Structure of the Molten $NaCl-MgCl_2$

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With potential parameters adjusted to reproduce the experimental structure factor of molten $MgCl_2$ reasonably, molecular dynamics simulations of the molten $NaCl-MgCl_2$ were carried out. The structure of this system was investigated by comparison of experimental with computational results.

1. Introduction

The thermodynamic properties of multivalent cations in molten salt mixtures are important when these cations are recovered by electrolysis. Most multivalent cations are stabilized in the molten salt solvents, that is, their thermodynamic activities decrease. According to the Nernst equation, a decrease of the activity brings about a negative shift of the redox potential (E):

$$E = E_0 + RT/nF \ln(a_{M^{n+}}/a_M) \quad (1)$$

where E_0, F, n, $a_{M^{n+}}$ and a_M are a standard decomposition potential, Faraday constant, an electron transfer number, and the activity of an ion M^{n+} and a product M, respectively. We were interested in the reason of such a stabilization of multivalent cations. Molecular dynamics (MD) simulations give information about the microscopic structure in real space, while diffractional methods give us structural information in reverse space.

This paper deals with molten $NaCl-MgCl_2$, whose thermodynamic properties were obtained by emf measurements [1, 2]. Brooker and Huang guessed the structure of this system from Raman spectroscopy [3, 4]. Moreover, the structure of molten $MgCl_2$ was studied by X-ray diffraction and neutron diffraction [5, 6].

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2. Computation

For the pair potential between ions we employed the expression

$$u_{ij}(r) = z_i z_j e^2/4\pi\varepsilon_0 r + b A_{ij} \exp((r_i^0 + r_j^0 - r)/\varrho) \quad (2)$$

with valence numbers, z the elementary charge e, the dielectric constant of vacuum ε_0, the Pauling factor b, the ionic radii r^0 and the softness parameter ϱ. Sundheim and Woodcock's MD simulations of the molten $MgCl_2$ [7] gave a coordination number 3 of Cl and Mg which does not agree with the experimental results. Therefore we adjusted the parameters r^0 and ϱ to reproduce the experimental structure factor [5]. After that we made MD simulations of molten $NaCl-MgCl_2$ for 7 compositions (mole fraction x_2 of $MgCl_2$ = 1.00, 0.75, 0.52, 0.33, 0.23, 0.11, and 0.00) at 1100 K. The softness parameter was changed according to a rule proposed by Larsen and Førland [8].

In order to anneal the system we employed Woodcock's method [9] with the Verlet algorism for 3000 time steps (Δt = 1 fs). This was followed by 2000 time steps, using the isothermal MD simulation proposed by Nose [10]. The internal energy U, averaged over 2000 time steps, was calculated by

$$U = \Phi + \text{K.E.} \quad (3)$$

In this equation Φ and K.E. are the potential energy, where the coulomb energy was estimated by the Ewald method, and the kinetic energy, respectively. The enthalpy is given by

$$H = U + pV, \quad (4)$$

but in condensed matter pV can be neglected (pV is smaller than 0.1 kJ mol^{-1} in our case). The computa-

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tional mixing enthalpy was evaluated by

$$H_{mix} = H(x_1, x_2) - x_1 H_1 - x_2 H_2, \quad (5)$$

where H_1 and H_2 are the enthalpies of the pure components 1 and 2, respectively.

The number of isolated complexes $MgCl_4^{2-}$ was accumulated at every hundredths time step.

3. Results and Discussion

The structure factor ($Q\,i(Q)$) of the molten $MgCl_2$ was estimated by Debye's equation

$$Q\,i(Q) = \sum_i \sum_j f_i f_j \sin(Q r_{ij})/r_{ij} \exp(-b_{ij} Q^2), \quad (6)$$

where Q, f_i, b_{ij} nd r_{ij} wave number, the atomic scattering factor of ion i, a temperature and the distance between the ions i and j. The softness parameter ϱ and the ionic radii of Mg^{2+} were adjusted to reproduce the experimental structure factor [5]. Thus we obtained $\varrho = 0.022$ nm and $r^0_{Mg} = 0.085$ nm. The structure factors obtained experimentally and computationally are shown in Figure 1. At high Q, the phase of the structure factor becomes larger than the experimental one. The slightly shorter distance (see Table 1) between the Mg and Cl ions in the simulated system than in the experimental system might bring this discrepancy.

Figure 2 shows the pair correlation functions (pcfs) between Mg–Mg, Mg–Cl and Cl–Cl in pure $MgCl_2$ and in the most dilute ($x_2 = 0.11$) system. The characteristics of the pcfs are listed in Table 1. These figures and the table show that

(1) g_{MgMg} in the most dilute system has an isolated first peak, which indicates the presence of a dimer $Mg_2Cl_7^{3-}$.
(2) the first peak position of g_{MgCl} decreases with decrease of $MgCl_2$ content. The coordination number of Cl^- around Mg^{2+} is 4 at all compositions. The distance between Mg^{2+} and Cl^- in $MgCl_4^{2-}$ is shortest in the isolated $MgCl_4^{2-}$. Brooker and Huang estimated the fraction of isolated $MgCl_4^{2-}$ by Raman spectroscopy [4]. Their and our results are depicted in Figure 3. The inclination of these results shows good coincidence.
(3) with decrease of $MgCl_2$ content the second peak, which does not appear in pure $MgCl_2$, increases. Chloride ions at this second peak position coordinate to Na^+. Then, as the NaCl content increases, the interaction between Cl^- and Na^+ increases

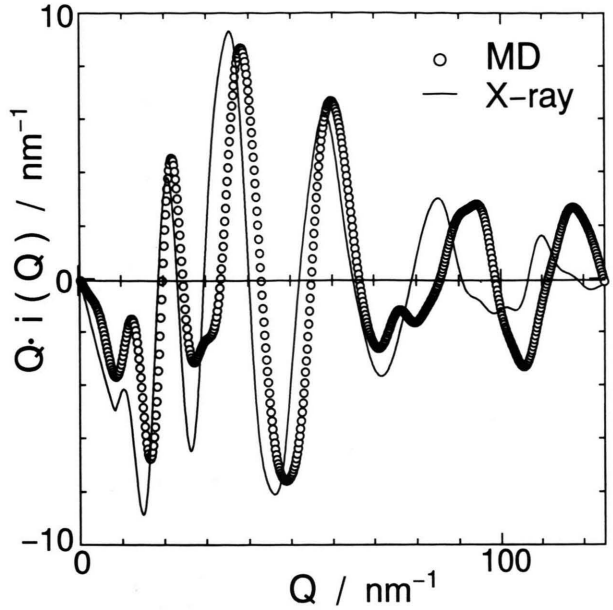

Fig. 1. Experimental and computed structure factor in molten $NaCl-MgCl_2$.

Table 1. Characteristics of the pair correlation functions. x_2 = mole fraction of $MgCl_2$.

x_2	Position of the first peak/nm			
	r_{MgMg}	r_{MgCl}	r_{ClCl}	∠ Cl–Mg–Cl
1.00	0.433	0.221	0.353	102°
0.75	0.427	0.217	0.343	106°
0.52	0.411	0.209	0.339	106°
0.33	0.405	0.205	0.335	107°
0.23	0.409	0.201	0.329	108°
0.11	0.403	0.197	0.329	109°

Table 2. Internal energy of molten $NaCl-MgCl_2$ simulated at 1100 K.

x_2	Number of ions			Internal energy/kJ mol^{-1}
	Mg	Na	Cl	
1.00	72	0	144	−2476.2 ± 2.3
0.75	66	22	154	−2060.0 ± 2.7
0.52	52	48	152	−1663.6 ± 3.1
0.33	35	70	140	−1331.3 ± 2.7
0.23	23	75	121	−1151.2 ± 2.9
0.11	11	89	111	−918.4 ± 3.3
0.00	0	108	108	−706.4 ± 1.6

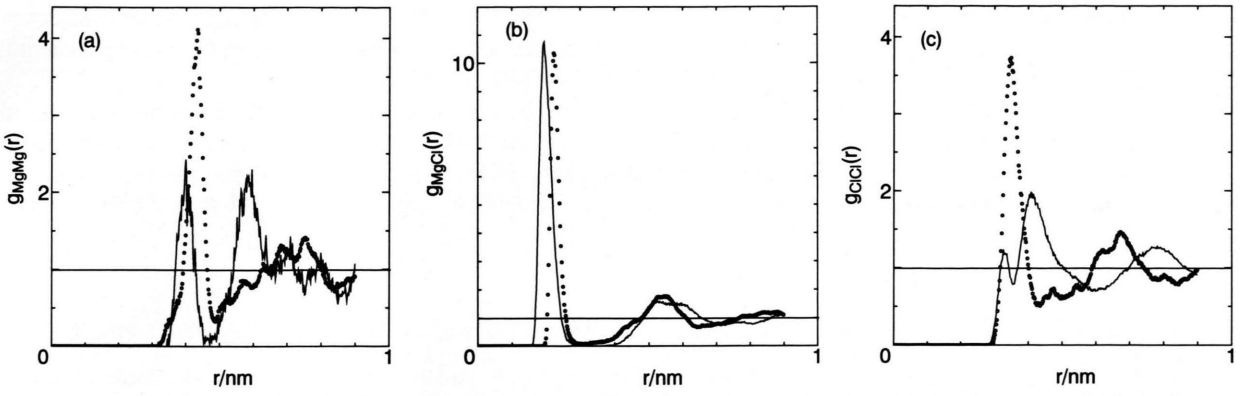

Fig. 2. Pair correlation functions in the molten $NaCl-MgCl_2$ for $x_2=1$ (circles) an $x_2=0.11$ (solid line). (a) g_{MgMg}, (b) g_{MgCl} and (c) g_{ClCl}.

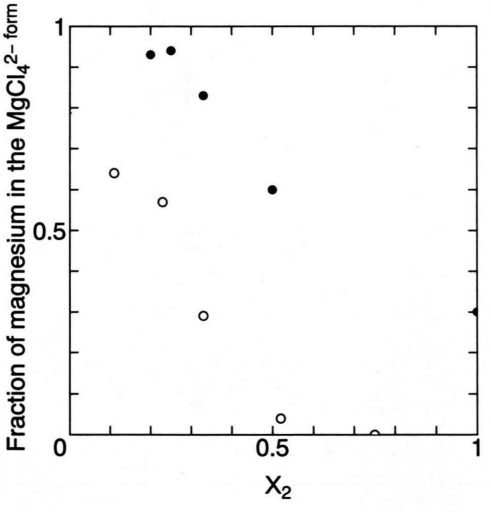

Fig. 3. Fraction of the isolated $MgCl_4^{2-}$. x_2 = mole fraction of $MgCl_2$. ●: experimental [3] and ○: computed (this work).

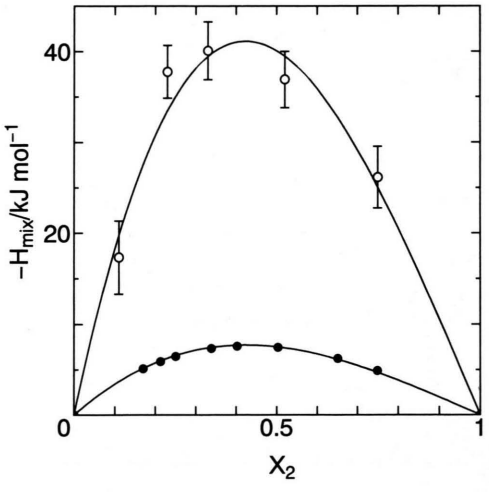

Fig. 4. Molar mixing enthalpy of the $NaCl-MgCl_2$. ●: experimental [1] and ○: computed (this work); solid lines: see text.

and the interaction between Cl and Mg^{2+} decreases. The shortest distance between Cl^- ions decreases with decrease of $MgCl_2$ content, and the angle between Cl–Mg–Cl becomes the angle of the tetrahedral configuration of $MgCl_4^{2-}$ with decrease of $MgCl_2$ content.

Figure 4 shows the estimated mixing enthalpy (H_{mix}) as well as the experimental one. Although the computed H_{mix} is about 5 times larger than the experimental one, these two mixing enthalpies are expressed by similar functions:

$$H_{mix}(\text{this work}) = -106.8\,(x_1 - x_1^3)\,\text{kJ/mol}, \quad (7)$$

$$H_{mix}(\text{experimental}) = -20.0\,(x_1 - x_1^3)\,\text{kJ/mol}. \quad (8)$$

The solid lines in Fig. 4 are drawn with these equations. According to Hoch [11], it is concluded that the atomic interaction in the simulated system is similar to that in the real system.

4. Conclusion

With the potential parameters which reproduced the experimental structure factor well, molten $NaCl-MgCl_2$ was well simulated. The simulated system explains the experimental results.

The fraction of isolated $MgCl_4^{2-}$, which was determined in this work, is similar to the experimental one [4].

The mixing enthalpy as a function of x_2 estimated by the MD simulation is similar to that estimated experimentally, Thus the atomic interaction in the simulated system is similar to that in the real system.

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