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DIALKYLIMIDAZOLIUM CHLOROALUMINATES: *AB INITIO* CALCULATIONS, RAMAN AND NEUTRON SCATTERING MEASUREMENTS

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Dialkylimidazolium Chloroaluminates: *Ab Initio* Calculations, Raman and Neutron Scattering Measurements

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Abstract

The Raman and neutron scattering spectra of 46 mol% $AlCl_3$ -54 mol% 1-ethyl-3-methyl imidazolium chloride (EMIC) and 67 mol% $AlCl_3$ - 33 mol% EMIC melts are presented. *Ab initio* molecular orbital calculations have been carried out on structures of chloroaluminate anion and EMI cation and the interaction between anion and cation.

Introduction

A new class of room-temperature molten salts, $AlCl_3$-1-ethyl-3-methyl imidazolium (EMI) chloride[1] has been receiving renewed interest since their recent application in the electroplating of Al on steel.[2] The chemistry of these systems is quite similar to that of the chloroaluminates and it has been shown that the ionic species formed are strongly dependent on the acidity or basicity of the melts. In basic solutions, i.e. $AlCl_3 < 0.5$, the major species is $AlCl_4^-$. The major equilibrium describing acid-base properties of tetrachloroaluminate ionic liquids is the dissociation of the tetrachloroaluminate anion:

$$2AlCl_4^- \rightarrow Al_2Cl_7^- + Cl^- .$$

At more acidic compositions, $Al_2Cl_7^-$, which consists of two $AlCl_4^-$ tetrahedra sharing a corner, becomes the predominant species. These species have been identified from electrochemical techniques,[3] NMR (^1H, ^{13}C, ^{27}Al, ^{35}Cl),[4-6] and IR.[7]

In this paper, we present results of Raman and neutron scattering experiments on selected melts as well as *ab initio* molecular orbital calculations of the structure and the vibrational modes associated with $AlCl_4^-$, $Al_2Cl_7^-$, and the EMI cation.

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Experimental Methods

A. Raman spectroscopy

The Raman spectra were measured using a Laser Ionics 1400-15 ion laser, SPEX model 1877 triple monochromator, Photometrics Model CH210 liquid nitrogen cooled CCD detector, and argon 457.9 and 476.5 nm excitation. The spectra taken for 46 and 67 mol% $AlCl_3$ - EMIC melts were recorded in the range of 150-750 cm^{-1}. The wavelength of 476.5 nm was used to measure spectrum for 46 mol% $AlCl_3$ melt. For 67 mol% $AlCl_3$ melt, two wavelengths of 476.5 and 457.9 nm were used because of the noise of background. When the 476.5 nm wavelength was used, the plasma was seen on the spectra at ~500 cm^{-1}.

The samples were prepared by mixing highly anhydrous $AlCl_3$ with EMIC at 60°C. The weighing and handling of the samples were done in a glove box, where the H_2O and O_2 levels were maintained at less than 2 ppm.

B. Neutron spectroscopy

Inelastic-scattering measurements were performed using the Low-Resolution Medium-Energy Chopper Spectrometer (LRMECS) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Two compositions, 46 and 67 mol% of $AlCl_3$ - EMIC melts, were studied at 25, 243 and 297 K with neutron incident energies of 60, 160 and 400 meV. (1 meV is equivalent to 8.066 cm^{-1}, and these two units of energy will be used interchangeably in this paper.) The measurements provided a characterization of the vibrational spectra of this system from 5 (40 cm^{-1}) to 350 meV (2823 cm^{-1}) for both the liquid and solid state.

C. Theory

The *ab initio* molecular orbital calculations[8] were carried out to determine equilibrium structure and harmonic vibrational frequencies. The polarized split valence 6-31G* basis was used. All of the *ab initio* molecular orbital calculations were done at the Hartree Fock (HF) level of theory. Computations were also carried out using the MNDO[9] (modified neglect of differential overlap) semiempirical molecular orbital method. The HF/6-31G* basis set is expected to give vibrational frequencies that are about 5 - 10% too high on the basis of previous studies of a large number of molecules. MNDO has done reasonably well in calculations of vibrational frequencies of chloroaluminates and organic molecules.

Results

A. Raman spectroscopy

The Raman spectra of $AlCl_3$-EMIC melts are presented in Fig. 1. The numerical values for the bands are given in Table 1. For the $AlCl_3$-EMIC melts the investigation was carried out at 25°C. Seven absorption bands were observed for the 46 mol% $AlCl_3$

- 54 mol% EMIC melt and 11 bands were observed for the 67 mol% $AlCl_3$ - 33 mol% EMIC melt in the measurement range of 150 - 750 cm^{-1}. Polarization measurements were also carried out and the results are listed in Table 1.

B. Neutron spectroscopy

Unlike Raman scattering, neutron scattering by atomic nuclei is not restricted by selection rules. The neutron spectra, after being averaged over a wide range of detector angles, represent the vibrational density-of-states (DOS) weighted by the nuclear scattering cross sections of the atomic species in the system. Since H has a scattering cross section 5-10 times larger than those of the others atoms in $AlCl_3$-EMIC melts, the observed spectrum reflects by and large the atomic motions that involve H atoms. Fig. 2 displays the observed neutron-weighted vibrational DOS obtained from the 60-meV runs for the 46 mol% $AlCl_3$ - 54 mol% EMIC and the 67 mol% $AlCl_3$ - 33 mol% EMIC at 25 K. The intensities are normalized to the total scattering cross section of the melts. The two spectra bear strong resemblance because the prominent features arise from motions involving the 11 H atoms in the EMIC cations. A close examination of the two spectra, however, reveals some subtle differences which are likely due to the different atomic vibrations associated with the $AlCl_4^-$ and the $Al_2Cl_7^-$ anions. The neutron spectra at higher energies obtained from the 160 and 400 meV runs show even smaller differences between the two compositions, indicating that the vibrational DOS above 60 meV are mainly due to motion of the cations.

C. *Ab initio* calculations

$AlCl_4^-$: Tetrachloroaluminate anion has been studied previously at the HF/6-31G* and MNDO levels of theory.[10,11] At the HF/6-31G* level, the anion has a T_d structure with a bondlength of 2.17Å. The HF/6-31G* vibrational frequencies were in good agreement with experimental measurements on the anion in various melts.[11] The HF/6-31G* Raman activity is shown in Fig. 3.

$Al_2Cl_7^-$: The $Al_2Cl_7^-$ anion has been the subject of several previous theoretical studies. Davis et al[12] reported a MNDO study of this anion including structure and vibrational frequencies. Curtiss[13] reported an *ab initio* molecular orbital study using the 3-21G basis set. Both studies found $Al_2Cl_7^-$ to have a C_2 structure with a bent AlClAl angle (MNDO: 124.9°; 3-21G: 132.4°). The HF/6-31G* calculations of this work also give a C_2 structure (AlClAl angle = 123.4°). The HF/6-31G* Raman activity is shown in Fig. 4.

1-ethyl-3-methyl imidazolium cation (EMI^+): At the HF/6-31G* and MNDO levels of theory the fully optimized cation has a structure with C_1 symmetry. The EMI^+ cation has 51 vibrational frequencies. The HF/6-31G* Raman active frequencies in the range 0 - 800 cm^{-1} are shown in Fig. 5. The HF/6-31G* structure is shown in Fig. 6.

$AlCl_4^-$ and EMI^+: The H_1 hydrogen of EMI cation (see Fig. 6) has a large positive charge suggesting that it is the most favorable position for interaction of the $AlCl_4^-$ anion. The corner-, edge-, and face- interactions of $AlCl_4^-$ with EMI^+ were considered in full optimizations at the MNDO level. The most stable structure was the face-bridged structure. The geometries of EMI^+ and $AlCl_4^-$ showed only small changes in the complex. The major shifts in the MNDO vibrational frequencies are listed in Table 2.

$Al_2Cl_7^-$ and EMI^+: Four possible structures for the complex between $Al_2Cl_7^-$ and EMI^+ were considered. Full optimizations were carried out at the MNDO level. The most stable structure was the face-bridged structure. The geometries of EMI^+ and $Al_2Cl_7^-$ also showed only small changes in the complex.

Discussion

The Raman spectra in Fig. 1 and frequencies in Table 1 are characterized by bands which are dependent on the $AlCl_3$ content of the melt as well as ones that do not change significantly with composition. The Raman active vibrational frequencies from the HF/6-31G* calculations are shown in Figs. 3 - 5. The two absorption bands at 181 and 350 cm^{-1} for 46 mol% $AlCl_3$ melt disappeared for 67 mol% $AlCl_3$. They are assigned to $AlCl_4^-$, because it is well known that $AlCl_4^-$ is the dominant species in the basic region. They are also in good agreement with the HF/6-31G* predictions for $AlCl_4^-$ of 188 and 353 cm^{-1}. The neutron spectrum of the 67 mol% $AlCl_3$ melt also shows a small drop in intensity at 186 cm^{-1} (23 meV) and 347 cm^{-1} (43 meV) as compared to the spectrum of the 46 mod% $AlCl_3$ melt (see Fig. 2). In addition, the spectrum of the 67 mol% $AlCl_3$ melt shows extra intensities near 153, 216 and 380 cm^{-1} (19, 27 and 47 meV). The HF/6-31G* calculations also predict weaker bands at 121 and 511 cm^{-1} which are not observed in both the Raman and neutron data. Four Raman bands were found for 67 mol% $AlCl_3$ melt (see Fig. 1). These bands are assigned to $Al_2Cl_7^-$ because this anion is known to be dominant in acidic melts. This is confirmed by the HF/6-31G* results which predict absorptions at 162, 311, 444, and 558 cm^{-1}. These are in good agreement with the experimental absorptions. The absorption bands of EMI^+ cation should be present in all of the melts. The bands at 241, 383, 596, and 700 cm^{-1} in Fig. 1 are assigned to EMI^+. The HF/6-31G* calculations predict vibrational frequencies at 249, 403, 632, and 700 cm^{-1} which are close to the observed bands. The neutron results indicate that the broad bands centered at 100 cm^{-1} (12.4 meV), 240 cm^{-1} (30 meV) and 298 cm^{-1} (37 meV) originate from H vibrations of the EMIC anions. The first band in the 40 - 130 cm^{-1} region arises from cooperative motions of the complex structure. Some of these modes are given as new frequencies in the $AlCl_4^-$....EMI^+ calculations in Table 2. Overall, the agreement between the predicted and observed frequencies is good and supports the existence of $AlCl_4^-$ and $Al_2Cl_7^-$ anions in the $AlCl_3$ - EMIC melts in the range 46 - 67 mol% $AlCl_3$.

The significant shifts from MNDO calculations in the vibrational frequencies due to interaction of a single anion ($AlCl_4^-$) with EMI^+ cation are shown in Table 2. The shifts are small (<20 cm^{-1}) with the exception of the 528 cm^{-1} band which split into 3 bands (499, 515, and 573 cm^{-1}). There is some evidence for a weak band at around 510 cm^{-1} in the Raman spectra.

Conclusion

A better understanding of the physical and chemical properties of $AlCl_3$ - EMIC melts has been achieved by combining *ab initio* calculations with Raman and neutron spectroscopy. $AlCl_4^-$ has a tetrahedral structure, $Al_2Cl_7^-$ has a C_2 structure (AlClAl bond angle = 123.4°), and EMI^+ has a C_1 structure. The Raman bands at 181, 350 cm^{-1} were assigned to $AlCl_4^-$ and the Raman bands at 162, 313, 429 and 562 cm^{-1} were assigned to $Al_2Cl_7^-$. The Raman bands of 241, 383, 596 and 700 cm^{-1} were assigned to EMI^+. The neutron results also agree qualitatively with these assignments. The calculations on the interaction of a single anion ($AlCl_4^-$ or $Al_2Cl_7^-$) with a single cation (EMI^+) show little effect on the structures; however, some of the vibrational frequencies were shifted.

Acknowledgments

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Table 1. Raman frequencies (cm^{-1}) of the $AlCl_3$-EMIC system

46 mol% $AlCl_3$	67 mol% $AlCl_3$
	162 dp
181 dp	
241 dp	241 dp
	313 p
350 p	
383 p?	387 p?
445 p	429 p
	504 dp
	562 dp?
597 p	593 p
	680 dp
701 dp	695 dp
	734 dp

Table 2. Comparison of frequencies (in cm^{-1}) of isolated ions and the $AlCl_4^-$ ....EMI^+ complex from MNDO calculations.[a]

	$AlCl_4^-$ ...EMI^+ complex	Isolated $AlCl_4^-$ and EMI^+
New freq.	6.4	
	18.4	
	20.9	
	41.2	
	74.4	
	93.1	
$AlCl_4^-$	109.9	107.8
	112.0	107.8
	499.5	528.2
	514.8	528.2
	572.9	528.2
EMI^+	135.0	122.5
	897.0	906.2
	964.0	945.1
	964.3	974.1
	1533.0	1518.1
	3380.4	3407.3
	3457.2	3440.5
	3468.9	3452.5

[a] The frequencies correspond to the ions listed in the first column. Only the frequencies that have the largest changes are listed. (The first six frequencies correspond to new modes).

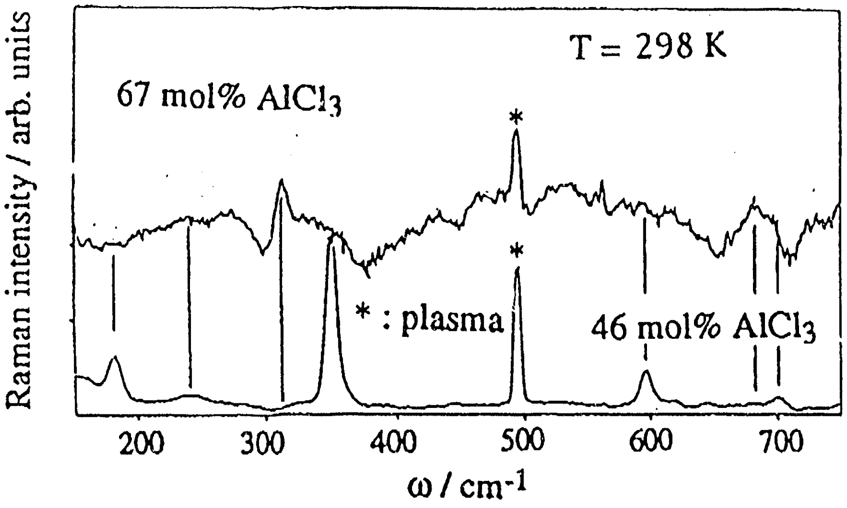

Figure 1. Measured Raman spectra of AlCl3 - EMIC.

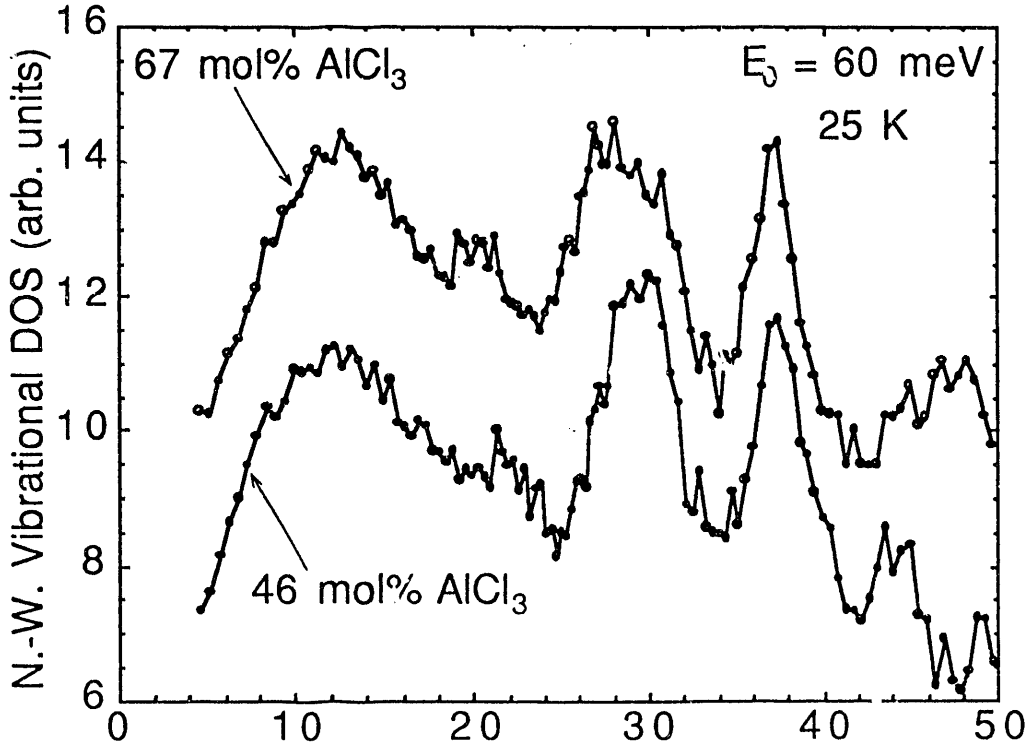

Figure 2. The observed neutron-weighted vibrational spectra of 46 mol% AlCl3 - 54 mol% EMIC and 67 mol% AlCl3 - 33 mol% EMIC at 25 K. The upper spectrum is displaced by 5 units in the vertical direction.

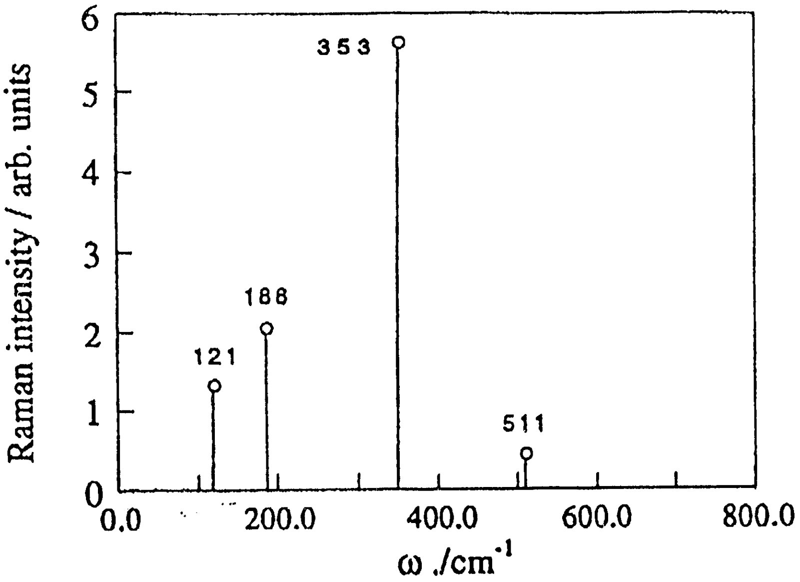

Figure 3. Calculated Raman activity of $AlCl_4^-$.

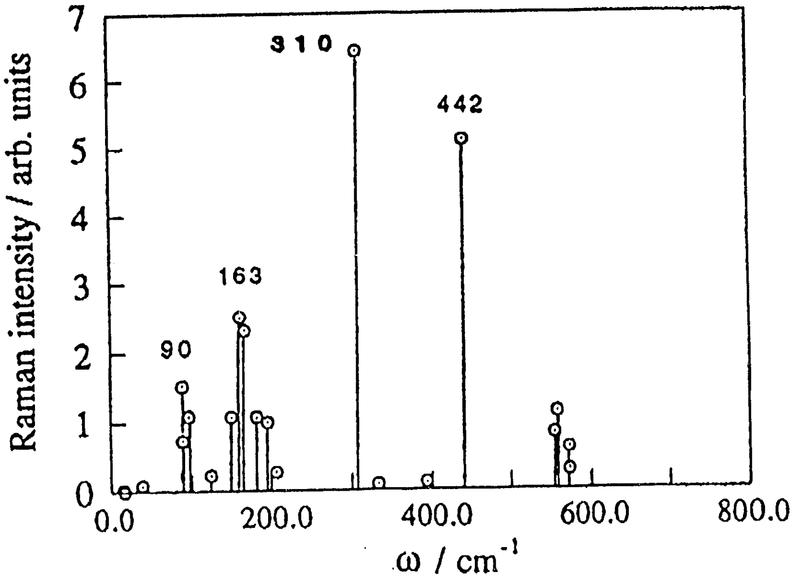

Figure 4. Calculated Raman activity of EMI^+.

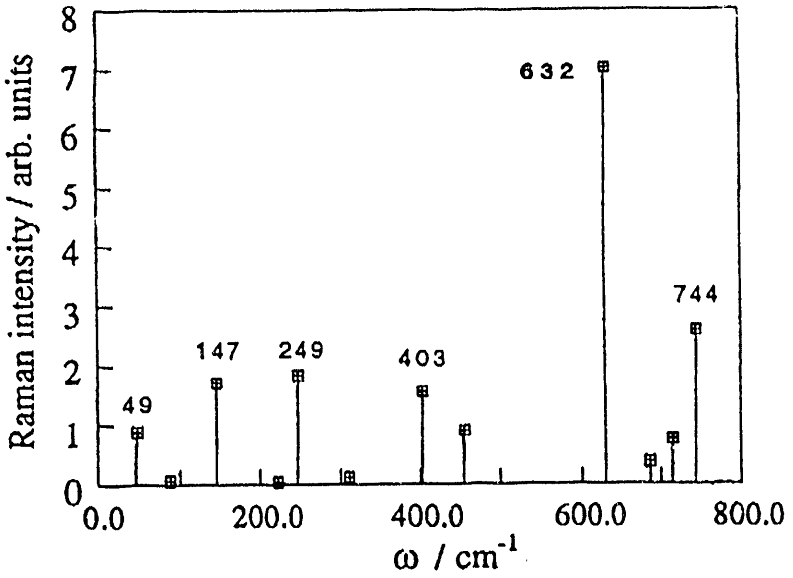

Figure 5 Calculated Raman activity of $Al_2Cl_7^-$.

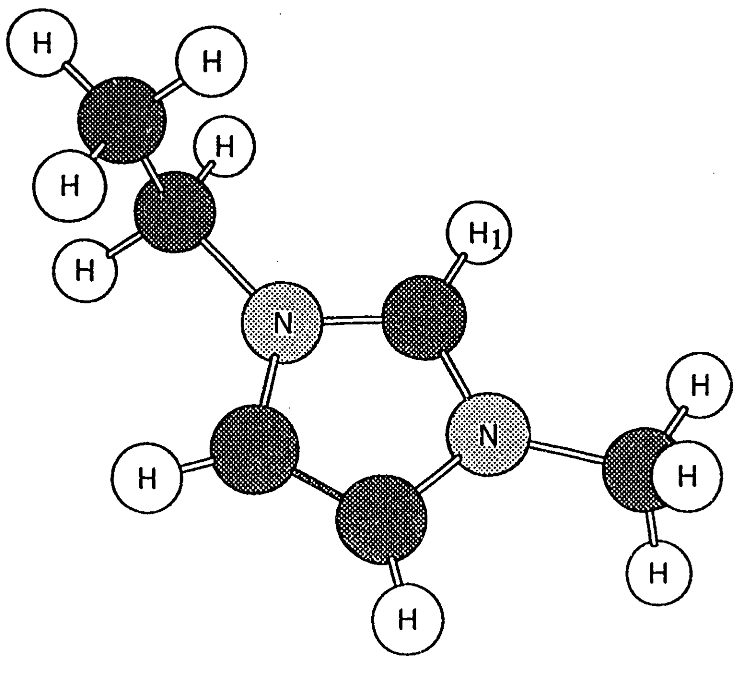

Figure 6. Structure of EMI cation from HF / 6-31G* calculations

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