extrapolation to very low temperatures even suggests the donicity order $NO_3^- > ClO_4^- > HCO_2^-$. The results in Table III help to conceptually separate the temperature-dependent shift contributions from those which do not depend on temperature. For example, the δ_f intercepts in both solvents are similar, but the slopes clearly show that the donicities of these amines diverge with increasing temperature. The liquid ammonia donicity decreases most rapidly, possibly due in part to its smaller molecular weight and greater mobility. Another consequence of the unequal slopes given in Table III is that certain temperatures produce identical values for δ_f and δ_{ip}. One such point occurs at about 289 K for $TlHCO_2$ in liquid methylamine. At this temperature it would not be possible to measure K_A for $TlHCO_2$ by using the methods employed here since the chemical shift would be independent of concentration.

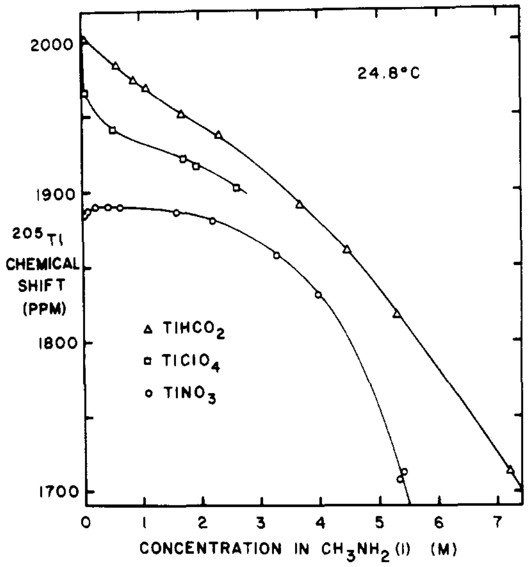

Figure 6. ^{205}Tl chemical shifts for thallium salts in liquid methylamine at high concentrations.

^{205}Tl chemical shifts were determined for high concentrations of all three salts in liquid methylamine (Figure 6). Resonance frequencies are found to decrease rapidly with increasing concentration as ions replace solvent molecules near Tl(I). However, the behavior of the shift for $TlNO_3$ concentrations below about 0.5 M is unexpectedly quite different from that observed for the other salts. Several explanations for this anomaly may be proposed. Assuming that Tl(I) exists predominantly in the form of ion pairs at the lowest concentrations studied, the rapid formation of ion triples or other multiple ion aggregates with increasing concentration might lead to the observed shift to high frequency. Alternatively, this shift may result from transitions between solvent-separated, solvent-shared, and contact ion pairs. Finally, a fundamental change in the structure of the associated species

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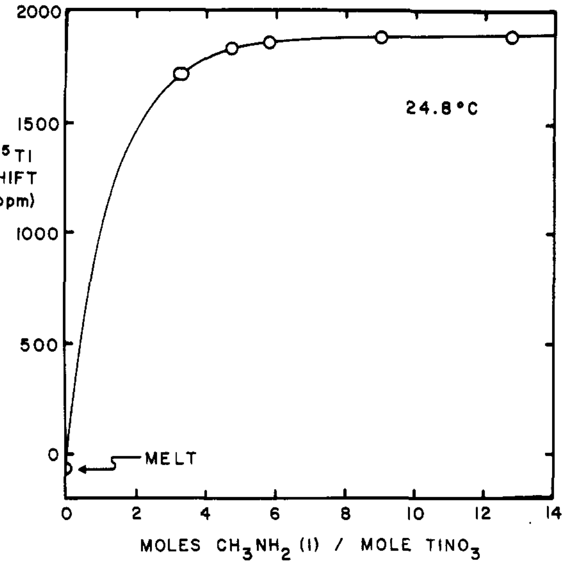

Figure 7. Plot of ^{205}Tl chemical shift against mole ratio of methylamine to thallium(I) nitrate at 24.8 °C.

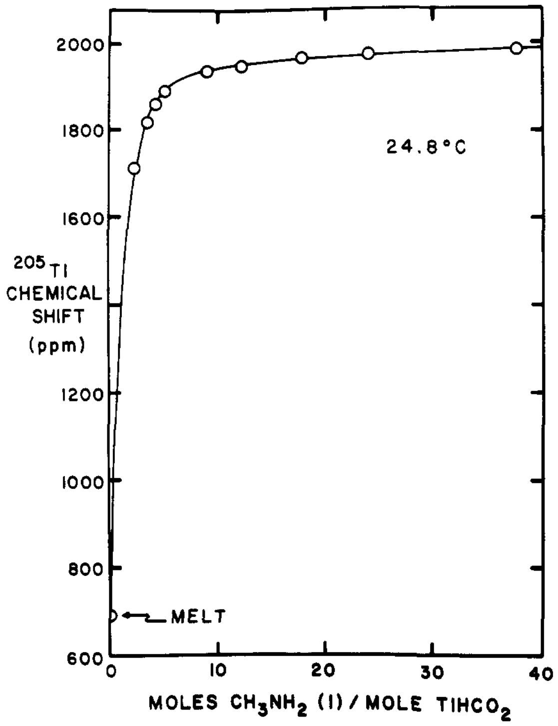

Figure 8. Plot of ^{205}Tl chemical shift against mole ratio of methylamine to thallium(I) formate at 24.8 °C.

may occur with increasing concentration. Such a structural change has been reported for the ammoniated $Tl^+NO_3^-$ contact ion pair as the number of solvating NH_3 molecules is reduced from three to two.[2,29,30] However, thallium(I) nitrate solutions below 0.5 M in liquid methylamine contain at least 40 solvent molecules per simple ion pair, so the probability of an analogous structural change in this case seems quite uncertain. At the present time, the source of the $TlNO_3$ shift anomaly below 0.5 M in Figure 6 remains unclear.

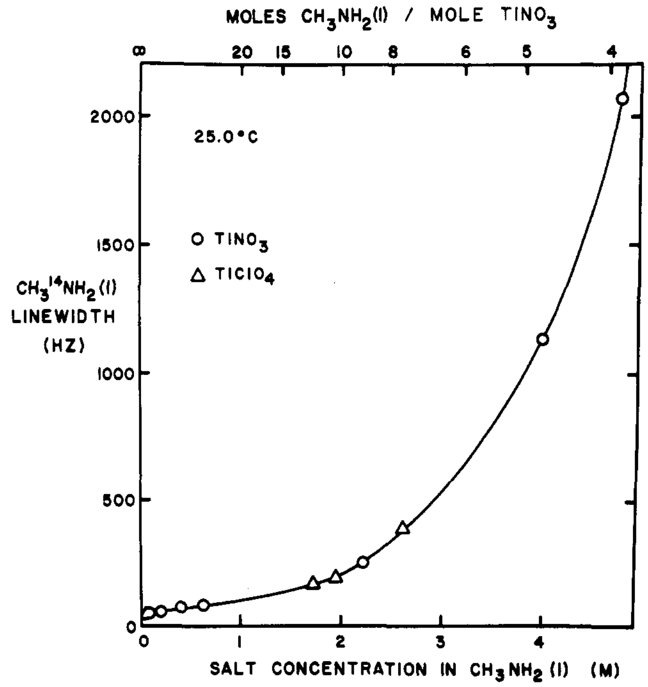

Figure 9. Dependence of the liquid methylamine ^{14}N line width on thallium(I) salt concentration at 25.0 °C.

As the concentrations of $TlHCO_2$ and $TlNO_3$ approach their maximum limits, the corresponding ^{205}Tl chemical shifts shown in Figure 6 decrease dramatically. This suggests the onset of incomplete solvation of the solute and may be examined by using plots of ^{205}Tl shift against solvent:solute mole ratio (Figures 7 and 8). In order to define a lower limit to these plots, temperature-dependent chemical shift data for $TlNO_3$[31] and $TlHCO_2$[32] melts were extrapolated to 24.8 °C. This procedure has been used previously[1] to estimate ^{205}Tl chemical shifts in hypothetical thallium salt solutions completely devoid of solvent. Figures 7 and 8 clearly show that the addition of liquid methylamine to pure $TlNO_3$ or $TlHCO_2$ initially induces a large ^{205}Tl chemical shift to high frequency. However, as a certain critical mole ratio is reached, Tl(I) apparently becomes "saturated" with solvent, and little further change in the shift occurs. Unfortunately, the $TlNO_3$ and $TlHCO_2$ solubilities prevent experimental definition of the curves at mole ratios between 0 and about 3. It is nevertheless clear that any reasonable curve drawn through the $TlNO_3$ or $TlHCO_2$ data contains two approximately linear regions which, when extrapolated, intersect at a mole ratio near 2 (and certainly less than 3). This may be compared with the value of 3 determined previously for the solvation number of the $Tl^+NO_3^-$ contact ion pair in liquid ammonia.[1] In acetonitrile/amine solutions, the primary solvation sphere of free Li(I) ion has been reported to contain four ammonia, but only three methylamine, molecules.[33] Thus, it appears that methylamine solvation numbers may be consistently smaller than those of ammonia. This probably results in part from steric crowding of the methyl groups in the solvation sphere. Furthermore, methylamine, with its greater donicity, probably cancels the cation charge more effectively than ammonia and decreases the tendency toward high solvation numbers.

Figure 9 shows the ^{14}N line width of liquid methylamine as a function of thallium(I) salt concentration. The line width increases dramatically, but smoothly, at high salt concentrations, suggesting slow exchange of solvent molecules about the solute. The width is independent of anion, which is also consistent with broadening due to slow solvent exchange. The methylamine ^{14}N chemical shift was found to be −369.0 ± 5.8 ppm and was independent of both anion and concentration.

The $^{14}NO_3^-$ line of $TlNO_3$ in liquid methylamine is quite narrow in dilute solutions but broadens at high salt concentrations (Figure 10). In contrast to similar data using liquid ammonia as the solvent,[2] the increase in line width with increasing concentration appears to be quite smooth and lacks singularities attributable to structural rearrangements in the associated solute species. In addition, the $^{14}NO_3^-$ chemical shift (−2.5 ± 0.5 ppm) was found

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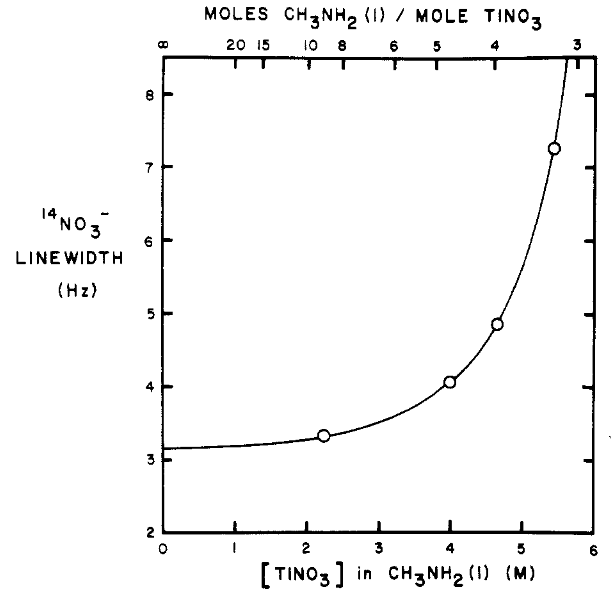

Figure 10. $^{14}NO_3^-$ line width as a function of $TlNO_3$ concentration in liquid methylamine.

to be constant over this concentration range, unlike the shift in liquid ammonia solutions which exhibited behavior consistent with a fundamental change in $Tl^+NO_3^-$ ion pair structure at a mole ratio near 3.[2] Overall, the ^{14}N data shown here provide no evidence for structural rearrangements of the associated $TlNO_3$ species in liquid methylamine over this concentration range. As suggested by the ^{205}Tl shifts of Figure 6, rearrangements might occur at concentrations below 0.5 M where accurate ^{14}N line width and chemical shift measurements were not possible due to the low inherent sensitivity of this nuclide. Structural changes might also be observable at solvent:solute mole ratios below 3:1 if matrix isolation techniques are used.

Previous studies of various salts in liquid ammonia have demonstrated the presence of mainly contact ion pairs.[1,2,34-36] The lower dielectric constant of liquid methylamine would be expected to promote contact ion pair formation in this solvent, and the large magnitudes of ΔH_A and ΔS_A determined for $TlClO_4$ are consistent with contact ion pairs. However, several other lines of evidence suggest the existence of solvent-shared or solvent-separated ion pairs. In contrast to results observed in liquid ammonia,[1] the methylamine proton chemical shifts of Figure 1 are anion independent, as expected if the anion interacts only weakly with the Tl(I) ion to which solvent molecules are bound. In addition, while Table III intercept values for δ_f (NH_3) and δ_f (CH_3NH_2) are similar, the intercept values of δ_{ip} (NO_3^-) in the two solvents are substantially different, suggesting differences in the nature of the associated species. As discussed above, a rearrangement of the $TlNO_3$ solvate at high concentrations in liquid methylamine is not supported by the ^{14}N data. However, a change in the geometry of a solvent-shared or solvent-separated ion pair might alter the ^{14}N shift and line width only very slightly. Alternatively, the ^{205}Tl chemical shift anomaly for $TlNO_3$ below about 0.5 M may result from a transition between solvent-separated, solvent-shared, and contact ion pairs. In this case, contact ion pairs would probably exist over the concentration range of the ^{14}N shift and line width measurements, and these data would indeed support the absence of $TlNO_3$ rearrangements up to 5.5 M.

The overall weight of evidence suggests the presence of solvent-shared or solvent-separated ion pairs for thallium(I) salts in liquid methylamine. Similar conclusions have been reported for other salts in this solvent.[16,37,38] The high methylamine donicity should inhibit the replacement of a solvent molecule in the primary solvation sphere by an anion. This effect apparently overcomes the tendency toward formation of contact ion pairs due to the low dielectric constant of this solvent.

Conclusions

By comparing relative ion solvation and association characteristics in liquid ammonia and liquid methylamine, the lower dielectric constant of the latter is observed to markedly increase the degree of association. While this result is hardly surprising in itself, the overall bulk solubilities of the salts investigated are found to be only slightly lower in liquid methylamine. This attests to the strength of the interaction between the associated species and the methylamine solvent molecules. Additional evidence for strong solvation may be found in the dramatic decrease in solvent exchange rates at high concentrations as demonstrated by the $CH_3{}^{14}NH_2$ line widths. Furthermore, it has been shown that approximately two methylamine molecules are sufficient to completely solvate the associated species at high concentrations, whereas three molecules are necessary in liquid ammonia. This increased solvating power accounts for the excellent solubilities of the salts studied, despite the rather low dielectric constant of the solvent.

The strong cation solvation which permits the high solubilities discussed above also appears to inhibit the formation of contact ion pairs in liquid methylamine. This result is somewhat surprising, especially since contact ion pairs are believed to exist in liquid ammonia, which has a much larger dielectric constant. However, the high donicity of methylamine might be expected to oppose closely associated ion pairs and is the dominant factor in this case.

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Registry No. $TlNO_3$, 10102-45-1; $TlHCO_2$, 992-98-3; $TlClO_4$, 13453-40-2.

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