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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 (MEI CI), are 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 AlCl₂⁻ 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], ³¹C NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation. The results indicate that AlCl₃⁺ in a Na⁺ₐ,MEI⁺ₐ,NaAlCl₃ 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)ₕ⁺ 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 'H[15]:

\[ R_{1,d} = N_n (\gamma_C/\gamma_H) T_{CH} \tau_{ef} \]  

where \( R_{1,d} = 1/T_{1,d} \) is the dipolar relaxation rate, \( N_n \) is the number of hydrogens attached directly to the carbon atom, \( \gamma_C \) and \( \gamma_H \) are gyromagnetic ratios and \( T_{CH} = 1.09 \ \text{Å} \). \( \tau_{ef} \) is the effective correlation time and varies exponentially with temperature. Equation (1) is operative while under the "extreme narrowing condition" \( (\omega \tau_{ef} < < 1) \) which is usually applicable for small molecules including the chloroaluminate melts[11].

\[ R_{1,d} = \eta R_1/1.988 \]  

(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]:

\[ R_1 = \left[ 3\pi^2 (2l+3)/10l(l-1) \right] e^2 Q q/\hbar^2 r_e \]  

(3)

where \( l = 3/2 \) for ²³Na and 5/2 for ²⁷Al, eq is the nuclear quadrupole moment, \( e^2 Q q/\hbar^2 \) 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:

\[ QCC = \left( \frac{e^2}{4\pi\hbar} \right) \]

(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 \( ^{13}C \) dipolar relaxation rates(\( R_{1\text{d},} \)) vs. quadrupolar \( ^{27}Al \) relaxation rates(\( R_1 \)) that pass through the origin as predicted by equation (5):

\[ R_{1\text{d},}(^{13}C)/N_{\chi} [(^{13}C)_{Y_c} (^{13}C)_{Y_2}]^{2} = R_1(^{27}Al)/\alpha \chi^2 \]

(5)

where \( \alpha = \left[ 3\pi/10 \right] (2I^2 + 3)/I(I^2 - 1) \left[ 1 + (z^2/3) \right] \), and \( QCC = \chi \).

In this study, the DSP method is applied to melts containing MEICI, AlCl₃, and EtAlCl₂. The inclusion of EtAlCl₂ provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in EtAlCl₂. 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 MEICI-EtAlCl₂ melts reported herein, we observe a linear plot of eqn. (5) that passes through the origin when applied to the terminal CH₃ carbon in EtAlCl₂ and one of the peaks in the \( ^{27}Al \) NMR of the melts.

RESULTS AND DISCUSSION

The ability of both AlCl₃ and EtAlCl₂ to form \( C_{2n} \) dimers[19, 20] led us to examine the \( ^{27}Al \) spectra of: (1) neat EtAlCl₂, (2) mixtures of MEICI-EtAlCl₂, and (3) ternary melts (\( N = AlCl₃/MEICI/EtAlCl₂ [21] \)). The neat EtAlCl₂ \( ^{27}Al \) 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 EtAlCl₂[21].

The MEICI-EtAlCl₂ (\( N = 0.5/0.5 \)) melt \( ^{27}Al \) 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 EtAlCl₂ for peak 1 (downfield) and Et₂AlCl₃ for peak 2.

EXPERIMENTAL

Materials

The 1-ethyl-3-methylimidazolium chloride (MEICI) and chloroaluminate molten salts were prepared as described previously [1]. Ethylaluminium dichloride (EtAlCl₂) 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

\( ^{13}C \) and \( ^{27}Al \) NMR spectra were recorded on a Varian XL-300 spectrometer at 75.43 or 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5°C. Pulse widths(90°) were typically 8.6 (75.43 MHz) and 7.6(78.15 MHz) μs. Longitudinal relaxation times were measured by the the inversion-recovery method 

(180°-τ-90°-T) with \( T > 10T_1 \). At least 12 delay times(τ) 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].

Fig. 1. \( ^{13}C \) Dipolar R1's vs \( ^{27}Al \) R1's(25 to 70°C) for Al peak 1 (127-131 ppm from Al(\( \text{H}_2\text{O})_2^{+} \)).
In this study, we first apply the DSP method to the CH$_3$ carbon in EtAlCl$_2$ and $^{27}$Al NMR peaks 1 and 2 from several melt combinations and neat EtAlCl$_2$. Fig. 1 contains the results for $^{27}$Al peak 1 (downfield) and Fig. 2 contains the results for $^{27}$Al 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 EtAlCl$_2$.

Furthermore, the slopes of these lines can be used to calculate the relative quadrupole coupling constants for the EtAlCl$_2$-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 EtAlCl$_2$, 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 EtAlCl$_2$ (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($H_2O$)$_6^{2+}$) and both the NCH$_3$ and ethyl terminal CH$_3$ groups of MEI. Fig. 3 contains the plots for the NCH$_3$ group in each melt and Fig. 4 contains data for the terminal CH$_3$ on the MEI ethyl group.

Fig. 2. $^{13}$C Dipolar R1's vs $^{27}$Al R1's (25 to 70°C) for Al peak 2 (102.5-103.0 ppm from Al($H_2O$)$_6^{2+}$).

Fig. 3. $^{13}$C Dipolar R1's vs. $^{27}$Al R1's (25 - 70°C) for NCH$_3$ carbon vs Al peak 2 (25 - 70°C).

Fig. 4. $^{13}$C Dipolar R1's for ethyl CH$_3$ carbon vs $^{27}$Al R1's (25 - 70°C) for Al peak 2.

The QCC's obtained from the slopes in Fig. 3 (MEI NCH$_3$) 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 CH$_3$ 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 $^{27}$Al peak R1's. This result is directly opposite to that found in MEICl-AlCl$_3$ 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 EtAlCl$_3$ takes precedence over the formation of complexes between EtAlCl$_3$ and the MEI$^+$ ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the CH$_3$ groups (NCH$_3$ and terminal CH$_3$ in the ethyl group) of MEI$^+$ in these melts.

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REFERENCES


