Investigation of Lithium Chloride/Ambient-Temperature 1-Methyl-3-ethylimidazolium Chloride−Aluminum Chloride Ionic Liquids. 1. Ion Interactions in a Neutral Tetrachloroaluminate Melt

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Ion interactions in a neutral ambient-temperature tetrachloroaluminate melt were studied using FTIR and NMR techniques at different lithium concentrations. The effect of lithium on the imidazolium cation is shown to be very small, but it strongly affects the $AlCl_4^-$ anion, leading to the perturbation of the T_d symmetry and the appearance of extra absorption peaks due to lithium interactions. The interactions are strong in the LiCl−ImCl−$AlCl_3$ melt, and the absorbances of the related vibration peaks are linearly dependent on the lithium concentration. Under high Li^+ concentrations, an obvious change in the conductivity, density, viscosity, and ^7Li NMR shifts is observed when the mole ratio of $AlCl_4^-$:Li^+ is less than 3.5:1 to 5:1, depending on different measuring techniques. A model with the formation of a network-like structure of Li^+/$AlCl_4^-$ under high Li^+ concentrations was proposed to explain the above changes.

Introduction

The lithium chloride/ambient-temperature 1-methyl-3-ethylimidazolium chloride−aluminium chloride ionic liquid system was recently shown to provide a promising medium for advanced lithium battery applications as a result of its inertness toward lithium, satisfactory conductivity, and good solubility of lithium chloride.[1,2] However, rather large changes in its physical properties have been observed in the melts with high lithium content.[1] This has a strong implication for battery applications, and thus we initiated the present detailed study of the structure of the 1-methyl-3-ethylimidazolium chloride−aluminium chloride melt with the addition of a large amount of lithium chloride up to the saturation of the melt at about 2.8 mol of $LiAlCl_4$/kg melt.

The basic structure of the chloroaluminate melt has been studied using Raman,[3] IR,[4,5] NMR,[6−9] and electrochemical techniques.[10,11] To assist in the interpretation and assignment of the IR and Raman absorption peaks, solid chloroaluminate compounds with well-characterized structures were used for comparison.[3−5] NMR techniques were used to study the ion interactions,[6−9] and electrochemical techniques were used for the determination of the equilibrium constant.[10,11]

Wilkes and co-workers extensively studied the physical properties,[12] NMR,[7,8] and electrochemical properties[11] of this melt. However, very little work has been done on melts with high concentrations of lithium chloride. The chemistry of chloroaluminate melts is strongly influenced by the acid/base properties of the melts. Neutralization occurs at equimolar concentrations of $AlCl_3$ and 1-methyl-3-ethylimidazolium chloride, and an excess of $AlCl_3$ or chloride in the melt would introduce acidic or basic properties, respectively.

Table 1. Infrared Frequencies of $LiAlCl_4$, ImCl, ImCl−$AlCl_3$, and ImCl−$AlCl_3$−LiCl Melts[a]

ImCl	ImCl-$AlCl_3$ melt (1:1)	ImCl−$AlCl_3$−LiCl melt (1:1.51:0.51)	$LiAlCl_4$[b] (200 °C)	$LiAl_2Cl_7$[b] (200 °C)
1170.9 (vs)	1166.6 (vs)	1167.3 (vs)		
1121.2 (ms)	1108.1 (ms)	1108.3 (ms)		
1090.1 (ms)	1088.0 (ms)	1087.8 (ms)		
1030.7 (w)	1031.7 (w)	1031.4 (w)		
960.1 (ms)	955.6 (ms)	958.6 (ms)		
835.8 (s)	833.3 (s)	832.4 (s)		
806.4 (vw)				
	802.6 (vw)	802.2 (s)	802 (ms)	791 (w)
759.4 (s)				
	743.6 (s)	743.4 (s)		
701.5 (ms)	700.7 (ms)	700.4 (ms)		
		679.2 (ms sh)	681 (ms)	683 (w)
647.9 (s)	646.6 (s)	647.2 (s)		
621.1 (s)	620.8 (s)	620.7 (s)		
597.5 (w)	596.7 (w)	567.5 (ms, sh)	550 (vw, sh)	570 (s, sh)
			518 (vw, sh)	
	488.6 (vs)	491.7 (vs, b)	475 (vs)	514 (vs)
		440.7 (ms, sh)		442 (w, sh)
			385 (vw)	381 (m)
			355 (vw, sh)	334 (w)
			300 (s)	305 (w, sh)
			170 (m)	168 (m)

[a] Symbols given in parentheses: vs = very strong, s = strong, ms = medium strong, w = weak, vw = very weak; sh = shoulder, b = broad. [b] Data taken from ref 5. (see also refs 16 and 17 for oxide absorption peaks).

The addition of large amounts of LiCl would lead to the formation of a basic melt and give rise to high viscosity. Thus, a lithium-enriched melt has to be neutralized with $AlCl_3$. This in turn would influence the structure of the melt and its physical properties. The present work, using FTIR and NMR techniques,

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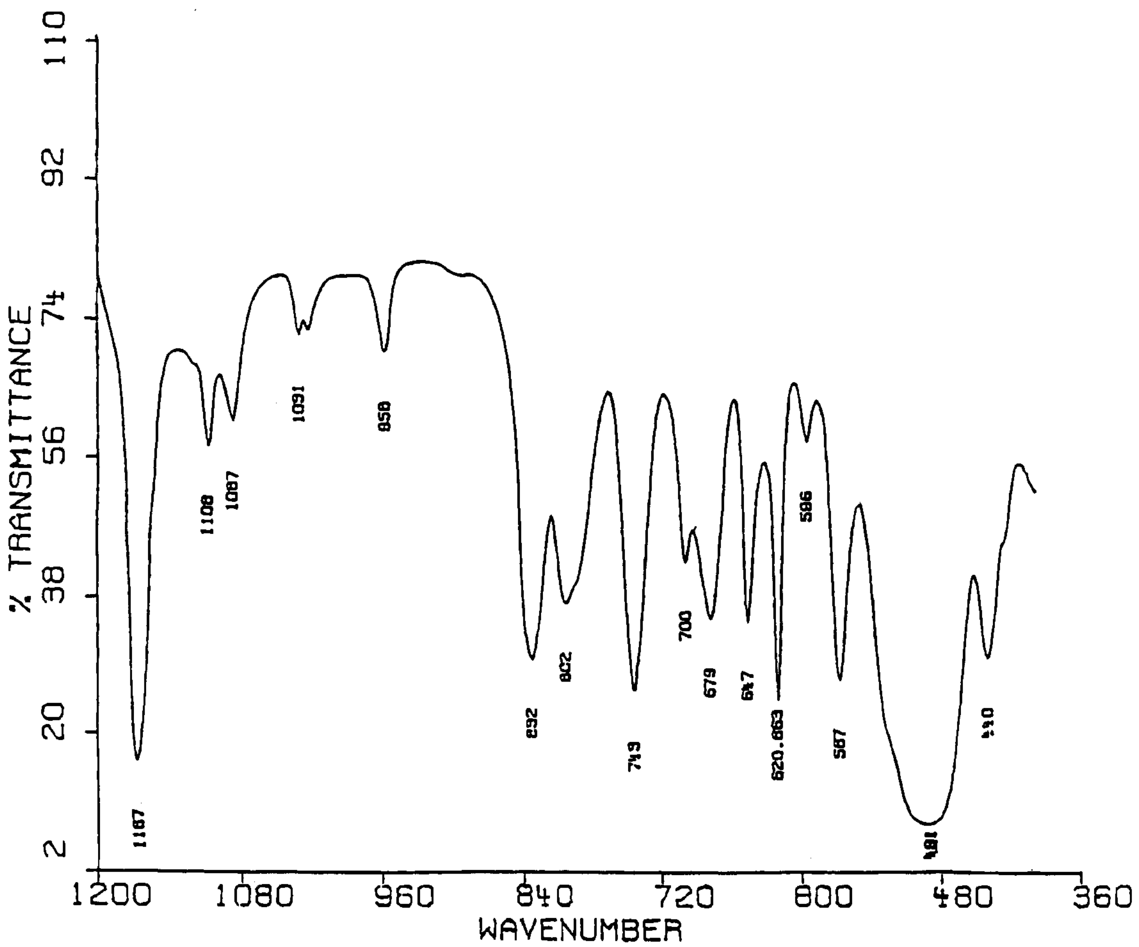
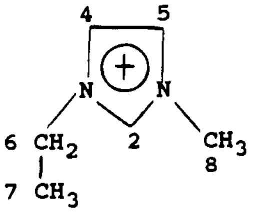


Figure 1. Infrared spectrum of neutral MeEtImAlCl$_4$ melt with LiAlCl$_4$. AlCl$_4^-$:Li$^+$ = 3.6:1.

Table 2. Assignments of ^{13}C NMR Resonances for the ImCl−AlCl$_3$ Melts[a]

ImCl−AlCl$_3$ (1:1.5)	ImCl−AlCl$_3$ (1:1)	ImCl−AlCl$_3$ (1:0.66)	ImCl−AlCl$_3$−LiCl (1:1.28:0.28)	assgnt[b]
134.280	134.983	136.434	134.677	C-2
124.058	123.905	123.783	123.905	C-4
122.377	122.209	122.270	122.224	C-5
45.596	45.519	45.137	45.504	C-6
36.947	36.993	36.611	36.947	C-7
15.235	15.296	15.510	15.250	C-8

[a] The resolution is 1.04 Hz (0.0153 ppm). [b] The numbers given under the assignment refer to the position of carbon in the imidazolium cation as follows:



will focus on how lithium interacts with a melt when LiAlCl$_4$ is added progressively to a high concentration. The changes in the phenomenological physical properties are monitored under different lithium concentrations, and a model is proposed to explain the trends observed.

Experimental Section

The purification of AlCl$_3$ and the preparation of 1-methyl-3-ethylimidazolium chloride and the chloroaluminate melt were described earlier.[12−14] The preparation of the melt for NMR and IR studies and all the experiments for measuring physical properties were carried out under a purified argon atmosphere in a drybox with a HE 493 Dri-Train. The lithium-enriched melt was prepared by the addition of lithium chloride to the neutral melt with co-addition of a stoichiometric amount of AlCl$_3$ with stirring. Lithium chloride was added slowly, and time was allowed for cooling prior to further addition of lithium chloride and AlCl$_3$. The lithium chloride used (BDH, AR) was purified by heating at 100 °C in a vacuum oven overnight prior to transferring to the drybox for storage and use.

The specific conductivities of various compositions of the melts were measured at 24 °C using a Radiometer conductivity meter, type CDM 2C, calibrated against a 0.1 M aqueous KCl standard. A closed and submersible all-Pyrex viscometer[12] was used for viscosity measurements. The viscometer was calibrated at different temperatures using cyclohexanol and ethylene glycol. Densities were measured using a 1.00 mL Pyrex pipet (DESAGA), and volumes were calibrated gravimetrically against distilled water. The volume of the pipet was 1 ± 0.006 mL, and all weighings were done using an electronic balance (Mettler, model AE101) placed inside the glovebox.

A JEOL GSX-270 NMR spectrometer was used to record the NMR spectra for ^{13}C, ^{27}Al, and ^{7}Li using C$_6$D$_6$, saturated Al$_2$(SO$_4$)$_3$ in D$_2$O, and saturated LiCl in D$_2$O as external standards, respectively. All external standards were sealed in 0.6 mm diameter, 5 cm long capillary tubes (Dade capiletes). The IR spectra were recorded by a Nicolet SX200 FTIR spectrometer.

Results and Discussion

Effect of Li$^+$ on Im$^+$. The effect of the presence of Li$^+$ on the structure of the melt was studied using FTIR and ^{13}C NMR, and the results obtained are shown in Tables 1 and 2.

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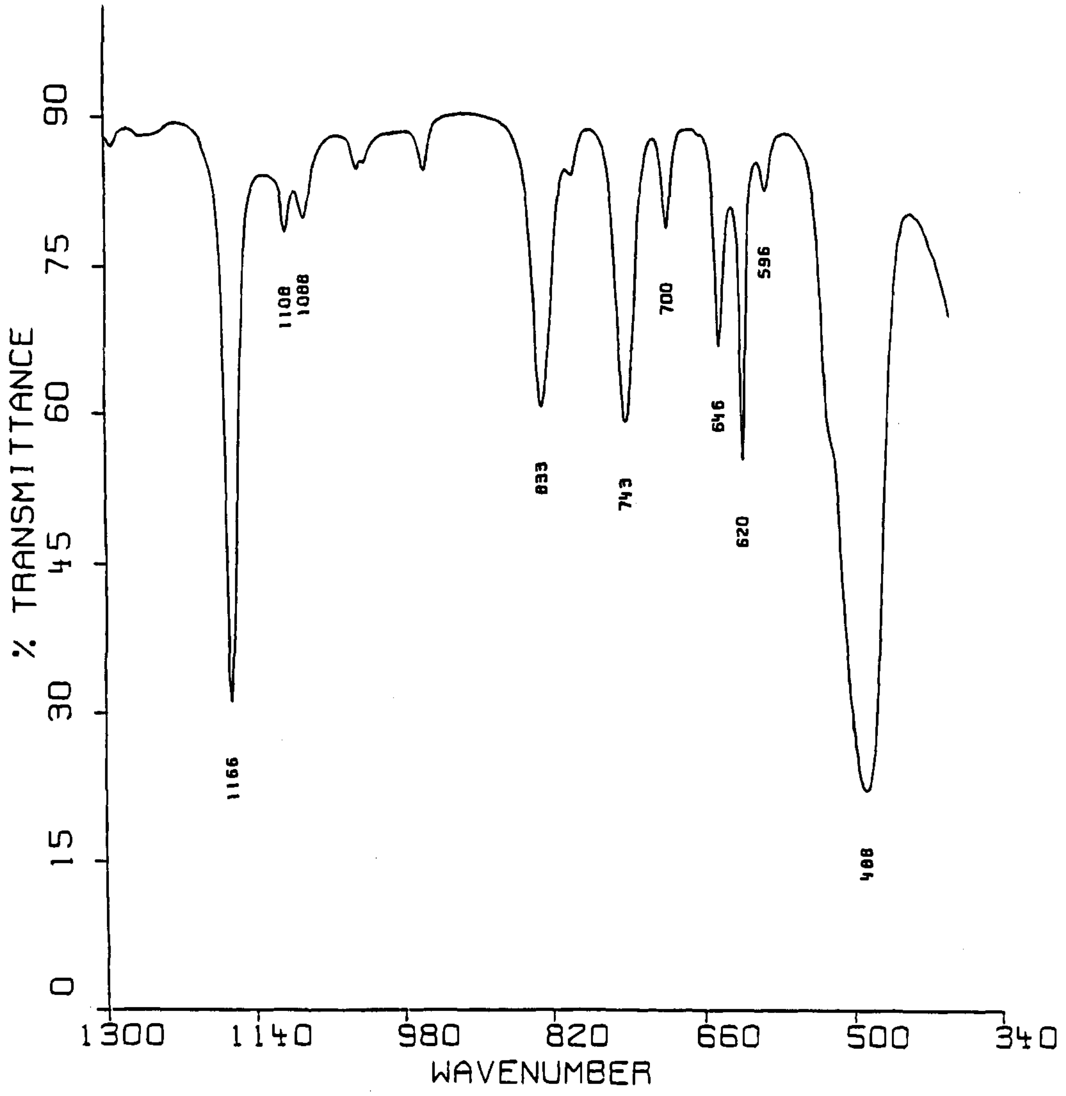

Figure 2. Infrared spectrum of neutral MeEtImCl$_4$ melt prior to addition of LiCl.

When the IR vibration frequencies of the neutral melt with and without the addition of lithium are compared, almost identical peaks are obtained in both cases, as indicated in Table 1. These absorption peaks are also found if only ImCl is used. Thus, no apparent interaction of the imidazolium ions with the lithium ions was shown to occur in the melt using the IR technique. Similar conclusions can be drawn from the ^{13}C NMR data as shown in Table 2. The chemical shifts of the lithium-enriched melt are in general close to those of the neutral melt for all carbon positions with the exception of C-7 at the side chain. This indicates that Li$^+$ interacts very little with Im$^+$ in the melt.

Effect of Li$^+$ on AlCl$_4^-$. The effect of Li$^+$ on AlCl$_4^-$ is mainly electrostatic, and the ionic interaction will perturb the symmetry of the AlCl$_4^-$ ion. The degree of interaction will be evident in the IR and NMR data. In comparison to the IR spectrum of the neutral melt (ImCl:AlCl$_3$ = 1:1), additional peaks were found for the LiCl−ImCl−AlCl$_3$ melt at 802.2, 679.2, 567.5, 491.7, and 440.7 cm^{-1} (Table 1).

Absorption peaks due to oxide impurities have been reported in earlier work[16,17] for high-temperature chloroaluminate melts. The purification procedure for lithium chloride as described in the Experimental Section seems to be able to remove these impurities to an acceptable level for use in the ambient-temperature chloroaluminate melts. The IR spectrum of the neutral melt before the addition of LiCl shows no trace of these additional absorption peaks (Figure 2), but they appear when LiCl is added. This is because the oxide bands (Al−O) are very strong. The purity of LiCl as assayed by argentine titration was 99.76% w/w (average of five titrations), and no oxychloride was found in the lithium chloride-enriched chloroaluminate melt as determined by an ASTM procedure,[18] which has a detection limit of less than 0.003% w/w. Moreover, no oxide peak was detected in the cyclic voltammogram of the lithium-enriched melt as described in the literature.[19]

In order to assign these five additional peaks, they are compared to those obtained using LiAlCl$_4$ and LiAl$_2$Cl$_7$ (Table 1). Although the 802 and 681 cm^{-1} peaks match well in both position and intensity those of LiAlCl$_4$, they could be due to the oxide impurities which absorb at the same positions.[16,17] The rest of the absorption peaks show a better match with those of LiAl$_2$Cl$_7$. The strong broad peak observed at 491.7 nm (Figure 1) may complicate the picture, as it is likely composed

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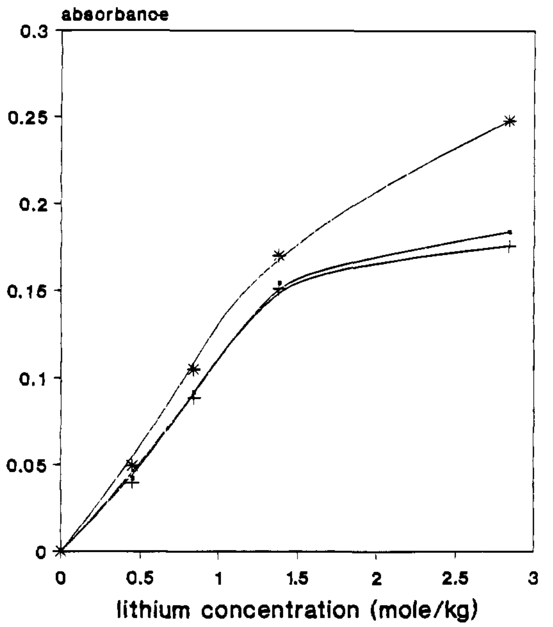

Figure 3. Concentration dependence of IR absorptions at 802 cm^{-1} ($*$), 679 cm^{-1} (□), and 567 cm^{-1} (+).

Table 3. NMR Line Widths and Chemical Shifts of ^{27}Al in Different Melts

molten salt	line width, Hz	chemical shift,[a] ppm
MeEtImCl$-$AlCl$_3$$-$LiCl (ImCl:AlCl$_3$:LiCl 1:1.36:0.36)	131.99	102.59
basic binary melt (ImCl:AlCl$_3$ = 1:0.66)	110.01	102.75
acidic binary melt (ImCl:AlCl$_3$ = 1:1.5)	655.0	101.55
neutral binary melt (ImCl:AlCl$_3$ = 1:1)	2.34	103.81

[a] Resolution 0.01 ppm.

of several underlying peaks. This may be due to the splitting of the $\nu_3(F_2)$ mode as reported by Rytter et al.[20] for molten $LiAlCl_4$ resulting from a lowering of the T_d symmetry of $AlCl_4^-$ due to the perturbation of the small and strongly polarizing Li^+ cation.

The above results might indicate that the interaction of lithium with the ImCl$-$AlCl$_3$$-$LiCl melt is somewhat intermediate between those of $LiAlCl_4$ and $LiAl_2Cl_7$. In other words, the T_d symmetry is perturbed strongly to such a degree that the formation of a bridging chloride as in $LiAl_2Cl_7$ is indicated. However, by following the variation of the absorbance at different lithium concentrations (Figure 3), we obtain linear curves for the 802, 679, and 567 cm^{-1} peaks with deviations at concentrations greater than 1.2 mol/kg. This indicates that the effect which may be due to the interaction of lithium or oxide impurities upon the addition of the lithium salt is quantitative and additive.

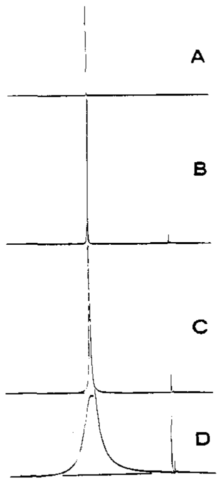

Figure 4. ^{27}Al NMR spectra of $MeEtImAlCl_4$ melts: (A) neutral melt (ImCl:AlCl$_3$ = 1:1); (B) basic melt (ImCl:AlCl$_3$ = 1:0.66); (C) neutral melt with $LiAlCl_4$ (ImCl:AlCl$_3$:LiCl = 1:1.27:0.27).

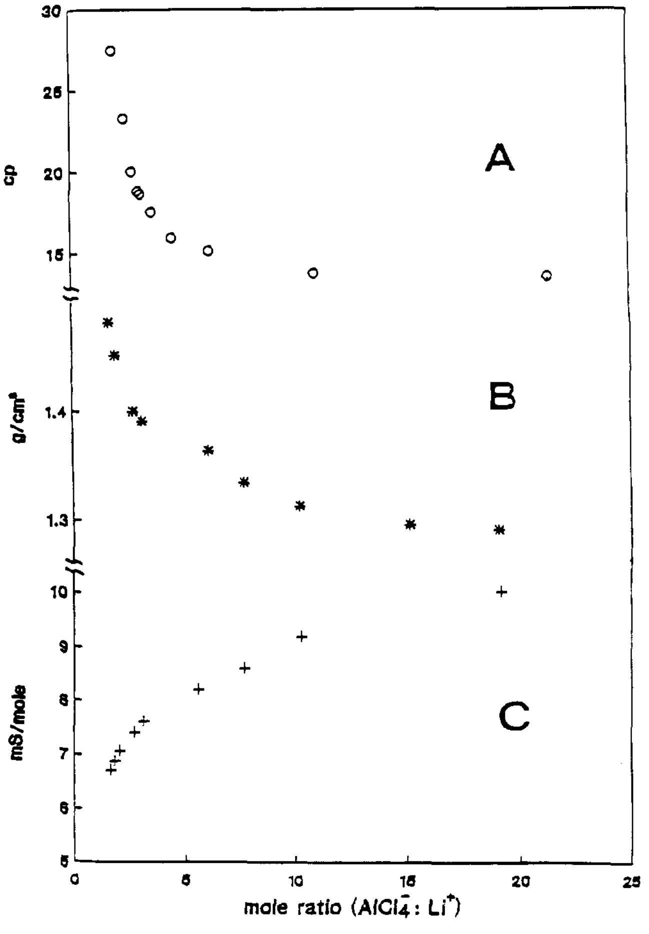

Figure 5. Variations of (A) viscosity, (B) density, and (C) molar conductivity at different $AlCl_4^-$:Li^+ mole ratios.

NMR was used to study the effect of lithium on $AlCl_4^-$, and the results of the ^{27}Al NMR work are shown in Table 3. Only one ^{27}Al resonance peak (Figure 4) was observed for basic, neutral, and Li^+-enriched melts in contrast with two peaks for the acidic melt. The chemical shifts for ^{27}Al do not differ much under different melt conditions. However, a large difference was observed in the line widths of the resonance signals from different melts. The neutral binary melt gave the sharpest line, and appreciable line broadening was found to occur when LiCl, ImCl, or $AlCl_3$ was added to the melt. The line broadening may be due to the change in viscosity, difference in chemical environment around the ions of study, and the occurrence of chemical exchange in the melts. The orders of change of viscosity, line width, and chemical shifts in the various melts under study are as follows:

viscosity: basic $\approx$ LiCl $>$ neutral $\approx$ acidic melts[1,2,12]

line width: acidic $\gg$ basic $\approx$ LiCl $>$ neutral melts (Table 3)

chemical shift: acidic $<$ basic $\approx$ LiCl $<$ neutral melts (Table 3)

The change in the chemical shifts reflects the degree of

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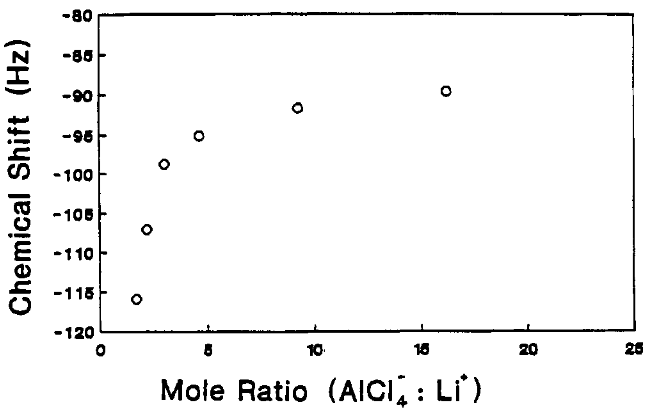

Figure 6. Variation of ^7Li NMR chemical shifts at different $AlCl_4^-$:Li^+ ratios.

deshielding at ^{27}Al, ranging from more shielding in the neutral melts with least disturbed $AlCl_4^-$ to the other extreme of acidic melts with the formation of the $Al_2Cl_7^-$ anion. The basic and LiCl neutral melts are somewhat intermediate between the two, as the $AlCl_4^-$ is slightly disturbed due to electrostatic interaction with excess Li^+ and imidazolium cations present in the LiCl and basic melts, respectively.

Many factors can affect the line width of the peak, such as viscosity and chemical exchange. For the neutral, LiCl-enriched neutral, and basic melts, the change in line width follows the same trend as the viscosity; thus viscosity is an important factor in these melts. However, the reason for line broadening in the acidic melt is different because of its exceptionally large value compared to those obtained in the other melts. It is likely due to the following chemical exchange:

$$AlCl_3 + AlCl_4^- \rightleftharpoons Al_2Cl_7^- \qquad (1)$$

The IR and NMR results indicate that the perturbation of the ideal tetrahedral symmetry of $AlCl_4^-$ by Li^+ in the ImCl−$AlCl_3$−LiCl melt leads to the occurrence of additional IR peaks, the splitting of the $\nu_3(F_2)$ mode of vibration, and peak broadening in the NMR resonances. The degree of interaction shows a linear dependence on the lithium concentrations. The NMR results indicate that the chemical environment at ^{27}Al of $AlCl_4^-$ in the LiCl neutral melts is similar to that obtained in the basic melts but very different from that obtained in the acidic melts, as indicated by the chemical exchange broadening of the NMR resonances.

Effect of High Li^+ Concentration. The addition of Li^+ to the ImCl−$AlCl_3$ melt was shown to effect a considerable change in the physical properties.[1,2] The conductivity was found to decrease, viscosity to increase, and density to increase upon increasing lithium concentrations. However, by plotting the change in the physical properties versus mole ratios of $AlCl_4^-$:Li^+ in the melt, we observed a very interesting trend (Figure 5) showing an obvious change in the physical properties when the ratio is less than 5. Thus, a structural change seems to be indicated in the melt at very high Li^+ concentrations.

NMR techniques are used to detect whether or not similar trends occur at the atomic level. The results are shown in Figure 6, which indicates obvious changes in the ^7Li NMR chemical shifts when the mole ratio of $AlCl_4^-$:Li^+ is less than 5.

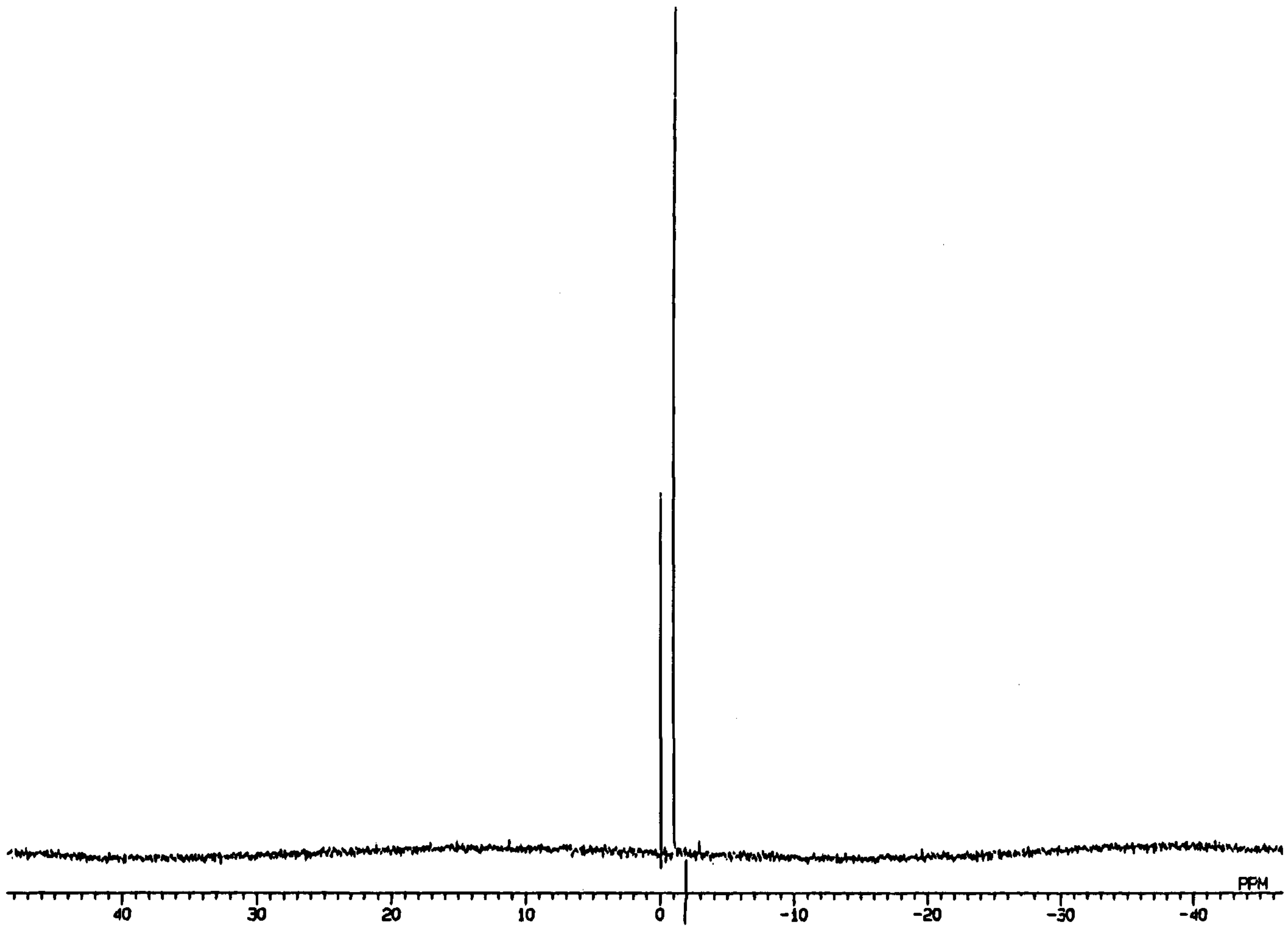

Figure 7. Typical ^7Li NMR spectrum of the $MeEtImAlCl_4$ melt with $LiAlCl_4$. $AlCl_4^-$:Li^+ = 3.6:1.

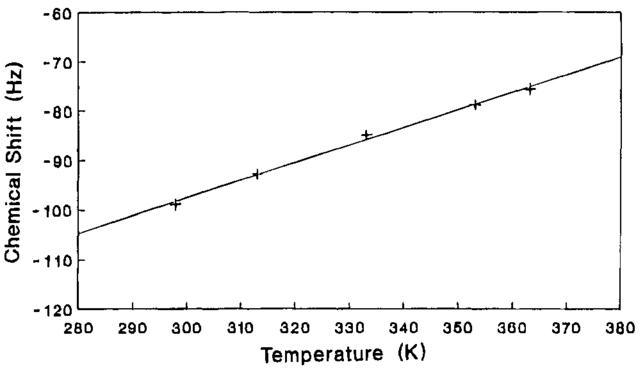

Figure 8. ^{7}Li NMR chemical shifts of the MeEtImAlCl$_4$ melt with LiAlCl$_4$ at different temperatures. AlCl$_4^-$:Li$^+$ = 3.6:1.

To further investigate the above effect, ^{7}Li NMR was used to probe the change in the environment around Li$^+$ when its concentration is high. A very narrow line was obtained and only one resonance peak was found to occur at different lithium concentrations (Figure 7) in addition to the external reference (saturated LiCl in D$_2$O) resonance at zero chemical shift. However, a significant change in the chemical shift occurred with a change in the lithium concentration (Figure 6). Again, an obvious change was observed when the AlCl$_4^-$:Li$^+$ ratio was less than 5:1. Thus, the structural change at high lithium concentrations led to a drastic increase in the shielding of the lithium ion and indicated the formation of a network-like structure at high lithium concentrations. At high temperature (Figure 8), the lithium ion was deshielded, and this was attributed to the breakup of the structure of the melt upon heating.

By plotting the slopes of the curves of the parts before and after the breaks of the curves at a mole ratio of 5:1 for both the physical properties and NMR data, we obtained a more accurate ratio. It is interesting to note that the use of different measuring techniques leads to slightly different ratios within the range of 3.5:1 to 5:1. This may be due to the fact that different properties are affected to slightly different degrees by the formation of an organized structure in the melt at high lithium concentrations.

The following model has been proposed to explain the above observation. The sudden change in the physical properties and NMR environment around Li$^+$ is due to a structural change of the melt at high lithium concentrations at mole ratios of about 3.5–5. At lower concentration of LiAlCl$_4$, i.e. many AlCl$_4^-$ ions around given Li$^+$ ions, it is essentially one structure, likely to be a complex of AlCl$_4^-$ around Li$^+$. However, when the lithium ion concentration is increased beyond a mole ratio (AlCl$_4^-$:Li$^+$) of 4.5, there is no longer sufficient space between the group of the Li/AlCl$_4$ complexes to allow them to move freely, and thus a network-like structure is formed. This leads to an increase in the intensity of the vibrational frequencies of the Li$^+$–Cl interaction and a drastic shift in the ^{7}Li NMR chemical shift when the AlCl$_4^-$:Li$^+$ mole ratio is decreased beyond about 4.

Conclusions

The results of the present study of ion interactions in lithium-enriched neutral tetrachloroaluminate melts of the 3-ethylimidazolium chloride–aluminium chloride system indicate that there is very little effect upon interaction at the imidazolium cation when Li$^+$ is added to the melt; this is supported by the NMR data.

The addition of Li$^+$ perturbs the AlCl$_4^-$ ion and leads to the broadening of the ^{27}Al NMR resonance. The degree of interaction depends on the lithium concentration, and the presence of the imidazolium ion does not seem to affect the general pattern of interaction. Considerable changes in the physical properties and ^{7}Li NMR chemical shifts were observed with the addition of lithium chloride, and an obvious change in both physical properties and atomic NMR data was observed when the mole ratio of AlCl$_4^-$:Li$^+$ was less than about 4.

A model was proposed wherein Li$^+$ and AlCl$_4^-$ are associated to form a complex at high AlCl$_4^-$:Li$^+$ ratios and they are independent of various other forms of interactions that may affect the physical and spectral properties of the melt. However, when the mole ratio is less than about 4, i.e., when Li$^+$ is added to exceed a given concentration ratio, a network-like structure is formed in the melt leading to the occurrence of a break in the physical properties, obvious changes in the concentration-dependent IR absorption peak intensities, and a large shift in the ^{7}Li NMR resonance.

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