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Neutron Diffraction Study of Aluminum Chloride Imidazolium Chloride Molten Salts

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ABSTRACT

The structure of molten mixtures of $(AlCl_3)_x$(1-ethyl-3-methylimidazolium chloride)$_{1-x}$ was investigated by neutron diffraction techniques for x=0.46, 0.50, 0.60 and 0.67. Results derived from earlier *ab initio* molecular orbital (6-31G* basis set) computations for $AlCl_4^-$, $Al_2Cl_7^-$, and EMI^+ were used to calculate the diffraction patterns; the calculated contributions of each species are thus obtained and the overall results are in good agreement with the measurements.

INTRODUCTION

Mixtures of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (EMIC) are technologically relevant room-temperature molten salts.(1,2) To understand their structure, we have initiated a series of studies involving neutron scattering, Raman spectroscopy,(4) ^{27}Al and ^{35}Cl NMR,(4) and ab initio calculations.(4) In this paper, we report results obtained by neutron diffraction measurements.

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EXPERIMENTAL

Neutron diffraction studies were carried out to obtain the structure and configuration of the ionic species. The measurements were made on the GLAD instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory. The samples were prepared by mixing highly anhydrous $AlCl_3$ with fully deuterated EMIC in a glove box, where the H_2O and O_2 levels were maintained at less that 2 ppm. The melts were sealed under vacuum in quartz tubes of 1 mm wall thickness and inner diameter of 3 mm. Four compositions, 46, 50, 60 and 67 mol% of $AlCl_3$, were selected. Measurements were made on each sample at room temperature, 298 K, followed by a similar measurement on an empty fused silica container of the same dimension and at the same temperature for purposes of instrument calibration and data normalization; measurements were also carried out on a 0.64 cm diameter vanadium standard and with the spectrometer empty, both at 298 K. The data were analyzed with standard procedures developed at Argonne for glass and liquid diffraction data incorporating simple corrections for multiple scattering and inelasticity effects.

The measured differential cross section per atom $d\sigma_a / d\Omega$ is reduced to the total structure factor $S(Q)$ according to

$$d\sigma_a / d\Omega = \langle \bar{b} \rangle^2 [S(Q) - 1] + \langle \overline{b^2} \rangle \tag{1}$$

where

$$\langle \bar{b} \rangle = \sum_i x_i \bar{b}_i, \tag{2}$$

and

$$\langle \overline{b^2} \rangle = \sum_i x_i \overline{b_i^2} \tag{3}$$

Here x_i denotes the concentration of the ith component and $\bar{b}_i$ and $\overline{b_i^2}$ are the mean and mean-square scattering amplitudes, respectively, for component i averaged over the nuclear isotopes and spins for that component. In the case of a multicomponent system, $S(Q)$ is, by definition, a weighted sum of partial structure factors, $S_{ij}(Q)$:

$$S(Q) = \sum_{ij} \sqrt{x_i x_j \, \overline{b_i}\,\overline{b_j}} S_{ij}(Q) / \langle \overline{b} \rangle^2 \tag{4}$$

RESULTS

Fig. 1 shows the structure factors $S(Q)$ as measured for the four solutions. These are rather similar over the range $Q > 5$ Å^{-1}. However, they show differences at relatively low Q, in the range 1-5 Å^{-1}, which must be due to the interactions between the anions Cl_4^-, $Al_2Cl_7^-$, and $AlCl_4^-$, and the cation, EMI^+.

The real space functions complement the reciprocal-space information. The total correlation $T(r)$ and the average pair distribution function $g(r)$ are derived from the function

$$D(r) = \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \tag{5}$$

from which it follows that:

$$T(r) = D(r) + 4\pi\rho r \tag{6}$$

$$g(r) = 1 + D(r) / 4\pi\rho r \tag{7}$$

The $T(r)$ and $g(r)$ for the four melts are shown in Figs. 2 and 3, respectively. Some information on the interatomic distances can be obtained from these plots. However, it is difficult to make a detailed interpretation because of the complex nature of the systems. The structures of $AlCl_4^-$, $Al_2Cl_7^-$, and EMI^+ were calculated by the *ab initio* molecular orbital (6-31G* basis set) method.(14) The $AlCl_4^-$ anion has a T_d structure with a Al-Cl bond length of 2.17 Å and Cl-Cl bond length of 3.54 Å. The $Al_2Cl_7^-$ anion has a C_2 structure with a bent Al-Cl-Al angle of 123.4 °. The Al-Cl distance in the bridge is 2.32 Å, and that of the terminal group is 2.13 Å. The EMI^+ cation has a structure with C_1 symmetry. which is shown in Fig. 4. The torsion angle of the terminal $-CH_3$, i.e., $H_6C_4N_2$ dihedral angle, of the ethyl group is 73 °. Selected geometrical parameters from the HF/6-31G* structure are listed in Table 1.

The major anions are expected to be $AlCl_4^-$ and Cl^- for the 46 mol%, $AlCl_4^-$ for the 50 mol%, $AlCl_4^-$ and $Al_2Cl_7^-$ for the 60 mol%, and $Al_2Cl_7^-$ for the

67 mol% $AlCl_3$ melt. If correlations between molecular orientations and positions can be neglected, $S(Q)$ takes the form:

$$S(Q) = f_1(Q) + f_2(Q)\left[S_c(Q) - 1\right] + 1 - \frac{\langle \bar{b}^2 \rangle}{\langle \bar{b} \rangle^2} \tag{8}$$

where $f_1(Q)$ is an intramolecular form factor, and $f_2(Q)$ and $S_c(Q)$ are an intermolecular form factor and a molecular center structure factor, respectively. For the first three compositions, the intramolecular part (first term in Eq. (8)) of the diffraction patterns were calculated for $AlCl_4^-$ and EMI^+. The results shown in Fig. 5 are in good agreement with the experiments over the range $Q > 3$ Å^{-1}; at lower Q, one would expect the intermolecular part to dominate (second term in Eq. (8)). For the 67 mol% $AlCl_3$ melt, the calculations were carried out for $Al_2Cl_7^-$ and EMI^+ again only for the intramolecular contributions. Fig. 6 shows both measured and calculated $S(Q)$: the calculations represent the measurements surprisingly well.

In conclusion, we have shown that it is possible to derive detailed information by combining experimental techniques probing the atomic structure and *ab initio* calculations of the structure of the main ionic species known to be present in the melts. For $Q > 3$ Å^{-1}, the interpretation that we propose has been validated: it remains to extract information about the interactions between anion and cation by analyzing $S(Q)$ in the range Q =1-3 Å^{-1}.

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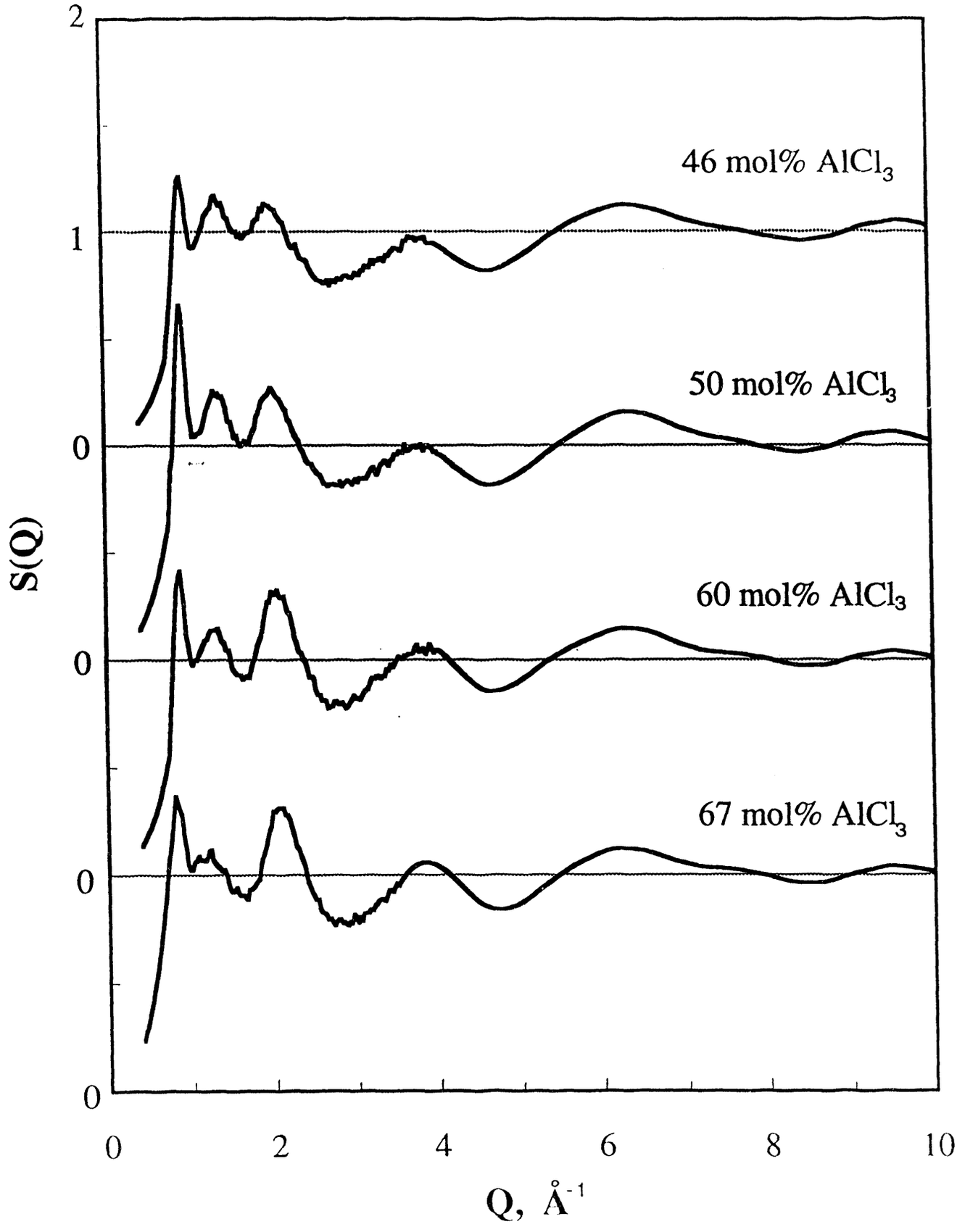

Fig. 1 Structure factors of $AlCl_3$-EMIC.

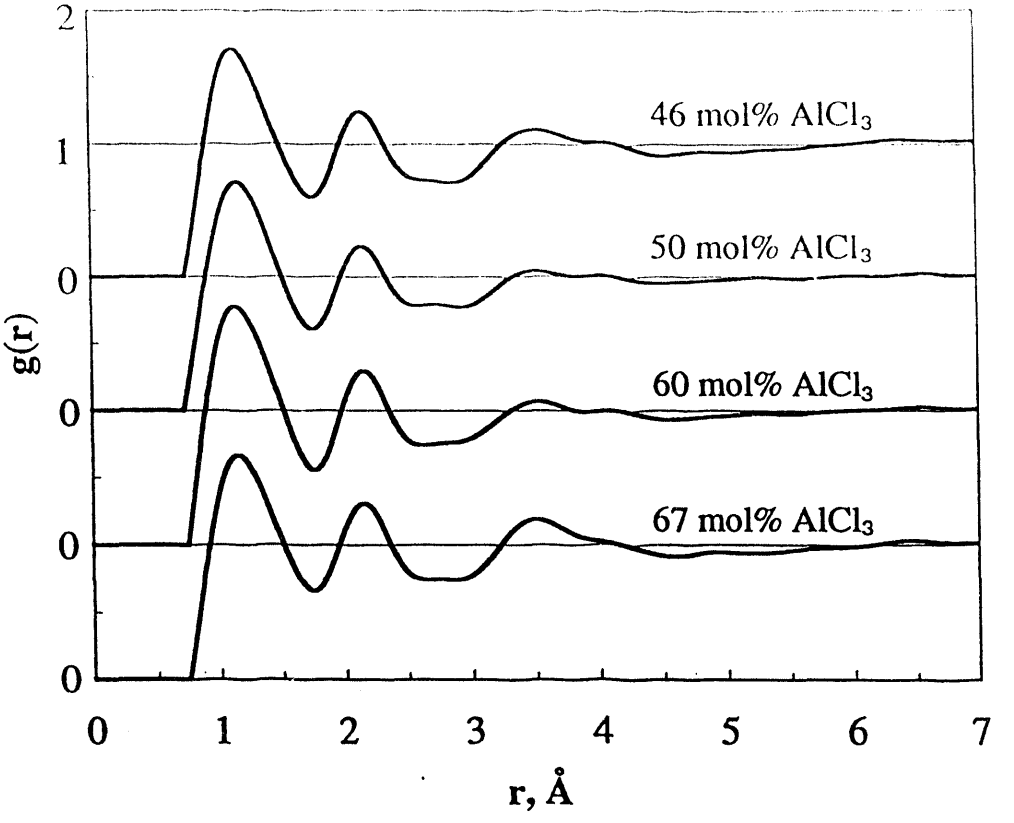

Fig. 2 Pair distribution functions of $AlCl_3$-EMIC.

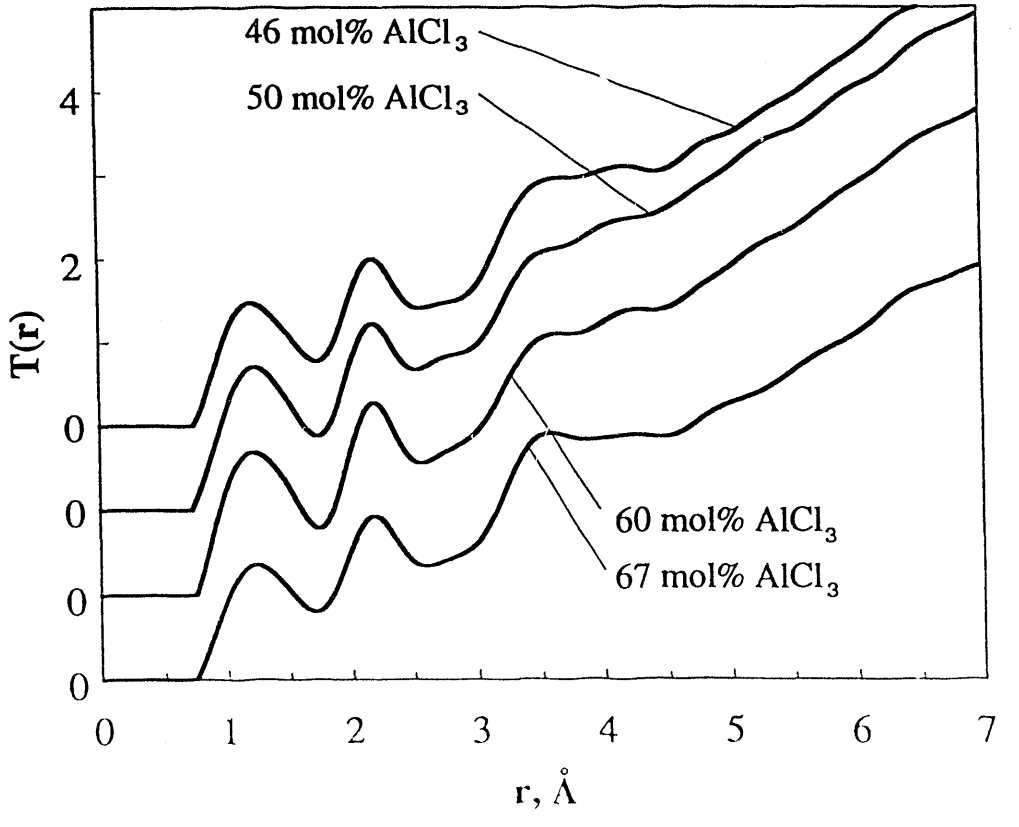

Fig. 3 Total correlation functions of $AlCl_3$-EMIC.

Table 1. EMI^+ geometry calculated by 6-31G* calculations.

Geometry	6-31G*
C_1N_1	1.32
C_1N_2	1.31
N_1C_2	1.38
N_2C_3	1.38
C_2C_3	1.34
N_1C_4	1.47
N_2C_5	1.48
C_5C_6	1.52
$<N_1C_1N_2$	110
$<C_1N_1C_2$	108
$<C_1N_2C_3$	108
$<N_1C_2C_3$	107
$<N_2C_3C_2$	107
$<C_1N_1C_4$	126
$<C_1N_2C_5$	126
$<N_2C_5C_6$	112

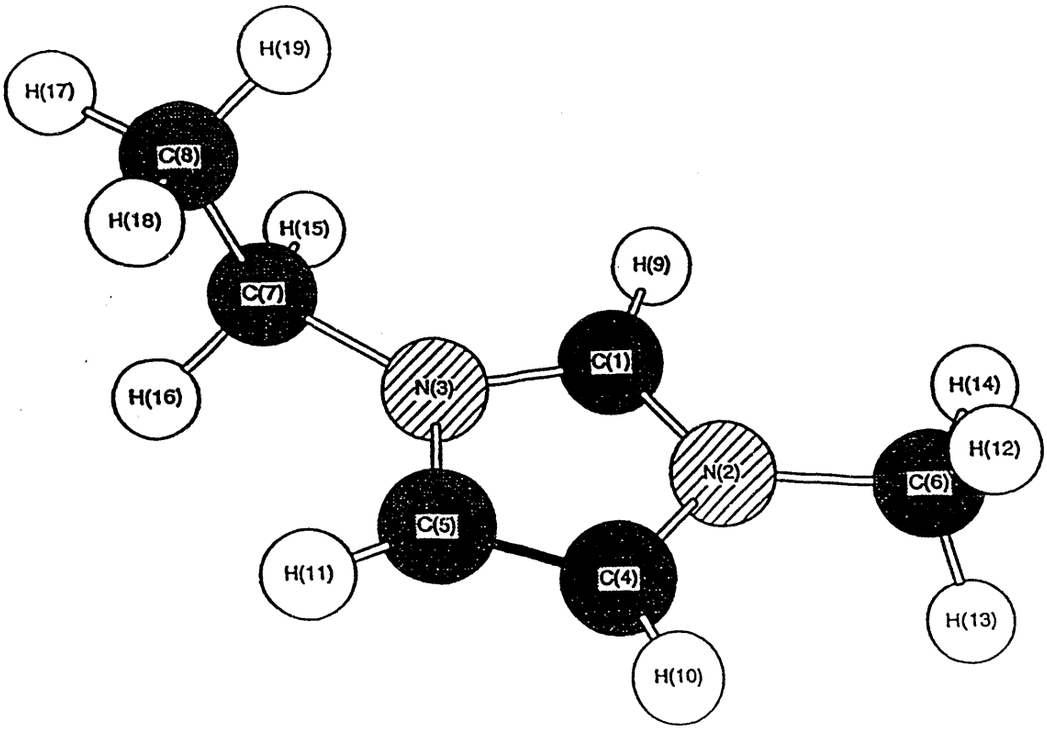

Fig. 4 HF/6-31G* optimized structure for EMI^+ cation.

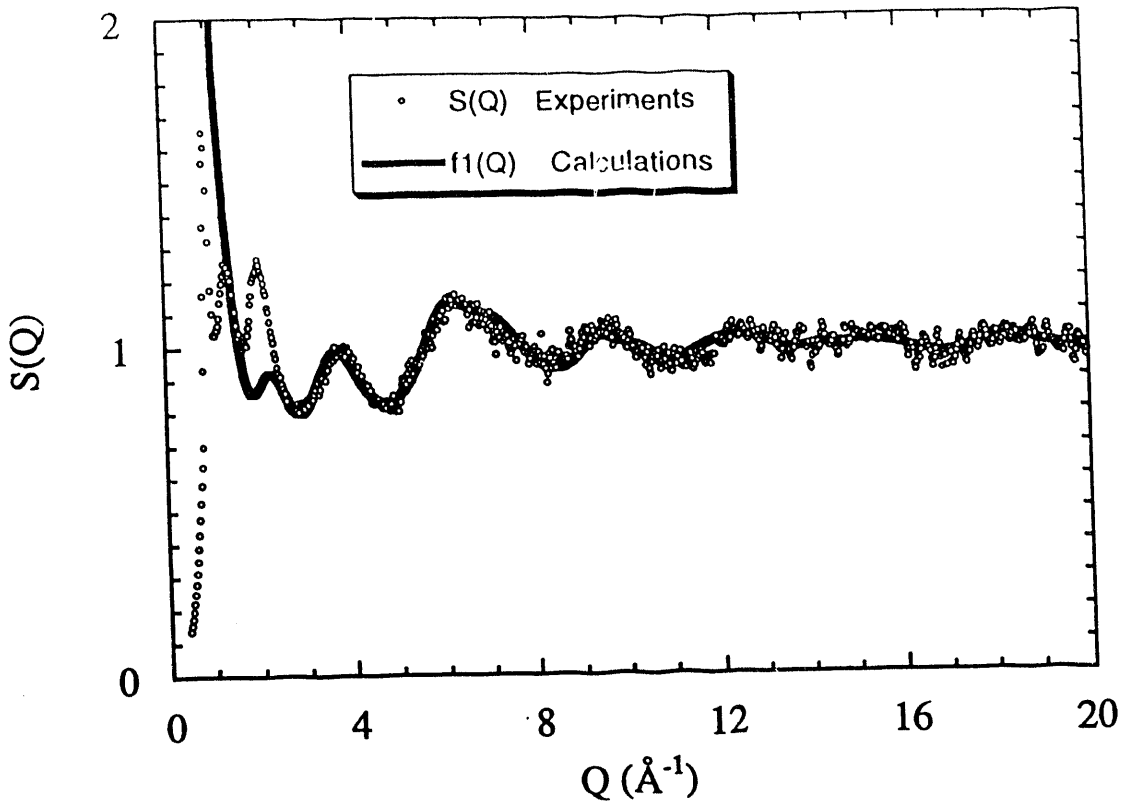

Fig. 5 Structure factors of 50mol% $AlCl_3$ melt.

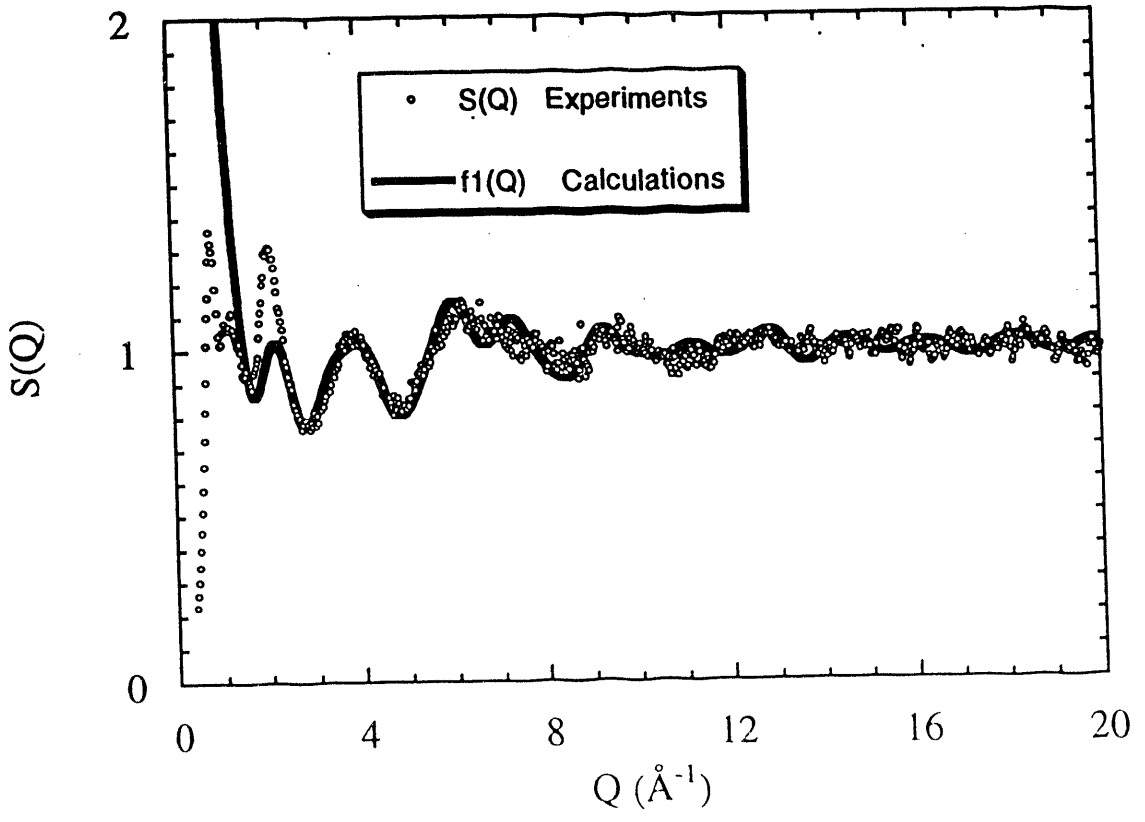

Fig. 6 Structure factors of 67mol% $AlCl_3$ melt.

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