MODEL STRUCTURES OF ALKALI METAL CHLORIDE MELTS

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ABSTRACT

Model structures of alkali metal chlorides, which incorporate clusters including tri-coordination spheres of $\text{Cl}^3'$ or $\text{Cl}^3+$ ions and outer-sphere ions of the $\text{M}_2\text{X}^+$ or $\text{MX}_2$ type are discussed. The geometric parameters of model structures ($\text{Cl}^3\cdot\text{M}_2\text{Cl}^+$) and ($\text{Cl}^3+\cdot\text{MCl}_2$) and potential energies of interaction between principal elements of these structures are calculated. In one of the calculated variants the model structure ($\text{Cl}^3\cdot\text{M}_2\text{Cl}^+$) parameters were found to be close to experimental values for the majority of alkali metal chlorides.

INTRODUCTION

As it was reported in (1,2), the best agreement between the calculated and experimental X-ray data for alkali metal (AM) halide melts is achieved by employing notions based on Zarzycki's model, whereas the quasi-lattice and autocomplex models yield much greater discrepancy between the experimental and calculated data (see ref. in (1,2)). For the majority of AM fluorides and chlorides the most acceptable clusters are quasi-crystalline ones with the structure of the NaCl type limited by the second-fourth coordination spheres (CS). For certain Rb and Cs halides, agreement is found between the calculated and experimental data when the clusters have the structure of the CsCl type and were limited by the second CS (2). These results are interesting from the crystallochemical viewpoint. The fact is that a cubic cluster of the NaCl type, incorporating three CS, designated as $C/3^*$, as well as a cluster of the CsCl type, limited by the second CS (a cuboctahedron) have smaller charges (+1 or −1) in comparison with clusters of other types:

- **type NaCl:** $\text{M}^+\cdot\text{6X}^-\cdot\text{12M}^+-\text{8X}^-\cdot\text{24M}^+-\text{24X}^-\cdot\text{12M}^+$...
  $+1 -5 +7 -1 +5 -19 +5 +17$

- **type CsCl:** $\text{M}^+\cdot\text{8X}^-\cdot\text{6M}^+\cdot\text{12M}^+-\text{24X}^-...
  +1 -7 -1 +11 -13$

The minimal charge of the clusters above dictates, consequently, their minimum-range interaction. It is also interesting to note that the structure of the NaCl type constructed from $\text{Cl}^3'$, for the central ion $\text{M}^+$ and $\text{Cl}^3+$, for the central ion $\text{X}^-$ is identical to the initial structure.
This work deals with AM chlorides and considers model structures containing Cl$_3^-$ and Cl$_3^+$ with more detail. However, the structures consisting only of a mixture of these clusters have remained outside the scope of this research. It is possible that immediately before melting the crystal lattice disintegrates into a combination of Cl$_3^-$ and Cl$_3^+$ clusters, but accounting for the features of such ionic systems as AM halides is difficult using this model. The experience of working with the autocomplex model (3,4) suggests that in order to account for the transport properties of AM halide melts, it is necessary to postulate the existence of outer-sphere interactions between clusters and elementary ions such as M$^+$, X$^-$, M$_2$X$^+$, MX$_2^-$. A similar idea of particle separation in the melt between structurally-ordered and disordered parts underlies the Eyring’s model (6-8) and is consistently implemented in work (9).

RESULTS AND DISCUSSION

This work presents the results of calculations for model structures (Cl$_3^-$·M$_2$Cl$^+$) and (Cl$_3^+$·MCl$_2$) incorporating M$_2$Cl$^-$ or MCl$_2$ ions. The crystallographical analysis demonstrates that the simplest way for such structures to organize is in a laminated structure where each layer is formed by translating the cluster in the plane to a distance of $\pm r = d$(M·X)$\cdot$i $\pm 3d$(M·X)$\cdot$j, where i and j are single vectors of axes lying on this plane. Inside the layer, the cluster is surrounded by four outer sphere (OS) ions, whereas between the layers these ions are missing. The ratio of Cl$_3$:OS ions is 1. Clusters located in neighbouring layers are shifted relatively each other. In this work the shift value is assumed equal to d(cl), i.e. to the distance between the nearest ions M$^+$ and X$^-$ in Cl$_3$. The parameters of these model structures are 1) distances d(M·X) in cluster – d(cl), 2) inside the layer (between the ions of the third CS of the cluster and OS ions) – d(cl) and 3) between the layers – d(l). The molar volume of the structure expressed through the above parameters is

$$V_m = \frac{N_A}{15} \cdot \left[2d(cl)+d(l)\right] \cdot \left\{\left[2d(cl)+d(os)\right]^2 + d(os)^2\right\} \quad [1]$$

By using the experimental values $V_m(m)$ for AM chloride melts,(1,10) and assigning two of the three parameters, it is possible to calculate the value of the third parameter in formula [1] and compare it with the location of maxima on curves of correlation functions G(r) obtained with X-ray data (11). For calculation of equilibrium values d(cl) and potential energy of cluster and OS ion interaction, the Pauling’s potential with parameters given in work (12) was used. The accuracy of this potential is sufficient for a qualitative analysis.

Table 1 demonstrates the calculated values of “crystal lattice” parameters $a_1$, $a_2$ and $a_3$ for the first, second and third cluster CS, respectively, as well as the weighted average magnitudes of these values d(cl) (the third-sixth columns). In the seventh-ninth columns are the $d_1(m)$ and $d_2(m)$ values corresponding to the first and second maxima on curves G(R) (11) and crystal lattice parameter d(cr) for infinite crystals (13).
Table I. Geometric parameters of clusters ClI3− and ClI3+ and values d1(m) and d2(m) for melts and d(cr) for infinite crystals of AM chlorides (in Å)

| MCl  | a1  | a2  | a3  | d(cl) | d1(m) | d2(m) | d1(cr) |
|------|-----|-----|-----|-------|-------|-------|--------|
| LiCl | 2.63| 2.42| 2.47| 2.34  | 2.44  | 2.27  | 2.34   |
| NaCl | 2.88| 2.78| 2.74| 2.68  | 2.69  | 2.61  | 2.68   |
| KCl  | 3.21| 3.07| 3.07| 3.04  | 3.00  | 2.98  | 3.03   |
| CsCl | 3.52| 3.52| 3.38| 3.39  | 3.29  | 3.29  | 3.39   |

* for structure of the NaCl type

It follows from these data that 1) as anticipated, the a1 values diminish from the first to the third CS in keeping with the decreasing coordination number (from 5 to 3); 2) an isolated cluster has the least size (r(cl) = a1V3) in comparison with a similar fragment of the infinite crystal (r∞(cl) = d1(cr)V3); 3) the d(cl) values with negatively charged clusters ClI3− are closer to experimental values d1(m) than with ClI3+, with the exception of CsCl.

Using d(cl) values given in Table I and assigning in turn d(l) and d(os) equal to d1(m) or d2(m) in equation [1] the missing parameters for the four variants were calculated: 1) d(l)=d1(m); 2) d(l)=d2(m); 3) d(os)=d1(m); 4) d(os)=d2(m). The calculated results are presented in Table II. Comparing the experimental values d1(m) and d2(m) with the calculated values d(l) and d(os) we can see that only in the first variant of calculation for structures of the (ClI3−·M2Cl+) type they are fairly close (with the exception of CsCl): d(l) is equal to d1(m) by definition, and d(os) is close to d2(m).

Table II. Geometric parameters of model structures (ClI3−·ClI3+) – A, and (ClI3+·MCl2) – B

| Variant Number | Type of structure | Calculated parameter | LiCl | NaCl | KCl | CsCl |
|----------------|------------------|----------------------|------|------|-----|------|
| 1              | A                | d(os)                | 3.96 | 4.35 | 4.44| 4.48 |
|                | B                | d(os)                | 4.34 | 4.53 | 4.57| 4.47 |
| 2              | A                | d(os)                | 3.36 | 3.74 | 3.88| 3.92 |
|                | B                | d(os)                | 3.71 | 3.90 | 4.00| 3.91 |
| 3              | A                | d(l)                 | 6.59 | 7.05 | 6.67| 5.96 |
|                | B                | d(l)                 | 7.85 | 7.60 | 7.05| 5.94 |
| 4              | A                | d(l)                 | 2.70 | 3.12 | 3.19| 2.71 |
|                | B                | d(l)                 | 3.51 | 3.49 | 3.46| 2.69 |

The data presented in Tables I and II were used to calculate the (ClI3–ClI3) interaction energies of clusters located in one or neighbouring layers, and the energy of (ClI3–OS ion)- bond within the layer. Apart from that, the parameters of the minimum of potential energy curves (Umin, dmin) were calculated for the interaction of neighbouring
layer clusters, and for the \((\text{Cl}_3-\text{OS} \text{ ion})\)-bond within the layer. It is these two latter kinds of interactions that mainly determine the values of parameters \(d(l)\) and \(d(os)\), respectively. The \(U^{\text{min}}\) values for \((\text{Cl}_3-\text{Cl}_3)\)-interaction of neighbouring layer clusters were found to be the closest to the values of energy \(U(l)\) for this type of interactions in the first variant (Table III, structural type \((\text{Cl}_3^+\cdot\text{M}_2\text{Cl}^-)\)), and for the \((\text{Cl}_3-\text{OS} \text{ ion})\)-bond – to the energy values \(U(os)\) in the third variant (Table IV, structural type \((\text{Cl}_3^+\cdot\text{M}_2\text{Cl}^-)\)).

Comparison of the data presented in Tables III and IV reveals that for the majority of MCl (with the exception of LiCl) the \(d(l)^{\text{min}}\) values are closer to the experimental values of \(d_i(m)\) than the \(d(os)^{\text{min}}\) values. The same is true for structures of the \((\text{Cl}_3^+\cdot\text{MCl}_2^-)\) type.

**Table III.** Energies and distances \(d(l)\) for the first variant – \(U(l)^{(1)}, d(l)^{(1)}\) and in the minimum of potential energy curves of \((\text{Cl}_3-\text{Cl}_3)\)-interaction – \(U(l)^{\text{min}}, d(l)^{\text{min}}\) (U-in kJ/mol)

| Type of structure | Parameter | LiCl | NaCl | KCl | CsCl |
|-------------------|-----------|------|------|-----|------|
| A                 | \(U(l)^{(1)}\) | 135.0 | 71.3 | 48.6 | 45.5 |
| A                 | \(d(l)^{(1)}\)* | 2.47 | 2.80 | 3.10 | 3.53 |
| A                 | \(U(l)^{\text{min}}\) | 119.2 | 69.4 | 46.7 | 45.5 |
| A                 | \(d(l)^{\text{min}}\) | 2.78 | 2.90 | 3.20 | 3.53 |

*\(d(l)^{(1)} = d_i(m)\)

**Table IV.** Energies and distances \(d(os)\) for the third variant \(U(os)^{(3)}, d(os)^{(3)}\) and in the minimum of potential energy curves of \((\text{Cl}_3-\text{OS} \text{ ion})\)-bond – \(U(os)^{\text{min}}, d(os)^{\text{min}}\)

| Type of structure | Parameter | LiCl | NaCl | KCl | CsCl |
|-------------------|-----------|------|------|-----|------|
| A                 | \(U(os)^{(3)}\) | -323.0 | -294.8 | -266.7 | -234.6 |
| A                 | \(d(os)^{(3)}\)* | 2.47 | 2.80 | 3.10 | 3.53 |
| A                 | \(U(os)^{\text{min}}\) | -329.5 | -301.5 | -269.9 | -242.2 |
| A                 | \(d(os)^{\text{min}}\) | 2.32 | 2.63 | 2.97 | 3.27 |

*\(d(os)^{(3)} = d_i(m)\)

**CONCLUSIONS**

On this basis, it is proposed that in the framework of this model the structural formation is determined by repulsion of the neighbouring layer clusters, but not by the \((\text{Cl}_3-\text{OS} \text{ ion})\)-attraction. This may be due to the fact that in addition to the minimum, the potential energy curves of \((\text{Cl}_3-\text{Cl}_3)\)-interactions include a maximum \((d^{\text{max}}>d^{\text{min}})\) - with the exception of \((\text{Cl}_3^+\cdot\text{LiCl}_2^-)\) structure. For this reason, the clusters formed in proximity of the melting point are unable to overcome the activation barrier whose values for the structure of the \((\text{Cl}_3^+\cdot\text{M}_2\text{Cl}^-)\) type are: NaCl and CsCl ~ 48, KCl ~ 56 kJ/mol. Only for the \((\text{Cl}_3^+\cdot\text{Li}_2\text{Cl}^-)\) structure the activation barrier value is comparatively small (~15 kJ/mol).
It is evident that distances $d(M-X)$ both inside the cluster and between clusters contribute in the $d_1(m)$ value. Only with LiCl the $d(l)^{\text{min}}$ value by far exceeds the $d_1(m)$ value. It is not ruled out that in more accurate evaluations these values may come closer together, but owing to the small value of the activation barrier it is the third variant or another type of structure, where the parameter values are determined by the (Cl3-OS ion) bond, that may turn out to be preferable for LiCl.

So, the value of experimental parameter $d_1(m)$ finds its physical explanation within the given simple model. However, drawing conclusions would be premature since more accurate calculations may correct the $d^{\text{min}}$ values. Concerning the physical reasons that may dictate the $d(os)$ experimental values, searching for them will require further calculations.

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