

Short Communication

Characterization of species in ethylaluminum dichloride molten salts by ^{27}Al NMR

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Abstract

A new room temperature melt containing 1-ethyl-3-methylimidazolium chloride (MEICl) and ethylaluminum dichloride (EtAlCl_2) contains EtAlCl_2 dimers and EtAlCl_3^- as determined by ^{27}Al NMR of neat EtAlCl_2 and a saturated LiCl-EtAlCl_2 solution at 60 °C. The ^{27}Al NMR peaks in the MEICl- EtAlCl_2 melt at 129 and 102 ppm are assigned to the dimers (*cis* and *trans*) of EtAlCl_2 (129 ppm) and EtAlCl_3^- (102 ppm), respectively. Semi-empirical calculations support the formation of EtAlCl_3^- over EtAlCl_2 dimer formation from Cl^- and EtAlCl_2 .

Introduction

Room temperature chloroaluminate melts contain a variety of charged species which have been identified by various spectroscopic techniques [1–11]. Recently, a new chloroaluminate room temperature molten salt system has been studied using Raman spectroscopy [12]. This melt is a mixture of ethylaluminum dichloride (EtAlCl_2) and 1-butyl-3-methylimidazolium chloride (BuMCl) and is liquid over a wide range of temperatures and melt compositions. A similar melt system containing 1-ethyl-1-methylimidazolium chloride (MEICl) and EtAlCl_2 has also been reported [13]. The ^{27}Al NMR of the MEICl- EtAlCl_2 melt, neat EtAlCl_2 and related melts provide evidence of the species found in this new melt [13].

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Experimental

Materials

The 1-ethyl-3-methylimidazolium chloride and chloroaluminate molten salts were prepared as previously described [9]. Ethylaluminum dichloride was purified by freeze-thawing under anhydrous helium gas atmosphere in a dry box. All molten salts preparations and manipulations were performed in a dry box. Samples were loaded into 5 mm sample tubes, capped and sealed with parafilm. They were then removed from the dry box and sealed immediately with a torch.

NMR measurements

^{27}Al NMR spectra were recorded on a Varian XL-300 spectrometer at 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5 °C. Pulse widths were typically 5–10 μs , and longitudinal relaxation times were measured by the inversion-recovery method ($180^\circ-\tau-90^\circ-T$) with $T > 10T_1$ [9]. For all melt samples, at least 12 delay times (τ) were used and relaxation times (in duplicate) obtained from a three parameter exponential fit of magnetization as a function of τ . All ^{27}Al chemical shift (δ) values reported herein are relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ [13].

Results and discussion

Spectral results

The ^{27}Al NMR of neat EtAlCl_2 at 60 °C and 78.15 MHz contains a broad peak at 128.5 ppm ($T_1 = 115 \mu\text{s}$) and a shoulder at 97 ppm ($T_1 = 147 \mu\text{s}$) which collapses into the broad downfield peak as the temperature is lowered to 30 °C [13]. The ^{27}Al NMR peaks at 128.5 and 97 ppm have been assigned to the dimer and monomer of EtAlCl_2 , consistent with the ability of this species to form C_{2h} dimers [13–15]. Similarly, the ^{27}Al NMR spectrum of a 0.5/0.5 (mole ratio) MEICl- EtAlCl_2 melt (Fig. 1) contains a broad peak at 129 ppm ($T_1 = 211 \mu\text{s}$) and a sharp peak at 102 ppm ($T_1 = 99 \text{ ms}$). Attempts to form EtAlCl_3^- by adding NaCl to neat EtAlCl_2 failed as NaCl is virtually insoluble in neat EtAlCl_2 . LiCl, however, is soluble and induces the dissociation of EtAlCl_2 dimers to form EtAlCl_3^- . The ^{27}Al NMR spectrum of a saturated solution of LiCl in EtAlCl_2 produces a single peak at 100.5 ppm ($T_1 = 1.53 \text{ ms}$) as shown in Fig. 1. Assignments of the ^{27}Al peak at 128–129 ppm to the EtAlCl_2 dimer and

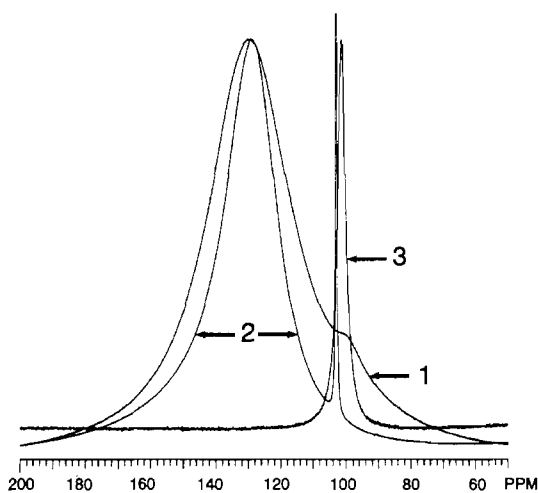


Fig. 1. ^{27}Al NMR spectra (78.15 MHz) of (1) neat EtAlCl_2 , (2) 0.5/0.5 $\text{MEtCl}/\text{EtAlCl}_2$ and (3) saturated $\text{LiCl}/\text{EtAlCl}_2$, all at 60°C .

the peak at 100–102 ppm to EtAlCl_3^- (C_{3v}) is consistent with both their coordination and symmetry [13–16].

Comparison of the ^{27}Al NMR spectra of these melts indicates that the 0.5/0.5 $\text{MEtCl}-\text{EtAlCl}_2$ melt contains a mixture of EtAlCl_2 dimers (broad downfield peak), EtAlCl_3^- and MEt^+ . The ratio of EtAlCl_2 dimer to EtAlCl_3^- at 60°C is 12:1 as indicated by the ratio of the integrated curve areas. The ^{27}Al NMR spectrum of a 0.4/0.6 mole ratio $\text{MEtCl}-\text{EtAlCl}_2$ melt at 60°C has the same peaks as the 0.5/0.5 melt, however the ratio decreases to 3:1 for the two main peaks (129/102 ppm), consistent with the formation of additional EtAlCl_3^- . A very weak third peak at 95 ppm is also observed in the 0.4/0.6 melt at 60°C . This narrow (long T_1) peak at 95 ppm is assigned to the $\text{Et}_2\text{Al}_2\text{Cl}_5^-$ species consistent with its likely concentration, coordination and chemical shift [16, 17]. This same species has previously been identified by Raman spectroscopy in $\text{BuMCl}-\text{EtAlCl}_2$ melts [12] at mole ratios greater than 1:1.

Model calculations

Semi-empirical calculations using the MOPAC [18] program package predict the general course of the reaction between EtAlCl_2 and Cl^- (eqn. (1)). Both AM1 [19] and PM3 [20, 21] (in parentheses) methods were used to calculate the heats of formation of each

$$(\text{EtAlCl}_2)_2 + 2\text{Cl}^- \rightleftharpoons 2\text{EtAlCl}_3^- \quad (1)$$

species. The results were -172.69 (-297.33) kJ for the *cis* dimer of EtAlCl_2 and -173.12 (-297.91) kJ for the *trans* dimer. The heat of formation of Cl^- is -157.57 (-214.34); EtAlCl_2 is -462.78 (-383.09) and EtAlCl_3^- is -918.83 (-934.24) kJ. The heat of reaction

for Cl^- reacting with the dimer of EtAlCl_2 to form EtAlCl_3^- and EtAlCl_2 is -125.79 (-46.04) kJ for the *cis* dimer and -125.37 (-45.49) kJ for the *trans* dimer. The heat of formation of EtAlCl_3^- is -298.49 (-336.81) kJ versus -172.69 (-297.33) kJ and -173.12 (-297.91) kJ for the *cis* and *trans* dimer formation, respectively. These results are in agreement with the formation of additional EtAlCl_3^- instead of dimer formation and free Cl^- as the mole ratio of Cl^- to EtAlCl_2 approaches 1:1.

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