MOLECULAR DYNAMICS CALCULATIONS OF MAX₄ MELTS
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ABSTRACT

Molecular dynamics calculations for MAX₄ melts are reported for two different sets of cation/anion radius ratios which were chosen so as to emulate melts such as chloroaluminates and fluoroyttriates. The results are expressed as radial distribution functions, the angular distributions of selected triplets and the number of ions which have particular integer values of the coordination numbers. For the small radius ratio, the A⁺³ ion is tetrahedrally coordinated and the structure of this completely ionic melt is consistent with the presence of X⁻, AX₄⁺, A₂X₇⁻ and A₃X₁₀⁻ species which equilibrate by the reactions 2AX₄⁺ ↔ A₂X₇⁻ + X⁻ and 3AX₄⁺ ↔ A₃X₁₀⁻ + 2X⁻. For the large radius ratio, the A⁺³ cations are mostly octahedrally coordinated and there is considerable bridging between AX₃⁻ⁿ moieties which leads to a tendency for long range order.

INTRODUCTION

The concept of complexing in binary molten salt mixtures has been used for structural interpretations of thermodynamic, spectroscopic and kinetic data in a class of strongly interacting melts such as the chloroaluminates.¹⁻⁷ The system NaCl-AlCl₃ is perhaps the most thoroughly studied complexing melt. Consequently, in this paper, we will focus largely on melts in which the interionic separations are similar to those expected in NaAlCl₄ melts. The main purpose is to explore the characteristic structures in this melt for comparison with those deduced from experiment. In addition, we will also examine the structures in a melt with a larger cation/anion radius ratio and a larger average coordination number of the A⁺³ ions.

MOLECULAR DYNAMICS COMPUTATIONS

Calculations were performed on an assemblage of 83 M⁺, 83 A⁺³ and 332 X⁻ ions which interacted according to the potential⁸
\[ u_{ij} = Z_i Z_j e^2 / r + B \exp[A(\sigma_i + \sigma_j - r)] \]  

where \( e \) is the electronic charge, \( Z_k \) is the integral number of charges on the \( k \)'th ion and has the same sign as the charge, \( r \) is the distance between ions, the constants \( A = 3.155 \text{Å}^{-1}, B = 0.190(10^{-12}) \text{erg} \) and \( \sigma_k \) is the 'radius' of the \( k \)'th ion. Two sets of radii were chosen with different values of \( \sigma_A / \sigma_X \) while keeping both \( \sigma_A + \sigma_X \) and \( \sigma_M + \sigma_X \) constant and at values which lead to interionic distances which correspond to those of Al\(^{+3}\)-Cl\(^-\) and Na\(^+\)-Cl\(^-\) respectively. The two sets of values of \( (\sigma_M, \sigma_A, \sigma_X) \) chosen (in Å) are potential 1 (1.352, 1.372, 1.578) and potential 2 (1.052, 1.072, 1.878).

The molecular dynamics calculations generated an ensemble of consecutive configurations of the 498 particles at about \( T = 500 \text{K} \). Details of the calculation which are for constant but very low pressure are discussed elsewhere. The time steps were \( 10^{-15} \) seconds and typically about \( 12,000 \) time steps were run after the temperature was stabilized. The radial distribution functions were averaged over all of these time steps whereas all the other calculated quantities were averaged over 1200 steps.

RESULTS AND DISCUSSION

In what follows we will define \( M^+ = 1, A^{+3} = 2 \) and \( X^- = 3 \) and the charges on these three ions will be understood when not explicitly stated.

A. Radial Distribution Functions (rdfs) and Coordination Numbers

The six calculated rdfs, \( g_{ij}(r) \), for MAX\(_4\) are plotted in Fig. 1 for the two potentials. In addition, we have also plotted \( N_{ij}(r) \), the number of ions of kind \( j \) about an ion of kind \( i \) within a radius \( r \). The value of \( N_{ij}(r) \) taken at the first minimum in \( g_{ij}(r) \) at \( r_0 \) is defined as the average coordination number, \( Z_{ij} \). In addition, we define a number \( n_{ij}^{(z)} \) which is the number of \( i \) ions which have exactly \( z \) \( j \) ions in their first coordination shell.

It is difficult to draw detailed conclusions based solely on rdfs, which is of course a pair distribution function. It is sometimes possible to infer such detail from a multiplicity of pair correlations (such as e.g. \( g_{23}(r) \) and \( g_{33}(r) \) to infer the tetrahedrality of \( AX_7^- \) moieties). However, as we will show, in order to extract much of the structural information requires a knowledge of higher order (i.e. triplet) correlations. With this limitation in mind we can examine the rdfs.

The values of \( g_{23} \) have steep narrow first peaks with maxima near \( 2 \text{Å} \) of about 10 and 18 and drop to very small values between \( 3.0 \) and \( 3.8 \text{Å} \). This characteristic can be expressed in terms of a potential of mean force, \( V_{ij}(r) \) which is defined as \( -kT \ln g_{ij}(r) \). A plot of \( V_{ij}(r) \) exhibits a potential well of about \( 6kT \). From this, one
would expect that an X anion in the first coordination sphere of an A cation will seldom 'escape' from that sphere without first entering the coordination sphere of another nearby A cation. The coordination number, \( Z_{23} \) for potential 1 is 5.8 and for potential 2 it is 4.0 suggesting tetrahedral coordination for the latter case and octahedral coordination for the former case.

With potential 1, the coordination number of 5.8 means that a significant fraction of the X ions must form A–X–A bridges. If the bridges are single and there are no free X anions, then the number of X ions in the first shell around an A which are part of a bridge is \( 2(Z_{23} - 4) \) which is also the coordination number of A about A, \( Z_{22} \). This is consistent with our results. For potential 2 there is very little bridging which is reflected in small first peaks in \( g_{22}(r) \) and small values of \( Z_{22} \). \( Z_{22} \) is non-zero because of a dissociation reaction we discuss later. The A–A correlations \( g_{22}(r) \) are therefore quite different for the two potentials. For potential 1 the first peak is sharp and located at about 4.5 Å with 3.6 coordination. For potential 2 the first peak at 4.7 Å is very small and there is a larger broad peak at about 6.2 Å.

Since the first maximum in \( g_{22}(r) \) for potential 1 is at about twice the distance to the first maximum in \( g_{23}(r) \) it follows that of the average of 5.8 X neighbors of A, 3.6 form a relatively straight A–X–A bridge from one A to another A under the first peak in \( g_{22}(r) \). The near linearity of the bridge suggests that the strongly repelling A cations remain far enough apart so that the A–A repulsions are at least partly shielded by intervening X anions.

One expects that the strong A–X attractions will dominate the tendency for close packing of X ions about A. The decrease in coordination number from 5.8 to 4.0 with an increase in the X–X repulsive core potential demonstrates the fact that the triple charges on A cations lead to the maximum possible packing of X anions in the first coordination shell within the limits set by the combination of anionic coulombic and core repulsions.

The first peaks in \( g_{33}(r) \) when compared with the peaks in \( g_{23}(r) \) indicate very different local structures for the two potentials. The ratios of the distances are consistent with an approximately octahedral coordination for potential 1 and tetrahedral for potential 2. This point will be amplified below.

B. Structural Implications

Coulombic forces together with steric effects determine the structure of ionic systems in general. In the present study one can show that i) repulsions between A cations should be more significant than between other like charge coulomb repulsions; ii) the A–X attraction will dominate over M–X attractions; and iii) the generated structures of X ions around A anions are sensitive to the core repulsions between X ions.
As discussed above, the analyses of $g_{23}$ and $g_{22}$ suggest an almost linear configuration for A–X–A bridges. To test this possibility, we calculated the distributions of angles of A–X–A triplets which are exhibited in Fig. 2 for the case in which the A–X distance is less than 3.0 Å. The results do show a predominance of angles close to 180° but indicate a significant fraction of triplets at much smaller angles (e.g., 30% at less than 150°). In any case, the small angular spread leads to the possibility that the structural correlations among the A cations could be of quite long range.

The tendency toward tight packing of the X anions about A cations appears to be energetically limited by two factors, i) the core repulsions between X ions which makes a positive energetic contribution and ii) the formation of A–X–A bridges and the consequent A–A positive repulsive energy when $Z_{23}$ is greater than 4. When the anion-cation radius ratio increases, the core repulsions between X ions is enhanced and $Z_{23}$ should tend to decrease. The number of bridges decreases as $Z_{23}$ decreases and the repulsions between A cations becomes energetically smaller. As expected, $Z_{23}$ is smaller for potential 2 than for potential 1. In order to determine the structure and symmetry of the X anions about the A cations we computed the angular distribution of X-A-X triplets which are plotted in Fig. 3. For potential 1 the distribution has maxima at angles close to 90° and 180° ($\cos \theta = 0$ and -1 respectively) which is consistent with octahedral symmetry. For potential 2 the maximum in the distribution lies close to the tetrahedral angle of 109°28' ($\cos \theta = -1/3$) as is expected for four coordination. In both cases, the spread in the distribution of angles is consistent with that expected for thermal motions.12.

The distribution $n^{(z)}_{23}$ of A cations as a function of the coordination number $z$ has also been calculated and is given in Table I. The results show that there is a broader distribution of coordination numbers for potential 1 than for potential 2 for which essentially all of the A ions are four coordinated. In many real molten salt systems, there is likely to be a distribution of coordination numbers, which in some cases might even be broader than that of potential 1. In such cases, it would be very difficult to interpret structure related measurements in a precise manner. A precise description requires one to specify not only the moieties which are present but also the relative amounts of all moieties.

The observation that most of the A–X–A angles are close to 180° and that the X–A–X angles are concentrated near 90° and 180° leads to the possibility that the long range A–A–A triplets should exhibit some regularity. A suggestion of this regularity can be found in the plots of $g_{22}$ for potential 1 where the second and third maxima are located at 1.4 and 2 times the first peak distance. This suggests that there is a preference for 90° and 180° angles in these triplets. To examine this point, the angular distribution of A–A–A triplets located within a sphere centered on A and having a 5.2 Å radius was calculated. The results are plotted in Fig. 4. The peaks at about 90° and 180° ($\cos \theta = 0$ or -1) indicate a tendency for
octahedral ordering up to at least the fourth nearest neighbors which are 9-10Å apart. However, there are other significant peaks in this angular distribution at 60°, 80°, and 102-110° which reflects complexities in the long range ordering and structures of these melts.

C. Complexing and Structure

A predominance of coordination numbers \( z_{23} = 4 \) or 6 is present for the two pair potentials. This result coupled with other studies underway suggest that there is a probable energetic preference for these values relative to 3 or 5. However, this preference is not absolute and other coordination numbers (such as e.g. 3 and 5) can be present for other pair potentials (e.g. for potentials intermediate between potentials 1 and 2). The tendency for a preferential coordination number, often ascribed to covalent or non-ionic bonding, can thus be shown to be a characteristic of purely ionic systems as well.

From earlier considerations, the first peaks in \( g_{22} \) (Fig. 1) are shown to be related to the formation of A–X–A bridges between the AXₙ moieties. The bridging anions by definition, are those X ions which have a nearest neighbor coordination number of 2. We have calculated the distribution of coordination numbers of the X ions, \( n^{(2)}_{32} \), which is given in Table II. For both potentials the expected number of bridging anions is close to the number of A–A nearest neighbor pairs (i.e. 83\( Z_{22}/2 \)).

The distribution of coordination numbers of X ions, \( n^{(2)}_{32} \), given in Table II and of A ions, \( n^{(2)}_{22} \) given in Table III for potential 2 indicate that many of the bridging anions are part of configurations which are complex and can be defined as \( A_2X^- \) or \( A_3X^{-10} \). For example, there are 13 bridging X ions and 13 X ions which are 'free' and have no A cations as nearest neighbors. Of the thirteen bridging anions, some belong to the 3 (+1) triplets with one A cation having two others as neighbors as given in Table III. If all A–A–A triplets have one of their three A–A pairs with a distance greater than 5.2Å then there are about 3 \( A_3X^{-10} \) species which have a total of 6 A ions with coordination 1 and 3 with coordination 2. This leaves 17 A cations with coordination 1 which can be part of 8.5 \( A_2X^- \) moieties. The number of bridges, 14.5 thus calculated is somewhat larger than the value of 13 given in Table II. This discrepancy can be related to the cutoff distance of 5.2Å for the results in Table III. Since there is obvious overlap between the two peaks on either side of this distance (see \( g_{22} \) for potential 2 in Fig. 1), this number, 14.5, includes unbridged A–A pairs associated with the broad peak at 6.2Å. These configurations are surprisingly similar to what has been postulated\(^1\) for NaAlCl₄ melts, reactions which involve complex species such as

\[
Cl^- + Al_2Cl_7^- \rightarrow 2AlCl_4^-
\]  \( (2) \)
The structures of the ionic species $A_2X_7^-$ or $A_3X_{10}^-$ are those of two or three $AX_4$ tetrahedra, respectively, which share one or two corners. (One possibility is that three tetrahedra share 3 corners to form an $A_3X_9$ species. The uncertainties in some of the data do not permit us to check this possibility at present.)

For potential 1, there is considerably more bridging as evidenced by the distribution of $A$ coordination numbers in table III. The bridging and the tendency for $A$-$X$-$A$ angles close to $180^\circ$ explains the distribution of the angles of the $A$-$A$-$A$ triplets exhibited in Fig. 4. However the presence of other peaks indicates that additional factors are also significant. The angular distribution of $A$-$X$-$A$ triplets indicates that significant numbers have angles which are substantially different from $180^\circ$ (i.e. $90\%$ less than $170^\circ$, $64\%$ less than $160^\circ$ and $30\%$ less than $150^\circ$). In addition, the spread in the angular distribution of $X$-$A$-$X$ triplets indicates that there is significant thermal motion and the concomitant tendency for the octahedra to distort. The presence of peaks other than at $90^\circ$ and $180^\circ$ in Fig. 4 is probably related to preferred structures based on small distortions of the angles of the octahedra and the $A$-$X$-$A$ bridges. Of particular interest in Fig. 4 is the sharp peak at $60^\circ$ which represents an equilateral triangle of three $A$ cations connected by bridging anions. When the $AX_n$ octahedra were stiffened to 'resist' distortion in another potential (which is not reported here) the peaks other than those at $\cos \theta = 0,-1$ in Fig. 4 become smaller, which is consistent with our suggestion that these other peaks, at least in part, represent distortions of the basic octahedral structure of $AX_n$ configurations for potential 1. The type of structural ordering indicated by Fig. 4 extends to quite long range (at least to 9-10Å) and appears to be related to bridging. Thus, we expect analogous long range ordering for potential 2 for compositions higher in the $AX_3$ component. For this case, an expected tendency for local tetrahedral configurations of the $AX_t^-$ species would propagate into the longer range distributions of the $A$-$A$-$A$ triplets. A more detailed analysis of bridging and structure in such systems is underway. In addition, the constancy of the average nearest neighbor coordination numbers of $A$ (such as 4 for potential 2) with a change of composition is not assured.

CONCLUSIONS

It has been shown that characteristics of binary $MAX_4$ melts such as chloroaluminates often ascribed to covalency and other non-ionic interactions between ions are present in an ionic solution. For potential 2 the $A$ cations are tetrahedrally coordinated and form $A_2X_7^-$ and $A_3X_{10}^-$ moieties analogous to species postulated to be present in chloroaluminates. For potential 1 there is considerable bridg-
ing and a tendency for long range octahedral-like order up to at least 10Å. The nearest neighbor coordination numbers and the symmetry of anions about the polyvalent cations do not completely account for the complexing observed in the present ionic molten salt solutions. From our results, many melts would be expected to have a distribution of coordination numbers for individual ions rather than a single value. This possibility means that it is generally difficult if not impossible to precisely define the structure of melts. Studies are underway of the influence of composition, different charges on the polyvalent ion as well as of radius ratios on the structures and energetics of melts which will include MX–AX₂ mixtures analogous to NaF-BeF₂, KCl-MgCl₂ and CaO-SiO₂ mixtures.

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Table I. The Distribution of $A^{+3}$ ions According to Their Coordination by $X^{-}$ ions ($n_{23}^{(z)}$) for $r \leq 3.0$ Å for Different Pair Potentials

| Potential/z | 4 | 5 | 6 | $Z_{23}^*$ |
|-------------|---|---|---|------------|
| 1           | 0 | 12| 71 | 5.8        |
| 2           | 83| 0 | 0  | 4.0        |

* $Z_{23}$ is the weighted average of various $n_{23}^{(z)}$.

Table II. The Distribution of $X^{-}$ Ions According to Their Coordination by $A^{+3}$ ions ($n_{32}^{(z)}$) for $r \leq 3.0$ Å for Different Pair Potentials

| Potential/z | 0 | 1 | 2 | $Z_{32}^*$ |
|-------------|---|---|---|------------|
| 1           | 5 | 108| 159| 1.5        |
| 2           | 13| 306| 13 | 1.0        |

* $Z_{32}$ is the weighted average of various $n_{32}^{(z)}$.

Table III. The Distribution of $A^{+3}$ Ions According to Their Coordination by $A^{+3}$ ions ($n_{22}^{(z)}$) for $r \leq 5.2$ Å for Different Pair Potentials

| Potential/z | 0 | 1 | 2 | 3 | 4 | 5 | 6 | $Z_{22}^*$ |
|-------------|---|---|---|---|---|---|---|------------|
| 1           | 0 | 2 | 7 | 22| 28| 22| 2 | 3.8        |
| 2           | 58| 23| <3| 0 | 0 | 0 | 0 | 0.4        |

* $Z_{22}$ is the weighted average of various $n_{22}^{(z)}$. 
1. Radial distribution functions, \( g_{ij}(r) \) and radius dependence of the average coordination numbers, \( N_{ij} \), calculated for MAX\(_4\) using potential 1 (solid line) and potential 2 (dashed line).
Fig. 2. Angular distribution of the A-X-A triplets in MAX_4 for a maximum distance of the A-X pairs of 3.0 Å. Potential 1 (solid line); potential 2 (dashed line).

Fig. 3. Angular distribution of the X-A-X triplets in MAX_4 for a maximum distance of the A-X pairs of 3.0 Å. The arrows indicate the angles at 90° and 109.47°. Potential 1 (solid line); potential 2 (dashed line).

Fig. 4. Angular distribution of the A-A-A triplets in MAX_4 for a maximum distance of the A-A pairs of 5.2 Å; potential 1 (dashed line), the solid line is for a potential in which the anion-cation radius ratio is somewhat larger than for potential 1. Note that this decreases the peaks at angles other than 90°. The arrows indicate the angles at 90° and 60°.