INTERACTION OF MCL MOLECULES WITH ENVIRONMENT IN CLUSTER MODEL OF ALKALI METAL CHLORIDE MELTS

V.G. Kremenetsky, D.V. Sidelnikov
Institute of Chemistry, Kola Science Centre RAS
14 Fersman Street
Apatity, Russia, 184209

ABSTRACT

Model structures of alkali metal chloride melts, which incorporate clusters including three coordination spheres of Cl⁻ or M⁺ ions (X³⁺ or M³⁺ single charged clusters respectively) and outersphere ions with M₂Cl⁺ or MCl₂⁻ common compositions are discussed (M – Li, Na, K, Cs). The analysis has shown that it is necessary to take into account opportunity of MCI molecule rotation formed owing to dissociation of outer sphere ions. In this part of work the interaction of MCI molecules with environment consisting of other MCI molecules and X³⁺ or M³⁺ clusters was studied. Equilibrium geometric parameters and potential energy were calculated for both types of interaction – (MCI-X³⁺) and (MCI-M³⁺). The environment of MCI molecule included 12 clusters and 14 MCI molecules (the first and the second coordination spheres of MCI molecule). Energies of transition from equilibrium structures to the "extended" structures (molar volumes of which are equal to the experimental molar volumes of MCI melts) and angles of MCI oscillations were calculated also.

LIST OF SYMBOLS

- cluster composed of alkali metal central ion M⁺ surrounded by three coordination spheres – M³⁺. Its composition – (M⁺•6X⁻•12M⁺•8X'),
- cluster composed of halide central ion X' surrounded by three coordination spheres – X³⁺. Its composition – (X'•6M⁺•12X'•8M+),
- outersphere particles with MCl₂⁻ common composition – MCl₂⁻,
- outersphere particles with M₂Cl⁺ common composition – M₂Cl⁺,
- model structure of melt composed only of M³⁻ clusters and M₂Cl⁺ particles – (M³⁻•M₂Cl⁺),
- model structure of melt composed only of X³⁺ clusters and MCl₂⁻ particles – (X³⁺•MCl₂⁻).

Other designations used in this work are:
- d(s) – crystal lattice parameter of the NaCl type,
- d(l) – distance between the nearest clusters located in adjacent layers (along axis Y in Fig.),

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• d(os) – distance between the cluster and nearest outersphere particle (along axes X or Z in Fig.),
• t – shift of clusters located in adjacent layers relatively each other (along axis Z in Fig.).

INTRODUCTION

Calculations were carried out in ChemObjects program generated by authors (1). The program is written mainly on C++ Builder and is intended for research of structural models which postulate existence in melts of stable particles with varied composition. The static characteristics of the given model - distances between building blocks, angles of rotation, molar volume, inner potential energies of particles, and potential energy of interaction were calculated.

In the literature there are a considerable number of publications, which operate with the concept of a structural particles stable in thermodynamic sense. The ChemObjects program allows to research structural features of such models in detail. With its help it is possible to estimate, as far as equilibrium structural performances of the given model correspond to experimental data. In ChemObjects there is a set of subprograms for the visual analysis and analytical handling of functions of major number of variables. These subprograms, for example, allow the determination of the localized or hard-to-reach areas of a multivariate surface of a potential energy, positions of local and global extremum on it, etc.

In our opinion, the analysis of those models that postulate derivation of rather large clusters in molten salts has a special interest. The viewed variant of cluster model is not realistic, but its research allows understanding some features of similar model structures. As it will be visible from the further presentation, such structures are not too easy to detect in MD experiments and consequently it is difficult to deny the statement about possibility of their existence.

The obtained information may be very useful for methods of MD and MC simulations. On the basis of these results it is possible to formulate requirements for carrying out of MD experiment and to organize purposeful searching of particles with this or that composition in MD equilibrium configurations.

RESULTS AND DISCUSSION

In this part of work we deal with one of variants of cluster model offered in (2-4). The composition of particles was specified earlier (5). Here the modified model structures of alkali metal chloride melts, which incorporate clusters including three coordination spheres of Cl⁻ or M⁺ ions (X³⁺ or M³⁺ single charged clusters respectively) and outersphere particles with the M₂Cl⁺ or MCI⁺ common compositions are discussed (M – Li, Na, K, Cs). In these structures, the ratio of M³⁺ clusters and outersphere M₂Cl⁺ ions (or X³⁺ and MCI⁺) is unity. Amongst the particles with the local structure of the NaCl type, the X³⁺ or M³⁺ clusters have the minimum charge. For instance, a cluster consisting of the central ion M⁺ and its first coordination sphere, i.e. a cluster of the
(M⁺·6X⁻) composition, has a charge of -5. If the second coordination sphere of M⁺ ion is also included, we obtain a cluster of the (M⁺·6X⁻·12M⁺) composition with the charge of +7. By adding sequentially the following coordination spheres we obtain a series of clusters with summary charges -1, +5, +9, +5, +17, -13, +11, etc. The minimum charge (-1) belongs to the aforementioned M3⁻ cluster of the (M⁺·6X⁻·12M⁺·8X⁻) composition. A similar cluster for the central X⁻ ion has the charge of +1 and its composition is (X⁻·6M⁺·12X⁻·8M⁺). It is designated as X3⁺.

As it was shown (5), average distances d(M-Cl) in clusters are rather close to experimental values but molar volumes of model structures with equilibrium values of geometric parameters are less than experimental data. The analysis has shown that it is necessary to take into account the opportunity of MCI molecule rotation formed owing to dissociation of outer sphere ions:

\[
M₂Cl⁺ → MCI + M⁺ \quad \text{and} \quad MCI₂⁻ → MCI + Cl⁻ \quad [1]
\]

However, previously we should have investigated the interaction of MCI molecules with environment consisting of other MCI molecules and X3⁺ or M3⁻ clusters. The present study is devoted to this task.

Initial (M3⁻·M₂Cl⁺) structure where ions are located in sites of a NaCl crystal lattice is shown in Figure 1.

![Figure 1. Model structure (M₃⁻·ClM⁺) (Click to enlarge)](image_url)

For calculations the Pauling’s potential was used. The parameters of this potential were determined from the experimental data for the crystal state of alkali metal chlorides (6). The accuracy of this potential was tested by calculating the equilibrium distances in MCI molecules and was found to be satisfactory to handle the problems dealt with in this work. The average error in the calculation of the equilibrium distance d(M-Cl) in MCI...
molecules was 0.3% (less than 0.001 nm), while the error of peak position determination of correlation curves, \( G(r) \), obtained using X-ray diffraction data is close to 2-4% (~0.005-0.01 nm).

Initially, the geometry of M3\(^-\) and X3\(^+\) clusters and MCI molecules were optimized by minimizing the potential energy of the given parameters. Then equilibrium geometric parameters and potential energy minimum in \( U^{\text{min}} \) were calculated for both types of interaction – (MCI-X3\(^+\)) and (MCI-M3\(^-\)). Interaction of clusters with a third ion (Cl\(^-\) or M\(^+\)) of the outersphere particle (MCl\(_2\)\(^+\) or M\(_2\)Cl\(^+\)) were not taken into account in this work; however this interaction may not affect the results significantly.

The environment of MCI molecule included 12 clusters and 14 MCI molecules from the first and the second coordination spheres of this molecule. Total number of parameters, which have been varied during searching of optimum geometry, is equal to eleven. Three of them characterize location of a barycentre of MCI molecule relatively of a cluster face. The slewing angle of molecules (\( \varphi \)) was varied in a perpendicular plane to a cluster face. It is this type of rotation which determines possibility of structure "extension", i.e. increasing of d(os) parameter.

The obtained values of potential energy \( U^{\text{min}} \) and equilibrium angles of rotation \( \varphi^{\text{min}} \) are given in Table I for both types of structures – (MCI-X3\(^+\)) and (MCI-M3\(^-\)). Apparently from the data in Table I, MCI molecules tend to occupy a position parallel to a cluster face with an angle equal to or close to zero.

| Type of structure | Parameters | LiCl | NaCl | KCl | CsCl |
|-------------------|------------|------|------|-----|------|
| (MCI-M3\(^-\))    | \( \varphi^{\text{min}} \) | 2\(^\circ\) | 0\(^\circ\) | 0\(^\circ\) | 0\(^\circ\) |
|                   | \( \varphi^{\varphi} \)  | 12\(^\circ\) | 10\(^\circ\) | 4\(^\circ\) | 4\(^\circ\) |
|                   | \( U^{\text{min}} \)     | -186.1 | -239.4 | -236.2 | -207.0 |
|                   | \( U^{\varphi} \)        | -120.6 | -121.1 | -140.8 | -146.4 |
|                   | \( \Delta U \)           | 65.5  | 118.3 | 95.4  | 60.6  |
| (MCI-X3\(^+\))    | \( \varphi^{\text{min}} \) | 2\(^\circ\) | 0\(^\circ\) | 0\(^\circ\) | 0\(^\circ\) |
|                   | \( \varphi^{\varphi} \)  | 8\(^\circ\) | 12\(^\circ\) | 4\(^\circ\) | 4\(^\circ\) |
|                   | \( U^{\text{min}} \)     | -113.8 | -211.8 | -228.2 | -206.0 |
|                   | \( U^{\varphi} \)        | -72.4  | -105.1 | -137.7 | -149.2 |
|                   | \( \Delta U \)           | 41.4  | 106.7 | 90.5  | 56.8  |

In addition to equilibrium structures, parameters of "extended" structures (molar volumes of which are equal to the experimental molar volumes of MCI melts) were calculated as follows. The molar volume \( V_m \) of the model structure expressed through the structure parameters is
\[ V_m = \frac{N_A}{15} \cdot \left\{ 2d(\text{cl}) + d(l) \right\} \cdot \left\{ (2d(\text{cl}) + d(\text{os}))^2 + d(\text{os})^2 \right\} \]  

where \(2d(\text{cl})\) is a size of cluster and \(N_A\) is Avogadro constant. Coefficient 15 has appeared in formula [2] due to the fact that the "elementary particle" of such model structures as \((\text{M}^3\text{Cl}_3\text{M}^3_2)\) and \((\text{X}^3\text{Cl}_3\text{M}^3_2)\) contains 15 MCI molecules, i.e. its molar volume is equal to \(15V_m\). The parameter \(t\) does not influence the value of molar volume. 

Using the experimental volumes \(V_m\) for alkali metal chloride melts and calculated values \(d(\text{cl})\) and \(d(l)\) it is possible to calculate the value of the \(d(\text{os})\) parameter. And further for this set of parameters it is easy to calculate equilibrium angles of MCI rotation \(\phi\) and potential energies \(U\) of MCI interaction with environment. They also are given in the Table with superscripts "ν".

The energies \(\Delta U\) given in the last table line are equal
\[ \Delta U = U^\nu - U^{\text{min}} \]

Values of these energies show, that transition from equilibrium model structure to "extended" structure demands the considerable energy expenditures. As the possibility of MCI molecule rotation, examination of potential energy surfaces has shown that for "extended" structures a hindered rotation only with vanishing angle of oscillations is acceptable. On the average, this angle is equal to 11° (for thermal fluctuations about 0.5\(RT_{\text{mel}}\)).

CONCLUSIONS

Within the framework of the given model, during melting the infinite crystal lattice disintegrates on assemblage of ions, molecules and clusters with new equilibrium parameters. Transition in this state is accompanied by emission of the fair quantity of energy. As calculations have shown, in equilibrium state the potential energy of clusters and molecules considerably exceeds the energy value of these particles in a crystal lattice. Possibly this excess energy may serve as a source of that energy which is necessary for structure expansion. Certainly, this supposition demands the further quantitative check by means of detailed calculations.

Here the detailed data about interaction of structure particles with each other were not given. From these data follows, that the surveyed model structure is rather rigid concerning the mutual shift of clusters (certainly it does not correspond to actual structure of salt melts). Nevertheless, it would be rather difficult to detect such particles in MD simulation, if the similar structure substantially existed. The value of a relative displacement of clusters of adjacent layers is incommensurable with cluster sizes. As a result period may appear very major. If a size of MD cell will be selected improperly then the structure will be exposed to self-destruction owing to violation of its periodicity. An additional problem is that the structure is anisotropic. This problem is easily solved, when properties of structure are known. But when we do not know anything, the situation becomes much worse.
Finally, it is necessary to note, that the observed model structure may be improved by changing the relationship between amounts of clusters and outersphere particles. Increasing the number of outer sphere particles will make the structure more disordered and mobile. However, we are interested by those model structures only that might be an intermediate between a crystalline phase and a disordered melt. This interest is based on those experimental facts that specify passing of reconfigurations in crystals near to melting point. In this connection there is a question, whether the process of a melting occurs through one or several intermediate stages? In this sense the viewed type of model structures is rather interesting, as admits possibility of build-up of the whole series of models. This fact was noted in reference (5) where the possibility of build-up of the model structure consisting exclusively of clusters M3" and X3+ was mentioned. This type of structure has property of self-similarity. That is the structure (M3"·X3+) is similar to the initial structure of NaCl type and on its basis it is possible to generate the complicated hierarchical structures.

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