NMR RELAXATION STUDIES OF MICRODYNAMICS IN CHLOROALUMINATE MELTS

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INTRODUCTION

Room temperature molten salts consisting of mixtures of AlCl₃ and 1-ethyl-3-methylimidazolium chloride (MEICl), of interest as aprotic solvents for studying a wide range of both organic and inorganic compounds [1-7]. These chloroaluminate molten salts possess considerable potential as battery electrolytes and various types of electrochemical agents [8-10].

The composition of a chloroaluminate melt has a considerable effect on its physical properties. The variations in physical properties of the melt are due to a combination of factors including ion-ion interactions [4], and Lewis acid-base properties. Chloroaluminate melts with AlCl₃ present in excess (mole fraction, N, of AlCl₃ > 0.5) are termed acidic with AlCl₃⁺ and Al₂Cl₇⁻ the predominant anions.

The use of NMR relaxation methods provides useful information about the dynamics and structure of various chemical systems and chloroaluminate systems in particular. In a previous work[11], ¹³C NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation. The results indicate that AlCl₃⁺ in a Na⁺ or AlCl₃⁺, AlCl₃, melt forms a complex by interacting with the C-2, C-4 and C-5 hydrogens on the MEI⁺ ring. This investigation was followed by studies [12,13] in which the Dual Spin Probe method [14] supported the existence of MEI(AlCl₃)ₙ, complexes in neutral (AlCl₃ = MEICl) and NaCl-buffered melts. ²⁷Al, ²³Na and ¹³C NMR relaxation results confirmed the presence of the chloroaluminate-MEI⁺ complexes and yielded ²⁷Al and ²³Na liquid state quadrupole coupling constants[12,13].

Application of the Dual Spin Probe(DSP) relaxation method typically requires knowledge of ¹³C dipolar relaxation rates which are defined by (1), the basic equation in which the ¹³C nucleus is relaxed by ¹H[15]:

\[ R_{1}^{dd} = N_{H}(\gamma_{C}/\gamma_{H})^{1/2}r_{CH}^{-4} \tau_{eff} \]  \hspace{1cm} (1)

where \( R_{1}^{dd} = 1/T_{1}^{dd} \) is the dipolar relaxation rate, \( N_{H} \) is the number of hydrogens attached directly to the carbon atom, \( \gamma_{C} \) and \( \gamma_{H} \) are gyromagnetic ratios and \( r_{CH} = 1.09 \) Å. \( \tau_{eff} \) is the effective correlation time and varies exponentially with temperature. Equation (1) is operative while under the "extreme narrowing condition" \((\omega_{p} \tau_{eff} < 1)\) which is usually applicable for small molecules including the chloroaluminate melts[11].

\[ R_{1}^{dd} = \eta R_{1}/1.988 \]  \hspace{1cm} (2)

The other part of the DSP method requires knowledge of quadrupolar relaxation rates for nuclei such as ²⁷Al and ²³Na. If there is a distortion from tetrahedral or cubic symmetry, nuclei such as ²⁷Al and ²³Na will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupolar relaxation rate in the "extreme narrowing region" is given by(3) [15,17]:

\[ R_{s} = [3\pi^{2}(2I+1)/10][1+(2/3)][e^{2}Q_{z}/h]^{2}r_{e} \]  \hspace{1cm} (3)

where \( I = 3/2 \) for ²³Na and 5/2 for ²⁷Al, eQ is the nuclear quadrupole moment, \( \epsilon \) is the maximum component of the electric field gradient tensor, and \( z \) is the asymmetry parameter of the electric field gradient tensor(\( z = 0 \) for AlCl₃).
The quadrupole coupling constant, QCC, is given by:

\[ QCC = [e^2Q/\hbar] \]

(4)

The DSP method has been applied to chloroaluminate melts[12,13] and has provided evidence that the ring hydrogens of MEI⁺ interact with the tetrachloroaluminate anion. The existence of these complexes has been supported by linear plots of \( ^{13}\text{C} \) dipolar relaxation rates(\( R_s \)) vs. quadrupolar \( ^{27}\text{Al} \) relaxation rates(\( R_i \)) that pass through the origin as predicted by equation (5):

\[ R_i \propto (1/2 \Delta || (2I + 3)/|\hbar (2I - 1)|) [1 + (z^2/3)], \]  

where \( \alpha = [3 \pi^2/10]||(2I + 3)/|\hbar (2I - 1)|[1 + (z^2/3)], \) and

QCC = \( \alpha \).

In this study, the DSP method is applied to melts containing MEICl, AlCl₃, and EtAlCl₄. The inclusion of EtAlCl₄ provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in EtAlCl₄. The existence of covalent bonding (or complexation) between quadrupolar and dipolar nuclei in a molecule results in a linear plot of eqn. (5) that passes through the origin. In the MEICl-EtAlCl₄ melts reported herein, we observe a linear plot of eqn (5) that passes through the origin when applied to the terminal CH₃ carbon in EtAlCl₄ and one of the peaks in the \( ^{27}\text{Al} \) NMR of the melts.

EXPERIMENTAL

Materials

The 1-ethyl-3-methylimidazolium chloride (MEICl) and chloroaluminate molten salts were prepared as described previously [1]. Ethylaluminum dichloride (EtAlCl₄) was obtained from Aldrich. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Samples were loaded into 5 mm sample tubes, capped in the dry box, removed, and sealed immediately with a torch.

NMR Measurements

\( ^{13}\text{C} \) and \( ^{27}\text{Al} \) NMR spectra were recorded on a Varian 6000 spectrometer at 75.43 or 78.15 MHz. Temperature measurements were calibrated against ethanol or ethylene glycol and are accurate to within \( 2^\circ \text{C} \). Pulse widths(90°) were typically 8.6 (75.43 MHz) and 16 (78.15 MHz) \( \mu \text{s} \). Longitudinal relaxation times measured by the the inversion-recovery method (180°-\( \tau \)-90°-T) with \( T > 10T_1 \). At least 12 delay times(T) were used and the results fitted to a three parameter exponential. NOE measurements were made using the gated decoupler method[18]. It is likely that the error in the NOE measurements is in the 5-10% range[18].

RESULTS AND DISCUSSION

The ability of both AlCl₃ and EtAlCl₄ to form C₂H₄ dimers[19,20] led us to examine the \( ^{27}\text{Al} \) spectra of: (1) neat EtAlCl₄, (2) mixtures of MEICl-EtAlCl₄, and (3) ternary melts (\( N = \text{AlCl}_3/\text{MEICl}\), EtAlCl₄)[21]. The neat EtAlCl₄, \( ^{27}\text{Al} \) NMR spectrum contains two peaks [21]. Peak 1 is a broad downfield peak that dominates the spectrum. The second peak (upfield) overlaps peak 1 and is only a fraction of peak 1 in total peak area. Peak 2 collapses into peak 1 as the temperature is lowered from 60 to 25°C. These two aluminum sites are consistent with the extent of monomer-dimer formation in liquid EtAlCl₄[21].

The MEICl-EtAlCl₄ (\( N = 0.5/0.5 \)) melt \( ^{27}\text{Al} \) NMR spectrum also has two peaks. In this case, peak 1(downfield) is very broad while peak 2 is very sharp, and has a low peak area. Peak 2 increases slightly in area and peak 1 broadens as the temperature is lowered from 70 to 0°C. We have previously[21] made the tentative assignments of EtAlCl₄ for peak 1(downfield) and Et₂Al₂Cl₄ for peak 2.

![Fig. 1. \( ^{13}\text{C} \) Dipolar R1's vs \( ^{27}\text{Al} \) R1's(25 to 70°C) for Al peak 1 (127-131 ppm from Al(H₂O)₄²⁺).](image-url)
In this study, we first apply the DSP method to the CH₃ carbon in EtAlCl₂ and ²⁷Al NMR peaks 1 and 2 from several melt combinations and neat EtAlCl₂. Fig. 1 contains the results for ²⁷Al peak 1 (downfield) and Fig. 2 contains the results for ²⁷Al peak 2. The fact that both plots are linear and pass through the origin, indicate that: (1) the DSP method is appropriate for these systems and (2) the species associated with each peak contains EtAlCl₂. Furthermore, the slopes of these lines can be used to calculate the relative quadrupole coupling constants for the EtAlCl₂-containing species in solution. The QCC values obtained from Fig. 1(Al peak 1) are 171, 119, 106 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat EtAlCl₂, respectively. The QCC values obtained from Fig. 2(Al peak 2) are 6.9, 20, 11 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat EtAlCl₂(repeated).

Results of the Dual Spin Probe method (eqn. [5]) applied to the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts indicate interactions between the Al-containing species in peak 2(102.5-103.0 ppm relative to Al(H₂O)₆⁺⁺) and both the NCH₃ and ethyl terminal CH₃ groups of MEI⁺. Fig. 3 contains the plots for the NCH₃ group in each melt and Fig. 4 contains data for the terminal CH₃ on the MEI ethyl group.

Fig. 2. ¹³C Dipolar R1's vs ²⁷Al R1's(25 to 70°C) for Al peak 2 (102.5-103.0 ppm from Al(H₂O)₆⁺⁺).

Fig. 3. ¹³C Dipolar R1's vs ²⁷Al R1's(25 - 70°C) for NCH₃ carbon vs Al peak 2(25 - 70°C).

Fig. 4. ¹³C Dipolar R1's for ethyl CH₃ carbon vs ²⁷Al R1's(25 - 70°C) for Al peak 2.

The QCC's obtained from the slopes in Fig. 3(MEI NCH₃) are 1.7, 2.3 and 4.4 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts. The QCC's from
Fig. 4 (terminal CH₃ on the MEI ethyl group) are 1.6, 6.9 and 1.3 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts.

Finally, there is no correlation between the ring hydrogen dipolar R1's and any of the ²²Al peak R1's. This result is directly opposite to that found in MEICI-AlCl₃ systems [11,12].

CONCLUSIONS

Application of the DSP probe method to these mixed melt systems indicates a lack of complexation between the ring hydrogens of MEI⁺ and any of these aluminum containing species. These and previous results[21] suggest that the formation of various charged dimers containing EtAlCl₂ takes precedence over the formation of complexes between EtAlCl₄ and the MEI⁺ ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the CH₃ groups (NCH₃ and terminal CH₃ in the ethyl group) of MEI⁺ in these melts.

ACKNOWLEDGMENTS

This work was partially supported by a National Research Council and Summer Faculty Research Associateship to W. R. C. and a summer Graduate Fellowship to P. A. S.

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