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NMR MEASUREMENTS IN SOLUTIONS OF DIALKYLIMIDAZOLIUM HALOALUMINATES


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June 1992

(To be submitted to Proceedings of the Eighth International Symposium on Molten Salts, The Electrochemical Society)

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Abstract

$^{27}$Al and $^{35}$Cl NMR spectra of AlCl$_3$-1-ethyl-3-methyl imidazolium chloride (EMIC) melts were measured for initial compositions ranging from 50 to 67 mol% AlCl$_3$ at various temperatures. It was shown by changing the preacquisition delay time (DE value) that the dominant aluminum species are AlCl$_4^-$ in the melt formed by mixing 50 mol% AlCl$_3$ with EMIC and Al$_2$Cl$_7^-$ in the 67 mol% AlCl$_3$ melt. In the equimolar mixture, the chemical shift of $^{27}$Al NMR spectrum is 103.28 ppm and the line width is 22.83 Hz. In the 67 mol% AlCl$_3$ mixture, the chemical shift is 103.41 ppm and the line width is 2624 Hz. A third species observed at 97 ppm in the $^{27}$Al spectra for the 55 and 60 mol% AlCl$_3$ mixtures is identified to be a product of the reaction with residual water. The relaxation rates for each species in the melts were determined.

Introduction

Dialkylimidazolium chloroaluminates are promising new room temperature molten salts which, in addition to their importance for fundamental electrochemical studies, have potential applications for high-energy batteries and for carrying out chemical reactions. Recently, AlCl$_3$-1-ethyl-3-methylimidazolium chloride (AlCl$_3$-EMIC) has been used successfully for the electroplating of Al on iron steels.

The major equilibrium describing the acid-base properties of the tetrachloroaluminate ionic liquids is given in eqs (1) and (2). In basic solutions, i.e. when the AlCl$_3$ composition is less than 50 mol%, the major aluminum containing species is AlCl$_4^-$.

$$\text{Cl}^- + \text{AlCl}_3 \rightleftharpoons \text{AlCl}_4^- \quad (1)$$

$$\text{AlCl}_4^- + \text{AlCl}_3 \rightleftharpoons \text{Al}_2\text{Cl}_7^- \quad (2)$$

At more acidic compositions, Al$_2$Cl$_7^-$ becomes the predominant species when the AlCl$_3$ composition is approximately 67 mol%. The structure of the Al$_2$Cl$_7^-$ ion consists of two AlCl$_4^-$ tetrahedra sharing a corner chloride moiety. These species have been identified from electrochemical techniques, NMR ($^1$H, $^{13}$C, $^{27}$Al), and IR.

In order to understand the detailed structure and dynamics of AlCl$_3$-EMIC melts, we have initiated a series of measurements involving X-ray and neutron diffraction, Raman spectroscopy and nuclear magnetic resonance (NMR) of both $^{27}$Al and $^{35}$Cl. In this paper, we report results obtained by the latter technique.

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Experimental

The $^{27}$Al and $^{35}$Cl NMR spectra were recorded using a General Electric, GN-300 spectrometer and 10-mm probe that could be tuned for $^{27}$Al or $^{35}$Cl. The receiver coil was tuned to optimize the detection of $^{27}$Al resonances at 78.3MHz or $^{35}$Cl resonances at 29.5MHz. The $^{27}$Al NMR chemical shifts were referenced to an external Al(H$_2$O)$_6^{3+}$ standard. The $^{35}$Cl NMR chemical shifts were referenced to an external Cl$^-$ standard. The molten salts were obtained by mixing highly anhydrous AlCl$_3$ with EMIC at 60°C. The mixtures were prepared by weighing corresponding amounts of AlCl$_3$ and EMIC in a glovebox where the levels of H$_2$O and O$_2$ were maintained at less than 2 ppm. The water content was measured by IR and found to be less than 100 ppm.

Results

$^{27}$Al and $^{35}$Cl NMR spectra were recorded for five nominal compositions of the AlCl$_3$-EMIC molten salt system scanning the neutral melt to the acidic region. In what follows we will present results obtained for these mixtures and highlight the effect of compositional changes and time resolution.

A- Effect of composition changes The dependence of the $^{27}$Al NMR spectra on the initial AlCl$_3$ mol% was measured, at room temperature. The $^{27}$Al NMR spectrum of the 60 mol% AlCl$_3$ mixture is shown in Fig.1. In the neutral melt, the chemical shift is 103.28 ppm and the line width ($\Delta v_{1/2}$) is 22.83 Hz. With increasing AlCl$_3$ content, the chemical shifts become slightly larger and the line width markedly broader. At 67 mol% AlCl$_3$ mixture, the chemical shift is 103.41 ppm and the line width is 2624 Hz. The $^{35}$Cl NMR spectrum of the melt with a 60 mol% AlCl$_3$ is shown in Fig.2. At the equimolar mixture, only one $^{35}$Cl resonance was observed. An additional $^{35}$Cl resonance appears in more acidic melts.

B- Effect of time resolution It is possible to resolve species with substantially different line widths by varying the preacquisition delay time (DE), because the FID falls off more rapidly for species with large line widths than for species with sharp NMR resonances. This technique is particularly useful to resolve species at trace concentrations levels, provided that the species in question has a sharper line width than the line width(s) of the major component(s) of the molten salt. The $^{27}$Al NMR spectra obtained with a 300 μs DE value for two molten salts with different AlCl$_3$ contents are shown in Fig.3. The $\Delta v_{1/2}$ only for the 50 and 67 mol% AlCl$_3$ mixtures were found to be independent of the preacquisition delay time. In contrast, two partially resolved peaks are seen by varying the DE value for the melts with AlCl$_3$ composition from 55 to 64 mol%. A single sharp peak at 97 ppm is observed in the 55 mol% AlCl$_3$ mixture at preacquisition delay times longer than 2.25 ms. Similarly, for the 60 mol% AlCl$_3$ mixture, the sharp peak at approximately 97 ppm is observed at preacquisition delay times longer than 0.7 ms. The full peak width at half height, $\Delta v_{1/2}$, was constant for the peak at 97 ppm as the delay time was varied.

Discussion

The tetrahedral symmetry of the AlCl$_4^-$ species acts to minimize line broadening due to the quadrupole moment of the $^{27}$Al nucleus. In contrast, the lower symmetry of the Al$_2$Cl$_7^-$ ion, which is composed of two corner sharing AlCl$_4^-$ tetrahedron, results in efficient nuclear quadrupolar induced spin relaxation. The results shown in Fig.1 demonstrate the
substantial line broadening due to the presence of Al$_2$Cl$_7^-$ at AlCl$_3$ compositions greater than 50 mol%. In addition, the $^{35}$Cl spectra (Fig.2) support the formation of Al$_2$Cl$_7^-$, because the additional peak at 1800 ppm may be associated with the bridging chloride moiety in the Al$_2$Cl$_7^-$ ion.

At room temperature, the spectra for the 50 and 67 mol% AlCl$_3$ mixtures were unaffected by increasing the DE value. This implies that only one aluminum species exist for these melt compositions. If it is assumed that only one species is formed, then the value of $1/T_2^*$ is obtained from eq.(3),

$$M_A = M_0 \exp\left(-\frac{1}{T_2A^*}\right)$$
$$M_B = M_0 \exp\left(-\frac{1}{T_2B^*}\right)$$

where A refers to AlCl$_4^-$ and B to Al$_2$Cl$_7^-$. Furthermore, $M_A,M_B$ are the total magnetic moments for species A and B, respectively. Plots of ln $M_A$ and ln $M_B$ vs. DE were found to be linear. The relaxation rate, $1/T_2A^*$, of 65.7 s$^{-1}$ is obtained for the AlCl$_4^-$ species from the slope for the 50 mol% AlCl$_3$ mixture. The corresponding $1/T_2B^*$ is 8500 s$^{-1}$ for the Al$_2$Cl$_7^-$ species from the 67 mol% AlCl$_3$ mixture. For the 55-64 mol% AlCl$_3$ mixtures, the $\Delta \nu_{1/2}$ values changed with the DE values indicating that more than one aluminum containing species is present in these solutions. However, using a DE value greater than 2.25 ms for the 55 mol% AlCl$_3$ mixtures produced no further reduction in the $\Delta \nu_{1/2}$ which indicates that the delay time resolution is adequate at a DE value of 2.25 ms. For DE values greater than 2.25 ms, the ln $M$ vs. DE plot shows a single exponential decay. The value of $1/T_2^*$ for the third component at 97 ppm is 503 s$^{-1}$. Maciel et al. concluded that this narrow peak corresponded to AlCl$_4^-$ in AlCl$_3$-BPC system. However, we believe that this peak is due to another species, because the chemical shift is low, 97 ppm, and the concentration of this species is quite small, 0.3%. This third aluminum containing species at 97 ppm is considered to be result from the minute water in the initial mixtures. As mentioned earlier, IR measurement of these mixtures revealed less than 100 ppm of H$_2$O. For the 60 mol% AlCl$_3$ mixture the ln M vs. DE plot shows a single exponential decay for delay times greater than 0.7 ms and provides the value of 854 s$^{-1}$ for $1/T_2^*$.

Conclusion

From the present $^{27}$Al and $^{35}$Cl NMR study, we have shown that the dominant aluminum species are AlCl$_4^-$ in the equimolar mixture and Al$_2$Cl$_7^-$ in the 67 mol% AlCl$_3$ mixture. In the acidic melts (>50 mol% AlCl$_3$), very small amounts of a third species exist. This third species is determined to be a product of the reaction with residual water contained in the initial mixtures. The concentration of the Al$_2$Cl$_7^-$ ion increases as expected with the degree of acidity. The relaxation rate $1/T_2^*$ of AlCl$_4^-$ is $\sim$70 s$^{-1}$, and of Al$_2$Cl$_7^-$ is $\sim$8500 s$^{-1}$, consistent with the symmetry of these two ionic species and a nuclear quadrupole-electric dipole relaxation mechanism.

Acknowledgment

This work was performed under the auspices of the US Department of Energy, Division of Materials Science, Office of Basic Energy Sciences, under contract No. W-31-109-
ENG-38. S. Takahashi was supported by Nisshin Steel Co., Ltd, and acknowledges Argonne for hospitality. We wish to thank R.A. Osteryoung, J. S. Wilkes, P. Trulove and N. Koura for numerous discussions.

Reference
Fig. 1 $^{27}$Al NMR spectra of 60 mol% AlCl$_3$ mixture at room temperature.

Fig. 2 $^{35}$Cl NMR spectra of 60 mol% AlCl$_3$ mixture at room temperature.
Fig. 3 $^{27}$Al NMR spectra with 300 $\mu$s DE value for AlCl$_3$ - EMIC mixtures at room temperature.
(a) 60% - 40% ; (b) 67% - 33%
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