Ionic Structure and Interactions in 1-Methyl-3-Ethylimidazolium Chloride/AlCl₃ Molten Salts

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ABSTRACT

Room temperature chloroaluminate molten salts formed by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) with AlCl₃ are of interest as electrolytes and non-aqueous reaction media. We have done NMR, IR, and theoretical studies on this system to elucidate the still unresolved picture of ionic structure and interactions in these melts. NMR studies of MEI⁺ in melts of various composition (determined by the mole fraction, N, of AlCl₃ used in forming a melt) were originally explained by a stack model. In this model, the anions (Cl⁻ and AlCl₄⁻ in basic melts and AlCl₄⁻ and Al₂Cl₇⁻ in acidic melts) are located between stacked "parallel" MEI⁺ ring planes. However, IR and Raman spectra were interpreted as evidence that Cl⁻ formed ion pairs with MEI⁺ by a H-bonding interaction through the H on the C-2 in the ring, disputing the stack model. Our IR studies now indicate that while the hydrogen on the C-2 does interact with the Cl⁻, it is clearly not the only point of interaction. It appears that the Cl⁻ affects the hydrogens at C-4 and C-5 members of the ring as well. Semi-empirical molecular orbital calculations support a model in which Cl⁻ interacts with two MEI⁺'s while occupying an equilibrium position approximately equidistant between the C-2's of adjacent near parallel MEI⁺'s.

INTRODUCTION

One of the most widely studied room temperature melt systems is the 1-methyl-3-ethylimidazolium chloride-AlCl₃ (MEICl-AlCl₃) melt which is liquid at room temperature for compositions between 33-67 mole% AlCl₃ (1,2). This melt exhibits acid-base chemistry which can be controlled by varying the composition. When the mole fraction of AlCl₃ (N) used in preparing the melt is less than 0.5, it contains an excess of Cl⁻ and is basic. For compositions N > 0.50, the melt is considered acidic because it contains an excess of Al₂Cl₇⁻. In N = 0.50 melt the melt is neutral, containing only AlCl₄⁻ anions.
This melt exhibits several attractive features such as a large electrochemical window and high conductivities. The structure of MEI+ is shown below:

A better understanding of the physical and chemical properties of these melts has been sought through investigation of the ion-ion interactions in these melts. The crystal structure of the iodide analog, MEII, has been reported, and based upon the C-2 hydrogen-iodide distance, an interaction involving hydrogen bonding through the C-2 hydrogen has been suggested (3). Previous investigations have used this model to explain variations in the IR spectra of basic MEICI-AlCl₃ melts (4). In this work we studied both normal and deuterated MEI+ in melts of various composition. We studied the effects of solvent addition and replacement of the C-2 hydrogen with methyl. Our studies indicate that the changes in the IR spectra may not be attributed entirely to hydrogen bonding interactions between the MEI+ and Cl− anion. Semiempirical molecular orbital calculations have been used to support our experimental evidence for this conclusion. Other possible structures in which the interaction is not a hydrogen bond have been considered.

**EXPERIMENTAL**

**General Procedures:** The preparation of the melts has been presented earlier(1). Benzene-d₆ (Aldrich) and dichloromethane-d₂ (Aldrich) were used as received. Benzene (Aldrich, HPLC grade) and dichloromethane (Baker, HPLC grade) were purified by refluxing over P₂O₅ for several days followed by fractional distillation.

The IR spectra were recorded on an IBM model 32 FTIR spectrometer. The solutions were run between two NaCl plates (Wilmad, 41 x 32 x 6 mm) as thin films or with lead spacers of appropriate size. All loading of IR cells was done in a He-filled dry box with less than 10 ppm H₂O/air.

**Preparation of 2-d₁-MEICI:** A solution of 4 g of MEICI was allowed to stand in 10⁻³ mL of d₂-H₂O for 3 days. The water was evaporated under reduced pressure and then, to remove the remaining water, the resulting material was suspended in benzene and distilled until the distillate was clear. Analysis (IR) of the material dried by this procedure showed that there was still a small amount of water present so the material was suspended in about 30 mL benzene and treated with about 0.5 mL of thionyl chloride. After standing for 0.5 h, the benzene and thionyl chloride were removed under reduced pressure and the resulting semi-solid was stored under vacuum overnight. The material prepared in this manner showed no
water when analyzed by IR, and its $^1$H-NMR spectrum showed only a small peak, c.a. 0.04 proton for the hydrogen at C-2.

Theoretical Considerations: Theoretical calculations were carried out using the standard AM1 (5) and MNDO (6) models as incorporated in the MOPAC program (7). Geometries were fully optimized using the DFP method (8) and refined by minimizing the scalar gradient of the energy (9). True minima were characterized by the absence of negative force constants (9), and vibrational frequencies were calculated for the normal modes (10).

AM1 was preferred over MNDO due to the problem of excessive long range repulsions associated with MNDO and the capability of AM1 to reproduce hydrogen bonding (5,11). Unfortunately, there are, as of yet, no AM1 parameters for aluminum. Consequently, the MNDO parameters for aluminum were used in AM1 calculations involving the interaction of AlCl$_4^-$ ions with MEI$^+$. This less than ideal procedure is justified in this study since the AM1 results for AlCl$_4^-$ are similar to MNDO results (12) and the interaction between AlCl$_4^-$ and MEI$^+$ is primarily electrostatic in nature or involves only the chlorine atoms. There is no direct interaction of aluminum with the MEI$^+$ and essentially no change in bonding to aluminum is involved.

RESULTS AND DISCUSSION

I. Experimental

The vibrational spectra of the MEICl-AlCl$_3$ ambient temperature melts carried out by Tait and Osteryoung (4) were re-examined. They found that the IR spectra of MEI$^+$ in acidic and neutral melts were the same, but that in basic melts some bands were apparently shifted. They proposed that Cl$^-$ forms a hydrogen bond with the C-2 hydrogen of the MEI$^+$ cation to explain this shift. In other work (3) the crystal structure of MEII suggested that an interaction occurs between the I$^-$ and the C-2 hydrogen.

In $^1$H NMR studies the proton chemical shifts of the C-2 hydrogen show the largest changes as the composition of the melt is changed. This provides supportive evidence for the hydrogen bonded complex, but it was noted that the chemical shifts of the hydrogen at 4 and 5 ring positions are also affected by melt acidity (Fig. 1). Our results suggest that Cl$^-$ is interacting with the $\pi$ orbitals of the imidazolium ring instead of hydrogen bonding at the C-2 hydrogen.

Our conclusions are based on an analysis of the CH and CD stretching bands in the IR spectrum, in particular the behavior of the rather broad band at 3049cm$^{-1}$. The intensity of this band decreases as the mole fraction of AlCl$_3$ in the melt is increased (Fig. 2). It also decreases with the addition of benzene-d$_6$ and dichloromethane-d$_2$ (Fig. 3). In neutral melt, this band does not appear (Fig. 2). Its frequency appears at higher wavelengths in the
MEIBr-AlBr₃ basic melt (Fig. 4). The IR spectrum of N=0.50 MEICl-AlCl₃ melt is unaffected by the addition of benzene-d₆ or dichloromethane-d₂ and is identical to the neutral MEIBr-AlBr₃ melt. Thus, we conclude that the 3049cm⁻¹ band is due to MEI⁺ which is interacting with Cl⁻. Since the tetrahaloaluminate ion is the predominant ion in neutral melt, the IR spectra give no information on the interaction between the ions at this melt composition.

To determine whether the band previously assigned to the C-2 hydrogen stretch perturbed by a bonding interaction is a correct assignment, melts were prepared using the 1,2-dimethyl-3-ethyl imidazolium chloride salt (MMEICl). This salt is similar to MEICl except the C-2 proton has been replaced with a CH₃ group -- a group with which no hydrogen-bonding interaction is expected. The IR spectrum of an N=0.33 melt prepared from MMEICl shows the 3049cm⁻¹ band (Fig. 5). The intensity of this band decreases as the melt is titrated to neutrality (Fig. 5). This is the same behavior as was found for the 3049cm⁻¹ band observed in the IR of MEICl-AlCl₃ basic melts. These results indicate that the 3049cm⁻¹ band cannot be due solely to the C-2 proton stretch perturbed by hydrogen bonding but must involve other vibrations. The spectrum of the N=0.50 MMEICl-AlCl₃ melt differs from the MEICl-AlCl₃ melt. In the IR spectrum of MMEICl-AlCl₃ neutral melt, the band centered around 3119cm⁻¹ seen in the MEICl-AlCl₃ melts is not observed. We thus conclude that this band in MEI⁺ results from the C-2 proton stretch (Fig. 6).

Another band appears at 1595cm⁻¹ whose intensity increases as the melt is titrated from basic toward neutral (Fig. 7). The change in intensity of this band is opposite to what is observed for the 3049cm⁻¹ band. This band has been assigned to an imidazolium ring stretch vibrational mode. The changes in the band intensity indicates that the interaction of MEI⁺ with Cl⁻ inhibits this vibrational mode. The intensity of this band increases as the melt is neutralized because of the conversion of Cl⁻ to AlCl₄⁻ which appears to interact weakly with the MEI⁺ cation (1).

If the interaction between Cl⁻ and the hydrogen at C-2 hydrogen were due to hydrogen bonding, this should be readily observable by examination of the IR spectrum of material with a deuterium at C-2. The C-2 deuterium vibration will shift away from the vibrations of the other C-H bonds in the molecule so that changes in its vibrational frequencies would be easy to see. The IR spectrum of pure 2-d₁-MEICl, N=0.0, in which hydrogen bonding might be important, showed an IR peak at 2267cm⁻¹ for the C-2 deuterium bond and C-H vibrations as a broad band in the region from 2990 to about 3200cm⁻¹ with a maximum at 3058cm⁻¹. The IR spectra of N=0.33 and N=0.50 melts of 2-d₁-MEICl/AlCl₃ are shown in Fig. 8. The IR spectrum of the N=0.50 melt shows the C-2 deuterium stretch at 2350 cm⁻¹. In the spectrum of the N=0.33 melt, this band is reduced in intensity and a new band at 2283cm⁻¹ has appeared, presumably due to an interaction of the C-2 deuterium with Cl⁻. However, this shift
in frequency due to Cl\(^-\) interaction also appears for the vinylic C-H stretching frequencies. If the interaction were due to only hydrogen-bonding, no significant shifts would be expected in the C-4 and C-5 hydrogen stretching frequencies. In the spectrum of the N=0.50 melt, the C-4 and C-5 hydrogen stretching bands appear at 3170 and 3149 cm\(^{-1}\). In the spectrum of the N=0.33 melt, these bands are reduced in intensity and the broad Cl\(^-\)-interaction band at 3079 cm\(^{-1}\) appears. Thus the C-H stretches on C-2, C-4, and C-5 are all being affected by Cl\(^-\) in essentially the same way. We conclude that this non-specific interaction cannot be characterized as hydrogen bonding.

II. Theoretical

While AM1 and MNDO are parameterized using gas phase data, MNDO results were previously shown to be consistent with the experimental IR spectra of the Al\(_2\)Cl\(_7\) in molten KAl\(_2\)Cl\(_7\) (14). For the isolated MEI\(^+\) ion, AMI results (Fig. 9) again provide a reasonable model of the 2900–3300 cm\(^{-1}\) region of the experimental IR spectrum results for the N=0.50 AlCl\(_3\) melt, in which there is no Cl\(^-\) to interact with the MEI\(^+\). While the intensity of the C-2 hydrogen stretch is overestimated, its position, as well as the positions and relative sizes of alkenyl and alkyl C-H stretches, are well represented.

When a Cl\(^-\) was positioned to hydrogen bond to the C-2-hydrogen and the geometry optimized, the C-2-hydrogen and H-Cl distances optimizing at 1.56 and 1.40 Å, respectively. Consequently, the C-2-hydrogen stretch was strongly coupled with the H-Cl stretch; two vibrations appearing at 1565 and 711 cm\(^{-1}\). These results are no doubt exaggerated due to AM1 underestimating the stability of the chloride anion (\(\Delta H_f = -37.7\) kcal/mol calcd, -55.9 kcal/mol exptl [15]). Interestingly, however, when an AlCl\(_4\) \(^-\) was substituted for the Cl\(^-\), the interaction between one chlorine atom and the C-2 hydrogen was strong enough to shift the C-2-hydrogen stretch from 3118 cm\(^{-1}\) in the isolated MEI\(^+\) to 2492 cm\(^{-1}\) in the complex. This shift is too large to be explained fully by the change in reduced mass. While this result is again exaggerated due to the treatment of the complex as a totally isolated ion pair, it is reasonable to expect that a hydrogen bond between a Cl\(^-\) and the C-2 hydrogen would cause a larger red shift in the C-2-hydrogen stretch than to 3049 cm\(^{-1}\).

According to AMI calculations, the \(\psi_r\) orbital of the C-2 contributes 50% of the lowest unoccupied molecular orbital (LUMO) of the isolated MEI\(^+\). When a Cl\(^-\) was centered above the ring and the geometry optimized, the Cl\(^-\) shifted to form a covalent bond with the C-2. The heat of formation for this covalent species was 4.6 kcal/mol less than that for the "hydrogen bonded" complex, and the frequency of the C-2 hydrogen stretch was predicted to be 2951 cm\(^{-1}\). When a second MEI\(^+\) was positioned parallel to the first MEI\(^+\), with the Cl\(^-\) centered between the two rings, and the geometry fully optimized, a minimum was located with the Cl\(^-\) located slightly in
front of the two C-2's and nearly equidistant from both (C-2-H 2.48Å, C-2'-H 2.42Å). This complex was predicted to be 8.4 kcal/mol more stable than the covalent C6H11N2Cl species plus an isolated MEI+. The C-2-hydrogen stretch for the complex was red shifted relative to that of the isolated MEI+, its frequency being 3107cm⁻¹. It is not unexpected that this is higher than the 3049cm⁻¹ observed experimentally, since calculated vibrational frequencies are typically too high (10).

CONCLUSION

In basic melts of MEICl and AlCl₃, Cl⁻ interacts with MEI⁺ to cause similar shifts in the frequencies of the C-2, C-4, and C-5 hydrogen stretches. This nonspecific interaction cannot be characterized as hydrogen bonding. In fact, it is consistent with a stack model for the interaction of MEI⁺ with the anions in the melt.
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12. The MNDO heat of formation for AlCl₄⁻ is -273.4 kcal/mol, the Al–Cl bond length is 2.15 Å, and the atomic charges on Al and Cl are 0.90 and -0.47, respectively. The corresponding AM1 results are -263.2 kcal/mol, 2.07 Å, 0.64 and -0.41.

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Fig. 1: Proton chemical shifts in MEICl-AlCl₃ melt vs N at 30°C (•) H-2, (A) H-4 and H-5 (average of unresolved doublet), (■) N-CH₂ protons, (o) N-CH₃ protons, (A) CH₃ protons. The chemical shifts were referenced to Me₂SO external reference (13).

Fig. 2: IR spectra of CH bands of MEI⁺ in MEICl-AlCl₃ melt at: (a) N=0.50, (b) N=0.40, (c) N=0.33.

Fig. 3: IR spectra of CH bands of MEI⁺ in N=0.33 melt and nonaqueous solutions of this melt. (a) dichloromethane-d₂, (b) benzene-d₆, (c) neat melt.
Figure 4: IR spectra of CH bands of MEI⁺ in two different N=0.33 room temperature melts. (a) MEIBr-AlBr₃, (b) MEICl-AlCl₃.

Figure 5: IR spectra of CH bands of MMEI⁺ in MMEICl-AlCl₃ melt at: (a) N=0.33, T=140°C, (b) N=0.50, T=100°C.

Figure 6: IR spectra of CH bands of (a) MEI⁺ and (b) MMEI⁺ both in N=0.50 melt.
Figure 7: IR spectra showing the 1595 cm\(^{-1}\) band as function of N for a MEICl-AlCl\(_3\) melt:
(a) N=0.50, (b) N=0.40, (c) N=0.33.

Figure 8: IR spectra of 2-\(d_1\)-MEICl-AlCl\(_3\) melt at:
(a) N=0.33, (b) N=0.50.

Figure 9: IR spectra of MEICl-AlCl\(_3\) of different compositions. The bands obtained using AM1 calculations for the gas phase MEI\(^+\) are shown as straight lines.