

Dual spin probe NMR relaxation studies of ionic structure in 1-ethyl-3-methylimidazolium chloride–AlCl₃ molten salts

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Abstract

Room temperature molten salts consisting of 1-ethyl-3-methylimidazolium chloride (MEICl), AlCl₃ and NaCl are of interest as electrochemical agents. Results of ²⁷Al and ¹³C NMR dual spin probe (DSP) relaxation studies of these ionic ligands support the existence of interactions between MEI⁺ and AlCl₄⁻. The dual spin probe method is used to determine liquid state quadrupole coupling constants of 0.821 and 2.10 MHz for the neutral (MEICl=AlCl₃) and neutral buffered (Na⁺_{0.22}MEI⁺_{0.78}AlCl₄⁻) melts.

Introduction

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

The composition of the chloroaluminate melt, i.e. the relative proportions of AlCl₃ and MEICl, 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 (apparent mole fraction AlCl₃ (N) > 0.5) are termed acidic with AlCl₄⁻ and Al₂Cl₇⁻ the predominant anions. At neutral (MEICl=AlCl₃) composition [11] the only detectable anion is AlCl₄⁻. The addition of NaCl as a ternary component to an acidic chloroaluminate melt buffers

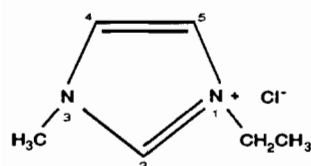


Fig. 1. MEI cation (positions are labeled).

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the medium to neutrality, producing AlCl₄⁻ as the only anion [12]. Thus, a neutral buffered melt is composed of MEI⁺, Na⁺ and AlCl₄⁻. The proportions of MEI⁺ and Na⁺ in the ionic liquid are determined by the composition of the AlCl₃–MEICl binary to which NaCl was added. A 0.55 melt buffered with NaCl has the composition Na⁺_{0.22}MEI⁺_{0.78}AlCl₄⁻.

The use of ¹³C NMR relaxation studies yields considerable information about the dynamics and structure of chemical systems in general and the chloroaluminate melts in particular [13]. The basic equation for ¹³C dipolar relaxation in which the ¹³C nucleus is relaxed by ¹H is given by [14]

$$R_1^{dd} = N_H (\hbar \gamma_C \gamma_H)^2 r_{CH}^{-6} \tau_{eff} \quad (1)$$

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, γ_C and γ_H are magnetogyric ratios and $r_{CH} = 1.09 \times 10^{-8}$ cm. τ_{eff} is the effective correlation time and varies exponentially with temperature.

Equation (1) is operative under the ‘extreme narrowing condition’ ($\omega \tau_{eff} \ll 1$) which is usually applicable for small molecules including the chloroaluminate melts [13]. The determination of R_1^{dd} as a function of temperature provides activation energies (E_a) which are indicative of a molecule’s ability (or inability) to move through the medium [15]. Consequently, the E_a results can support the existence of interactions between an ion such as MEI⁺ and its nearest neighbors (Cl⁻, AlCl₄⁻ or Al₂Cl₇⁻).

In a similar manner, a nucleus of spin greater than 1/2 that relaxes primarily through a quadrupolar mechanism can also be used as a NMR ‘probe’ to monitor

isotropic molecular tumbling. If there is a distortion from cubic symmetry, nuclei such as ^{27}Al will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupole interaction is affected by the reorientation motion of the ^{27}Al containing molecule (complex ion in our case) and the quadrupolar relaxation rate in the 'extreme narrowing region' is given by [14, 16]

$$R_1 = 1/T_1 = [(3/10)\pi^2(2I+3)/I^2(2I-1)][1 + (z^2/3)] \times [e^2Qq/h]^2\tau_c \quad (2)$$

where $I=5/2$ for ^{27}Al , eQ is the nuclear electric quadrupole moment, eq is the maximum component of the electric field gradient tensor, and z is the asymmetry parameter of the electric field gradient tensor. The quadrupole coupling constant (QCC) is the collection of terms given by eqn. (3).

$$QCC = e^2Qq/h \quad (3)$$

There are several problems associated with the determination of QCC , particularly in the case of ^{27}Al , for which there are few reports of compounds in the liquid and solid state [17]. If, however, a secondary spin probe such as ^{13}C is available in the complex, it is possible to equate τ_{eff} from eqn. (1) and τ_c from eqn. (2), providing that the motion is isotropic within the 'extreme narrowing region' [18, 19]. This allows the calculation of QCC , assuming that z^2 approaches zero.

A previous ^{13}C NMR relaxation study [13] supports the existence of $\text{MEI}(\text{AlCl}_4)_n^{(n-1)-}$ complexes in chloroaluminate melts. In this study, the dual spin probes ^{13}C and ^{27}Al are used to further detail the molecular dynamics and possible structure of these chloroaluminate complexes.

Experimental

Materials

The 1-methyl-3-ethylimidazolium chloride and chloroaluminate molten salts were prepared as previously described [1]. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in a dry box. Samples were loaded into 5 or 10 mm samples tubes, capped and sealed with parafilm. They were then removed from the dry box and sealed immediately with a torch. Viscosity and density measurements have been described elsewhere [13].

NMR measurements

^{27}Al and ^{13}C spectra were recorded on a JEOL FX90Q (23.29 and 22.49 MHz) spectrometer as described previously [13]. Temperature measurements were calibrated

against methanol or ethylene glycol and are accurate to within 0.5 °C. Pulse widths were typically 15.7 (^{27}Al) and 18.5 (^{13}C) μs . Longitudinal relaxation times were measured by the inversion-recovery method ($180^\circ\text{-}\tau\text{-}90^\circ\text{-}T$) with $T > 5T_1$. For all melt samples the experiments used at least 12 delay times (τ) and relaxation times were obtained from least-squares fits of the magnetization as a function of τ . NOE (η') measurements were made using the gated decoupler method [20] in which the fully decoupled spectrum is compared with one in which decoupling is present only during the acquisition time. It is likely that the error in the NOE measurements is in the 5–10% range [20].

Results

^{27}Al relaxation mechanisms

The change in ^{27}Al relaxation rates over the temperature range of 0–70 °C is shown in Figs. 2 and 3 for 0.50 ($\text{MEICl} = \text{AlCl}_3$) and 0.55 NaCl-buffered ($\text{Na}^{+0.22}\text{MEI}^{+0.78}\text{AlCl}_4^{-}$) melts. The anion in these melts is AlCl_4^{-} . The ^{27}Al Arrhenius plots contain distinct (linear least-squares regression coefficients are 0.999 for Figs. 2 and 3) exponential temperature regions (Table 1) as is the case for the ^{13}C relaxation results in the $\text{Na}^{+0.22}\text{MEI}^{+0.78}\text{AlCl}_4^{-}$ melt [13]. Table 1 contains a summary of the activation energies which are indicative of the interactions between the ^{27}Al containing moiety and the surrounding medium. Previous evidence [6, 13, 21] supports the existence of hydrogen bonds involving Cl^{-} or AlCl_4^{-} in the chloroaluminate melts as evidenced by results of solid state, ^{13}C NMR and viscosity studies [13, 21].

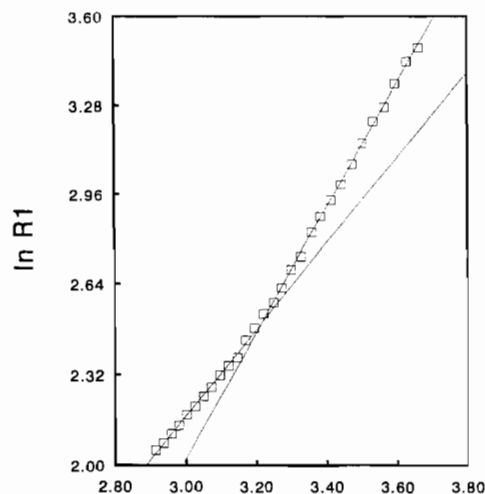


Fig. 2. Relaxation rates (^{27}Al) vs. $1000/T$ (in K) for 0.50 melt ($\text{MEICl} = \text{AlCl}_3$).

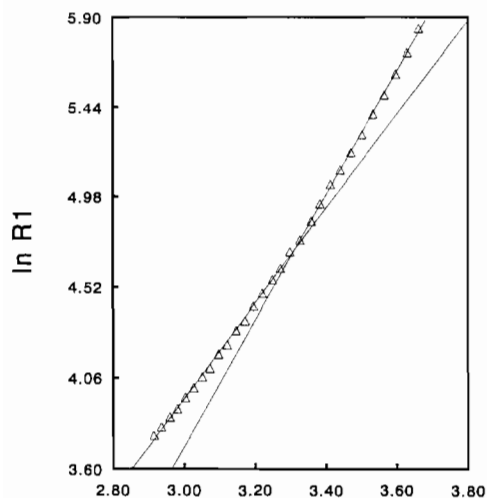


Fig. 3. Relaxation rates (^{27}Al) vs. $1000/T$ (in K) for $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melt.

TABLE 1. Activation energies and related temperature ranges for chloroaluminate melts at 23.29 MHz

| | Melt | |
|--|---------------------------------|--|
| | 0.50 (MEICl = AlCl_3) | $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ |
| Temperature range ($^\circ\text{C}$) | 0–40 | 0–27.5 |
| E_a (kJ) | 18.4 | 26.4 |
| Temperature range ($^\circ\text{C}$) | 40–70 | 27.5–70 |
| E_a (kJ) | 12.6 | 20.1 |

Determination of the ^{27}Al QCC

There are few reports in the literature of QCC for ^{27}Al complexes or compounds in the liquid state. The apparent distortion from octahedral symmetry has produced a range of values such as 32.9 MHz for alumichrome [22], 23.3 MHz for triethylaluminum [18] and 0.49 MHz for $\text{Al}(\text{acac})_3$ [19]. These results were obtained by either using the solid state QCC [22], assuming an effective correlation time [18], or by using a dual spin probe method [19]. The dual spin probe (DSP) method requires that the molecular tumbling is isotropic and the τ_{eff} in eqn. (1) is identical to τ_c in eqn. (2). If this is true, then QCC is determined from ^{13}C R_1^{dd} s and from ^{27}Al R_1 s, assuming that $z=0$. This last assumption may introduce a small error into the determination of QCC , however, the known tetrahedral symmetry of AlCl_4^- provides good support for this assumption.

In this study, we will assume that the $\text{MEI}(\text{AlCl}_4)_n^{(n-1)-}$ complexes [13] provide a basis for the use of the DSP method. If this assumption is valid, the combination of ^{13}C relaxation data from the nucleus

of MEI^+ can be used to determine the $QCC(=\chi)$ for the associated AlCl_4^- species. This is accomplished by plotting the ^{13}C dipolar relaxation rates at each temperature versus the Al relaxation rates over the temperature range 0–70 $^\circ\text{C}$. If $\tau_{\text{eff}} = \tau_c$, then from eqns. (1) and (2)

$$R_1^{\text{dd}}/N_{\text{H}}(\hbar\gamma_{\text{C}}\gamma_{\text{H}})^2\tau_{\text{CH}}^{-6} = R_1(^{27}\text{Al})/\alpha\chi^2 \quad (4)$$

$$\text{where } \alpha = [3\pi^2(2I+3)/10I^2(2I-1)][1+z^2/3]$$

Consequently, a plot of R_1^{dd} versus $R_1(^{27}\text{Al})$ will have a zero intercept and a slope, S , equal to eqn. (5)

$$S = N_{\text{H}}(\hbar\gamma_{\text{C}}\gamma_{\text{H}})^2\tau_{\text{CH}}^{-6}/\alpha\chi^2 \quad (5)$$

or the $QCC(=\chi)$ equals eqn. (6)

$$QCC = \chi = (\hbar\gamma_{\text{C}}\gamma_{\text{H}})(N_{\text{H}}/\alpha S)^{1/2}\tau_{\text{CH}}^{-3} \quad (6)$$

The ^{13}C NMR dipolar relaxation rates, R_1^{dd} were determined from NOE (η') measurements using eqn. (7) [23]

$$R_1^{\text{dd}} = \eta'R_1/1.988 \quad (7)$$

The results for the melts are plotted versus ^{27}Al R_1 s in Figs. 4 and 5 for the C4 (\approx C5) and C2 monoprotic carbons in the MEI^+ ring over the temperature range 20–70 $^\circ\text{C}$. The validity of eqn. (4) is verified with near zero intercepts and similar slopes for C4 (\approx C5) and C2 carbons. Use of eqn. (6) while assuming that $z=0$, yields QCC values given in Table 2.

Once the quadrupole coupling constants for the ^{27}Al in the anions have been determined, either ^{27}Al or ^{13}C relaxation rates may be used to evaluate the tumbling of the associated cations and anions. The average of the QCC values, i.e. those determined by relaxation of C2 and C4 in the MEI^+ cation, $(\text{C2} + \text{C4})/2$, for each

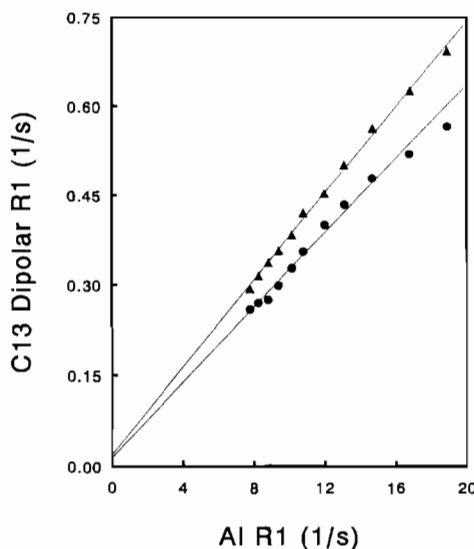


Fig. 4. ^{13}C R_1^{dd} s vs. ^{27}Al R_1 s from 20 to 70 $^\circ\text{C}$ for 0.50 melt: (●) = C2; (▲) = C4 (\approx C5).

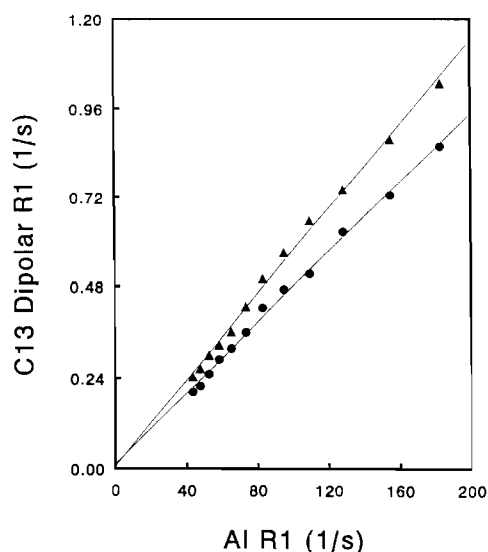


Fig. 5. ^{13}C R_1^{dd} s vs. ^{27}Al R_1 s from 20 to 70 °C for $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melt: (●) = C2; (▲) = C4 (\approx C5).

TABLE 2. ^{27}Al quadrupole coupling constants (MHz) and τ_c (ps) values for chloroaluminate melts

| MEI ⁺ carbon | Melt | |
|----------------------------|-----------------------------------|--|
| | 0.50 (MEICl = AlCl ₃) | $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ |
| C4 (\approx 5) | 0.789 | 1.99 |
| C2 | 0.852 | 2.20 |
| Av. QCC | 0.821 | 2.10 |
| Temperature range (°C) | 0–40 | 0–27.5 |
| τ_c | 48–18 | 80–27 |
| Temperature range (°C) | 40–70 | 27.5–70 |
| τ_c | 18–11 | 27–10 |

melt was used to calculate ^{27}Al correlation times, τ_c , over the temperature range 0–70 °C, as shown in Table 2. The higher average value of the ^{27}Al QCC (2.13 MHz) in the $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melt is to be expected, considering the ability of Na^+ to interact strongly with Cl^- , therefore distorting the tetrahedral symmetry around aluminum [24].

At 70 °C, the 0.5 (MEICl = AlCl₃) and $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melts have similar correlation times (10–11 ps), consistent with their similar compositions and mobility. As further evidence of their relative mobilities, measured viscosities for these melts between 0 and 70 °C are 42–6.7 and 57–0.20 cP for the 0.5 (MEICl = AlCl₃) and $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melts, respectively.

Despite the apparent success of the DSP method as applied to these systems, caution should be exercised as there are undoubtedly several circumstances that would lead to similar results despite a lack of interactions

in the melts. The most obvious case would occur when the individual species have the same correlation time fortuitously, rather than due to actual complexation between them.

Conclusions

In a previous study [13], agreement between ^{13}C relaxation times and a corrected Stokes radius obtained from diffusion measurements [25] supported the existence of $\text{MEI}(\text{AlCl}_4)_n(\text{Cl})_m^{(n+m-1)-}$ species in the $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$ melt. The results of this study, which includes the successful application of the DSP method in neutral and NaCl-buffered melts, supports the existence of a ^{27}Al and ^{13}C containing species.

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