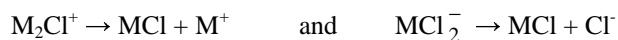# Interaction of MCl molecules with environment in the cluster model of alkali metal chloride melts

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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 of the M_2Cl^+ or MCl_2^- types were earlier discussed (1). In these structures the ratio of $M3^-$ clusters and outersphere M_2Cl^+ ions (or $X3^+$ and MCl_2^-) is unity. Amongst the particles with the local structure of the NaCl type the $X3^+$ or $M3^-$ clusters have the minimum charge. The basic purpose of this discussion consists of verification of physical validity of the given class of models.

As it was shown (1), 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 opportunity of MCl molecule rotation formed owing to dissociation of outer sphere ions:

$$M_2Cl^+ \rightarrow MCl + M^+ \qquad \text{and} \qquad MCl_2^- \rightarrow MCl + Cl^-$$

However previously we should investigate interaction of MCl molecules with environment consisting of other MCl molecules and $X3^+$ or $M3^-$ clusters.

The given study is devoted to the decision of this task. Calculation program ChemObjects is written on C++ Builder 6. The program allows to set types of chemical objects and its interaction potential. In the given work, the simple Pauling's potential was used. The parameters of this potential were determined from the experimental data for the crystal state of alkali metal chlorides. For this reason the accuracy of this potential was tested by calculating the equilibrium distances in MCl molecules and was found to be satisfactory to handle the problems dealt with in this work. The average error of determination of the equilibrium distance d(M-Cl) in MCl molecules was 0.3% (less than 0.001 nm), while the error of peak position determination at correlation curves G(r) obtained using the X-ray diffraction data is close to 2-4% (~0.005-0.01 nm).

Here equilibrium geometry of clusters is characterized by three parameters (1), i. e. each of three coordination spheres of a cluster has its own "crystalline" parameter d(M-Cl). Equilibrium geometric parameters and potential energy were calculated for both types of interaction – $(MCl \cdot X3^+)$ and $(MCl \cdot M3^-)$ where M = Li, Na, K, Cs. The environment of MCl molecule included 12 clusters and 14 MCl molecules from the first and the second coordination spheres. Total number of parameters, which have been varied during searching of optimum geometry, is equal to nine.

In addition to equilibrium structures, parameters of "extended" structures (molar volumes of which are equal to the experimental molar volumes of MCl melts) were calculated also. As to the possibility of MCl 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°.

Here the rotation plane of molecules was perpendicular a cluster face. Energies of transition from "equilibrium" structures to the "extended" structures are equal 65, 118, 95, 61 (M3- type) and 41, 107, 90, 57 kJ/mol (X3+ type) for LiCl, NaCl, KCl and CsCl respectively. Thus, this transition needs energy expenditures.

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. 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. In addition, it is desirable to study the effect of rotation plane orientation on a magnitude of activation barrier.

REFERENCE

1 V. Kremenetsky, in Molten Salts XIII/2002, **V.19**, p.448, The Electrochemical Society Proceedings Series, Philadelphia, PA (2002).