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^{27}Al and ^{13}C NMR Studies of Aluminum Chloride–Dialkylimidazolium Chloride Molten Salts

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Mixtures of 1-methyl-3-ethylimidazolium chloride and aluminum chloride form salts that are liquid at room temperature. As the proportions of organic chloride and aluminum chloride are varied, the ^{13}C NMR chemical shifts of the cation carbons change and the ^{27}Al line widths of the chloroaluminate anions change. The ^{13}C shifts may be explained by anion–cation interactions and the ^{27}Al line widths by the presence of more than one type of chloroaluminate anion. Temperature-dependent ^{27}Al NMR results show chemical exchange between chloroaluminate anions in the aluminum chloride rich molten salts.

Introduction

Molten salts prepared from aluminum chloride and organic chloride salts are currently of considerable interest because of their potential as electrolytes for high-energy-density batteries. Previous studies of mixtures of aluminum chloride and organic chlorides include $AlCl_3$–*n*-butylpyridinium chloride molten salts studied by ^{27}Al,[1] ^{13}C, and ^{1}H NMR[2] and Raman spectroscopy[3] and by electrochemical methods.[4] These studies indicate that for mole ratios of $AlCl_3$ and organic chloride up to 1/1 ("basic" melts), the important equilibrium is

$$M^+Cl^- + AlCl_3 \rightleftarrows M^+AlCl_4^- \qquad M^+ = \text{pyridinium cation} \tag{1}$$

Because the equilibrium constant is much greater than 1, the main species present at a 1/1 mole ratio is $M^+AlCl_4^-$. As the $AlCl_3$ to organic chloride ratio exceeds 1/1 ("acidic" melts), $Al_2Cl_7^-$ forms according to the reaction

$$M^+AlCl_4^- + AlCl_3 \rightleftarrows M^+Al_2Cl_7^- \tag{2}$$

Recently we have prepared and studied some similar molten salts composed of mixtures of $AlCl_3$ and 1,3-dialkylimidazolium chlorides.[5] The melts prepared from $AlCl_3$ and 1-methyl-3-ethylimidazolium chloride have the advantage of being liquid at room temperature over a considerable composition range, of mole fraction of $AlCl_3$ = 0.3–ca. 0.6. For this range of compositions, we have investigated the ^{27}Al NMR line widths ($\Delta\nu_{1/2}$) and ^{13}C NMR chemical shifts at 31 °C and have studied these same features over the extended range of mole fraction of $AlCl_3$ = 0–0.66 at a temperature of 90 °C. We express melt composition in terms of apparent mole fraction of $AlCl_3$, realizing that molecular $AlCl_3$ probably does not exist in the melts. The change in the ^{13}C NMR chemical shift of the C-2 atom of the imidazole ring with change in composition is expected to be a sensitive indicator of the degree of positive charge situated on the imidazole ring between the two nitrogen atoms, which should be affected by cation–anion interactions. In addition, the $\Delta\nu_{1/2}$ values for the ^{27}Al NMR line widths can be related to the Al-containing anions present at various compositions of the molten salts.

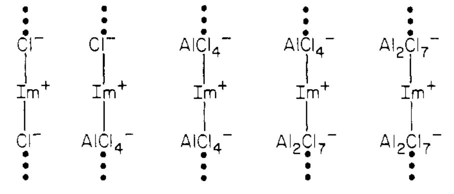
Experimental Section

The 1-methyl-3-ethylimidazolium chloride and chloroaluminate molten salts were prepared by methods described earlier.[5]

The ^{27}Al and ^{13}C NMR spectra were recorded by using a Nicolet NT-150 NMR spectrometer and a 12-mm probe that could be tuned for ^{27}Al or ^{13}C. The ^{13}C NMR chemical shifts were referenced to an external Me_4Si standard. Positive shifts indicate decreased shielding. The exchange-averaged ^{27}Al spectra shown in Figure 4 were taken on a JEOL FX90Q NMR spectrometer.

Results and Discussion

The relative chemical shifts of the imidazolium ring carbons (positions 2, 4, and 5) and of the $N-CH_3$ and $N-CH_2CH_3$ carbons were measured at 90 °C for mole fraction of $AlCl_3$ = 0–0.66 and at 31 °C for mole fraction of $AlCl_3$ = 0.3–0.56. A typical spectrum with assignments is shown in Figure 1. At both temperatures, by far the greatest change in chemical shift with composition was observed for the C-2 resonance. This was as expected since molecular orbital calculations show carbon-2 of the imidazolium cation to have by far the smallest electron density, and thus, this is the carbon affected to the greatest degree by cation–anion interactions. A plot of the ^{13}C chemical shift for this carbon atom vs. mole fraction of $AlCl_3$ in the molten salt solutions at 90 °C is shown in Figure 2. A large decrease in chemical shift is observed as a 1/1 mole ratio mixture of $AlCl_3$–imidazolium chloride is approached. If each imidazolium cation is coordinated with two anions,[6] then there are five possible environments for the cation, designated **1**–**5**.



1 **2** **3** **4** **5**

Species **1**–**5** are not discrete but represent portions of oligomeric chains of alternating cations and anions. Since the different species are evidently in a fast chemical-exchange regime, the observed chemical shifts should be the population-weighted average of the various species present. In order to fit the data in basic melts (mole fraction of $AlCl_3$ = 0–0.5), the chemical shifts of three different species are required: **1**, **2**, and **3**. The chemical shift of species **1** is that of the pure dialkylimidazolium chloride, while the chemical shift of species **3** is the shift observed in a mole fraction of $AlCl_3$ = 0.5 melt. On the basis of these two chemical shifts and the fact that the

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(1) Gray, J. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 7147–51.
(2) Robinson, J.; Bugle, R. C.; Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3776–9.
(3) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728.
(4) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 2723–5.
(5) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263–4.
(6) The average number of nearest anion neighbors of the imidazolium cation has been established by proton NMR experiments: Wilkes et al., unpublished results.

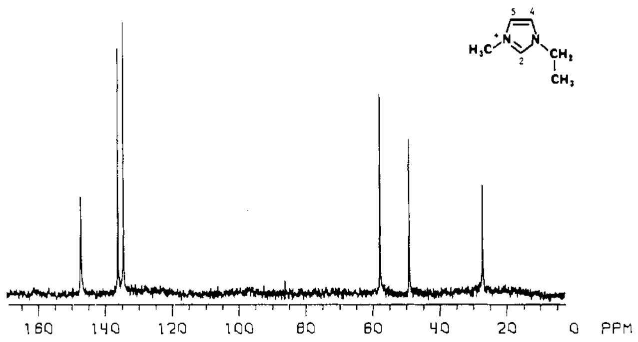

Figure 1. Proton-decoupled ^{13}C NMR spectrum of 1-methyl-3-ethylimidazolium chloroaluminate melt, where AlCl$_3$ mole fraction = 0.50 (temperature 90 °C, spectrometer frequency 37.734499 MHz). Assignments are (left to right) C-2, C-5, C-4, *N*-CH$_2$, *N*-CH$_3$, CH$_3$.

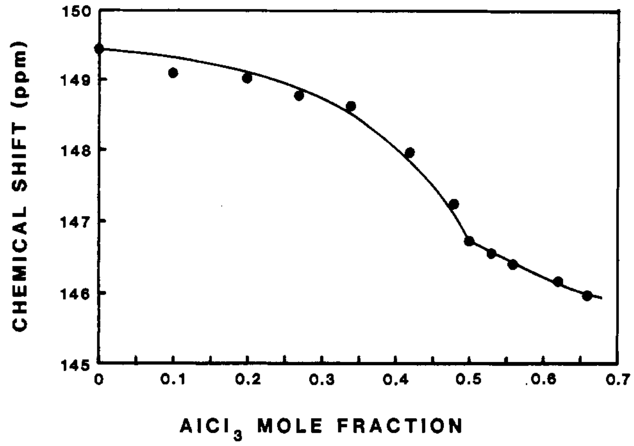

Figure 2. ^{13}C NMR chemical shifts of C-2 of 1-methyl-3-ethylimidazolium ion as a function of apparent mole fraction of AlCl$_3$. The solid lines are least-squares fits to eq 4 and 6.

sum of the mole fractions is equal to 1, the chemical shift curve shown in Figure 2 can be obtained for eq 3 and 4. An alternate model of the system in which only dimeric species were considered did not give a satisfactory fit to the ^{13}C chemical shift data or to the ^1H chemical shift data previously reported.[7] The values of δ_1 and δ_3 are the observed shifts at mole fraction of AlCl$_3$ = 0 and 0.5, respectively. δ_2 was obtained by a nonlinear least-squares fit to the data for basic melts. The X_i fractions were calculated from the stoichiometries indicated in eq 1 and 2, assuming a random distribution of anions.

$$\delta_{\text{obsd}} = \delta_1 X_1 + \delta_2 X_2 + \delta_3 X_3 \quad \mathbf{1, 2, 3} = \text{species; } X = \text{mole fraction} \tag{3}$$

$$\delta_{\text{obsd}} = 149.5X_1 + 149.0X_2 + 149.7X_3 \tag{4}$$

In the acidic melts (mole fraction of AlCl$_3$ = 0.5–0.66) the plot shows a relatively small change in chemical shift. This is because the AlCl$_4^-$ anion of species **3** is being replaced by the anion Al$_2$Cl$_7^-$ to form species **4** and **5**, which results in a smaller change in magnetic environment of the 2-carbon. The equivalents of eq 3 and 4 for the acidic region are

$$\delta_{\text{obsd}} = \delta_3 X_3 + \delta_4 X_4 + \delta_5 X_5 \tag{5}$$

$$\delta_{\text{obsd}} = 146.7X_3 + 146.1X_4 + 146.0X_5 \tag{6}$$

The values of δ_3 and δ_5 are the observed shifts at mole fraction of AlCl$_3$ = 0.5 and 0.66, respectively.

Table I. ^{27}Al Line Widths ($\Delta\nu_{1/2}$) at 90 °C for Various Compositions

mole fraction of AlCl$_3$	$\Delta\nu_{1/2}$, Hz	mole fraction of AlCl$_3$	$\Delta\nu_{1/2}$, Hz
0.11	231	0.50	2.34
0.20	202	0.53	87.5
0.27	176	0.56	277
0.34	110	0.62	504
0.42	39.8	0.66	655
0.48	30.5		

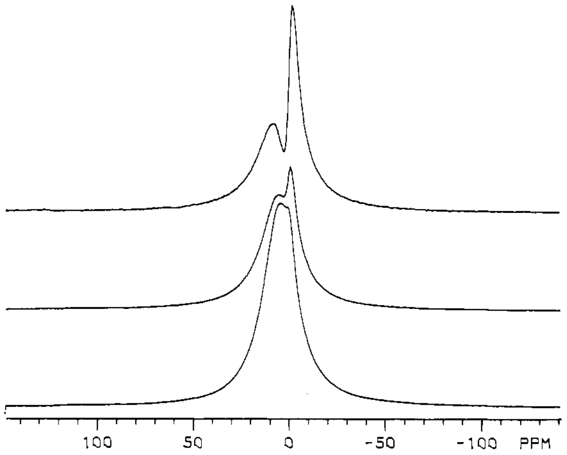

Figure 3. ^{27}Al NMR spectrum of a 1-methyl-3-ethylimidazolium chloride–AlCl$_3$ melt where aluminum chloride mole fraction = 0.56 and temperature is 30 °C. Preacquisition delay times are 1.00, 0.50, and 0.033 ms for the top, middle, and bottom scans, respectively (spectrometer frequency 39.103914 MHz).

The solid lines in Figure 2 are those predicted by eq 4 and 6.

The ^{13}C chemical shifts of the ring carbons C-4 and C-5 also decreased with increasing AlCl$_3$ for acidic melts, but in these cases the total change at 90 °C of about 1 ppm was analogous to the total change in chemical shift for the N–CH$_2$CH$_3$ carbons. This is indicative of a minimal change in the charge distribution in the imidazolium ring with change in composition.

At 90 °C over the entire composition range studied, only one ^{27}Al resonance was observed in each case. The measured ^{27}Al line widths, $\Delta\nu_{1/2}$, are given in Table I. On each side of the AlCl$_3$–imidazolium chloride equivalence point, the line width broadens markedly while, at exactly a 1/1 mole ratio mixture, the $\Delta\nu_{1/2}$ value is a relatively narrow 2.34 Hz. Previous studies of AlCl$_4^-$ and Al$_2$Cl$_7^-$ line widths have shown that the tetrahedral symmetry of the AlCl$_4^-$ species acts to minimize line broadening due to the quadrupole moment of ^{27}Al, while Al$_2$Cl$_7^-$ being larger and lacking tetrahedral symmetry is broadened by efficient nuclear quadrupole relaxation. Thus, we believe that the very narrow resonance for ^{27}Al at mole fraction of AlCl$_3$ = 0.5 is indicative of AlCl$_4^-$ of species **3** being the only aluminum-containing species, which exhibits little exchange broadening. At mole fractions of AlCl$_3$ greater than 0.5, the results show the presence of both AlCl$_4^-$ and Al$_2$Cl$_7^-$, which are undergoing exchange at 90 °C to give a single broadened peak. When the temperature is reduced to 31 °C for a sample of mole fraction of AlCl$_3$ = 0.56, two ^{27}Al resonances are just observable with a 100-ppm sweep width and a preacquisition delay time of 0.033 ms. As shown in Figure 3, by an increase in the preacquisition delay time to 0.50 ms and then to 1.00 ms, the narrow resonance can be separated. This is due to the selective reduction in the intensity of the broader Al$_2$Cl$_7^-$ resonance caused by the longer delay time.

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(7) Wilkes, J. S.; Levisky, J. A.; Pflug, J. L.; Hussey, C. L.; Scheffler, T. B. *Anal. Chem.* **1982**, *54*, 2378.

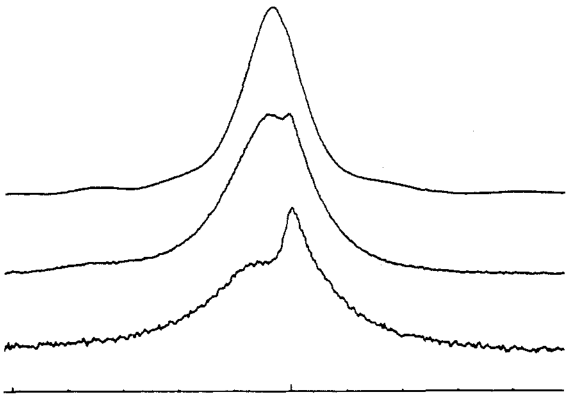

Figure 4. ^{27}Al NMR spectra taken at 88, 67, and 47 °C (from top to bottom). The spectra were obtained at 23.29 MHz with a preacquisition delay time of 1.5 ms. The mole fraction of $AlCl_3$ in this 1-methyl-3-ethylimidazolium chloride–$AlCl_3$ melt was 0.60.

Table I also shows a large increase in the ^{27}Al line width at 90 °C as the mole fraction of $AlCl_3$ is decreased from 0.5 to 0. A good part of this increase is undoubtedly due to increasing viscosity of the solutions that are richer in the organic halide. Preliminary results show that each decrement of 0.05 in $AlCl_3$ mole fraction in basic melts approximately doubles the absolute viscosity. The resulting increase in the correlation time for molecular reorientation broadens the line width.

The ^{27}Al spectra of a melt that was 0.60 in mole fraction of $AlCl_3$ were recorded at 47, 67, and 88 °C as shown in Figure 4. Under the conditions employed (observation frequency 23.29 MHz, scan width 10 000 Hz, 4K data points, and preacquisition delay time 1.5 ms), two broad ^{27}Al resonances were observed at 47 °C that gradually merged as the temperature was raised toward 90 °C, showing the effect of chemical exchange between the aluminum-containing species. Because of the decrease in viscosity with increasing temperature, the narrowing of the resonance lines is expected, but this cannot account for the coalescence of the resonances at high temperature.

In the manner of the butylpyridinium chloride–aluminum chloride study of Gray and Maciel,[1] the Nicolet NTCXCH computer program was used that calculates complete line shapes for a two-site exchange between components of different concentration. From a chemical shift difference of 350 Hz for the two resonances, mole fractions of 0.1 and 0.9 were obtained for narrow and broad components, respectively; the three simulated spectra were obtained as shown in Figure 5 by using the same frequency scale as that in Figure 4. These simulated spectra show the correct line shapes with the following values of τ, the preexchange lifetime, and the line widths of the narrow and broad components at 47, 67, and 88 °C: 0.0040 s, 95 Hz, 1200 Hz; 0.0013 s, 12 Hz, 710 Hz; and 0.0007 s, 10 Hz, 600 Hz. It should be noted that the mole fraction values used of 0.1 and 0.9 have to be artificially adjusted due to the discrimination of the broad-line component when a delay time of 1.5 ms is used, so they are not a true measure of the actual fractions of the anions.

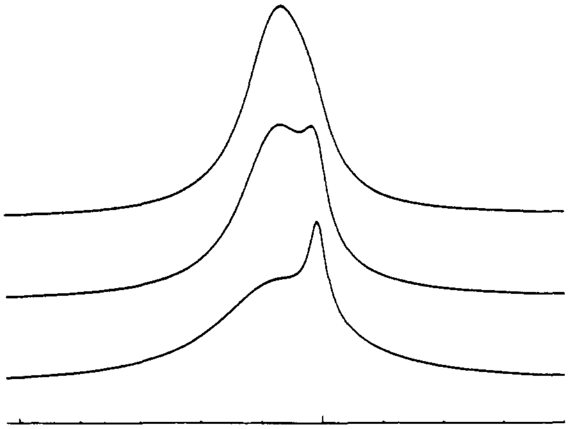

Figure 5. ^{27}Al NMR spectra calculated by using a two-site chemical-exchange simulation. The frequency scale used in this figure is identical with that used in Figure 4.

The chemical shift difference of 350 Hz used in the simulations was needed to give the right shape to the 47 °C ^{27}Al spectrum. If only the high-temperature results had been considered, the data could have been simulated more exactly by using a smaller chemical shift difference. This leads us to propose that a three-site or higher exchange mechanism occurs in the acidic melts at these temperatures. For this reason we believe the two-site-exchange simulations cannot be used to give an accurate value for the activation energy for this exchange. Perhaps a future ultrahigh-field NMR study of these melts will identify additional aluminum-containing species that will allow a more accurate simulation of the temperature-dependent resonances.

Conclusion

The ^{13}C chemical shifts and ^{27}Al line widths for various compositions of $AlCl_3$–dialkylimidazolium chloride molten salts show the effect of the presence of the anionic species $AlCl_4^-$ and Cl^- present up to mole fraction of $AlCl_3$ = 0.5, and the presence of the anionic species $AlCl_4^-$ and $Al_2Cl_7^-$ in the $AlCl_3$ mole fraction range 0.5–0.66. The change in ^{13}C shifts with mole fraction of $AlCl_3$ implies that each cation is associated with two anions.

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Registry No. M^+Cl^-, 65039-09-0; $AlCl_3$, 7446-70-0; $M^+AlCl_4^-$, 80432-05-9; $M^+Al_2Cl_7^-$, 87587-77-7.