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Investigation of thermodynamic properties of molten rare earth trichlorides by molecular dynamics method

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Abstract

The physical and thermodynamic properties of molten rare earth trichlorides were investigated by the molecular dynamics (MD) technique. In addition to a fully ionic model, partially ionic models, in which covalency was considered in the nearest unlike ion pair (cation–chloride ion), was used in the present work. The liquid structure, shear viscosity and enthalpy of molten YCl_3 and $LaCl_3$ calculated from the MD simulation were compared with the experimental data. It is concluded that the partially ionic model can better represent the experimental data than the fully ionic model. © 1997 Elsevier Science B.V.

1. Introduction

Recently, the use of molten chloride salts has been proposed in the fields of nuclear fuel cycle based on pyrochemistry [1] and the transmutation process of minor actinides with a proton accelerator [2]. Physical and chemical properties of molten salts must be known for the development of those technologies. The database of the physical properties of polyvalent metal chloride melts, however, is not enough for this purpose.

We have calculated the structure, electrical conductance and shear viscosity of molten YCl_3 by the MD method using a fully ionic model [3]. The calculated results from the fully ionic model, however, were in poor agreement with the experimental data. In the present work, the physical and thermodynamic properties for molten YCl_3 (m.p. 994 K) and $LaCl_3$ (m.p. 1131 K) were investigated by molecular dynamics (MD) simulations based on partially ionic models.

2. Calculation procedure

In the MD calculation, thermodynamic properties were obtained from 50000 steps data using 512 particle systems; shear viscosity and structure were obtained from 500,000 steps data using 1000 particle systems. Calculations were performed by the workstation SUN4 for the 512 particles system and the supercomputer VPP500 at JAERI for 1000 particles system. The step width used in the simulation was 5.0 fs (5.0×10^{-15} s).

The fully ionic potential used in the present simulation was ionic Busing-type potential with parameters proposed by Tatlipinar et al. [4],

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} + b(f_i + f_j)\exp\left[\frac{\sigma_i\sigma_j - r}{f_i + f_j}\right], \tag{1}$$

where z_i is electric charge. Other parameters such as f_i and σ_i are adjustable and were determined to reproduce the experimental structural and Raman scattering. On the other hand, the following potential [5], in which a combination of the Busing-type potential and covalent Morse potential (third term) was obtained, was used for the nearest unlike ion pair in the partially ionic model,

$$\phi_{ij}(r) = \frac{n_1^2 z_i z_j e^2}{r} + n_2 b(f_i + f_j)\exp\left[\frac{\sigma_i + \sigma_j - r}{f_i + f_j}\right] + D_M\{\exp[-2\alpha(r - r_0)] - 2\exp[-\alpha(r - r_0)]\}, \tag{2}$$

where D_M is the bonding energy at interatomic distance r_0

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and α corresponds to the sharpness of the potential curve. In Eq. (2), n_1 shows ionicity (between 0 and 1). In the present work, $n = n_1 = n_2$ was assumed for simplicity. It has been reported [6] that molten rare earth trichlorides have an octahedral structure, in which the cation is surrounded by six chloride ions, as a basic structure unit. Covalency between the cation and anion inside the octahedron is assumed in the partially ionic model. Parameters in the Morse potential (the third term in Eq. (2)) were selected so as to reproduce the liquid structure [7,8] and Raman scattering data [6,9]. As to all other interactions, Eq. (1) with the fully ionic model was used also in the partially ionic model.

The molar volume at atmospheric pressure and the internal energy U at zero pressure were obtained from an isothermal–isobaric (NPT) simulation. Enthalpy $H(T) - H(T_0)$ is equivalent to $U(T) - U(T_0)$ at zero pressure. On the other hand, the structure and shear viscosity were calculated from isothermal (NVT = constant) simulations as described in the previous report [3].

3. Results and discussion

3.1. Molten YCl_3

Molar volumes of molten YCl_3 calculated from the NPT simulation are shown in Fig. 1, together with the experimental data. The calculated values were deduced from the cell size averaging from 50 000 steps data at atmospheric pressure. The experimental value in Fig. 1 was extended to wider temperature range by use of the corresponding-states data correlation [10]. Volumes from the fully ionic model were larger than from the experimental curve. This must be due to extraordinary high pressure (2.8 GPa) obtained in the NVT simulation. On the other hand, the half ionic model ($n = 0.5$) showed an extremely smaller volume. The partially ionic model of $n = 0.67$ represents the best agreement with the experimental data.

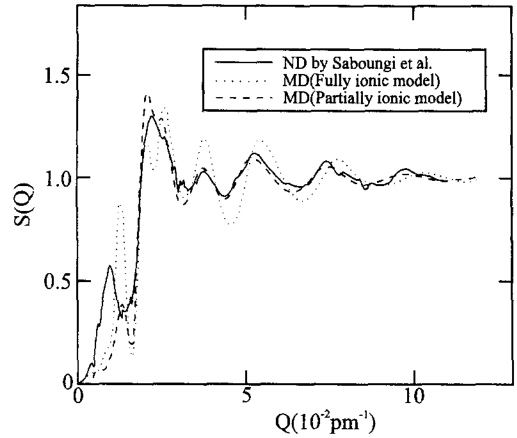

Fig. 2. Structure factor $S(Q)$ of molten YCl_3 by NVT simulation.

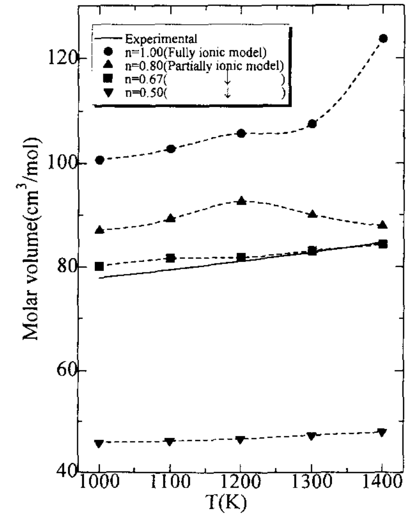

Fig. 1. Molar volume of molten YCl_3 by NPT simulation.

Structural factors of molten YCl_3 calculated from the isothermal NVT simulations were compared in Fig. 2 with the experimental data reported by Saboungi et al. [7]. It can be seen that the result from the partially ionic model ($n = 0.67$) gave a better fit to the experimental data.

The shear viscosity of molten YCl_3, calculated from the NVT simulations with various ionicities are shown in Fig. 3. Experimental shear viscosities of some rare earth trichlorides [11] are also plotted in Fig. 3, since the experimental data of molten YCl_3 has not been reported. Calculations using the fully ionic model and the partially ionic model of higher ionicity ($n > 0.70$) do not yield convergence values at 1000 K. The shear viscosity of molten YCl_3 from the partially ionic model ($n = 0.67$), which showed good agreement in molar volume, structure

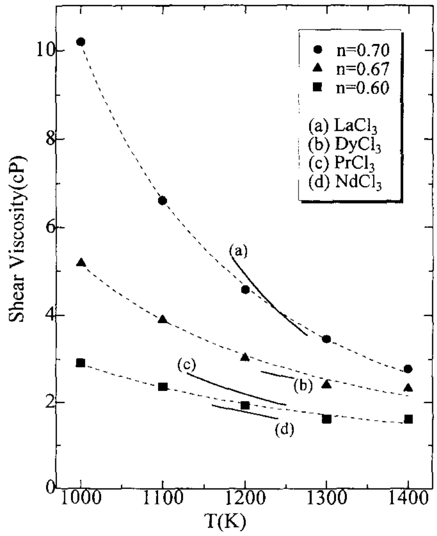

Fig. 3. Shear viscosity of molten YCl_3 by NVT simulation.

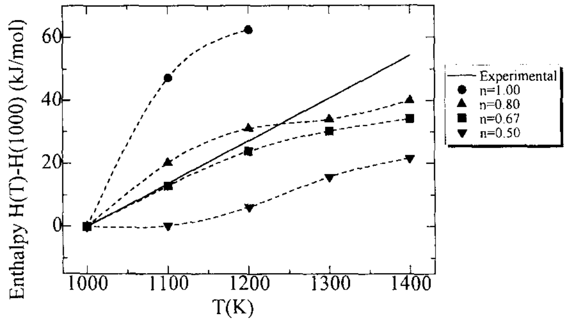

Fig. 4. Enthalpy $H(T) - H(1000)$ of molten YCl_3 by NPT simulation.

and enthalpy with the experimental data, is similar to that of molten $DyCl_3$. In the previous work [3], we speculated that the shear viscosity of molten YCl_3 must be close to that of molten $DyCl_3$, since both salts have the same crystal structure ($AlCl_3$-type) and similar melting points, volume change of melting, electrical conductance and molar volume.

The enthalpy ($H(T) - H(1000)$) of molten YCl_3 from the NPT simulation is shown in Fig. 4. Experimental data was taken from the recommended value by Barin [12]. In the fully ionic model, extremely higher values were obtained. The model $n = 0.67$ resulted in a good agreement with the experimental data below 1200 K, but slightly lower values at a higher temperature. Another partially ionic model, $n = 0.80$, also showed a relatively good agreement as a whole, especially better than the model $n = 0.67$ at a higher temperature. The model $n = 0.80$ gave a larger volume by ca. 10% than the experimental data and did not result in convergence for the calculation of shear viscosity. This means that the model (ionicity n) giving the best fit to the experimental data for some physical properties is not necessary unique.

3.2. Molten $LaCl_3$

In the simulation of molten $LaCl_3$, the model $n = 0.77$ gave the best agreement for the molar volume, structure and the enthalpy change with the experimental data. Fig. 5 shows the enthalpy ($H(T) - H(1150)$) of molten $LaCl_3$ calculated from the NPT simulation. The model $n = 0.77$, which is slightly more ionic than YCl_3, resulted in a good agreement with the recommended values [12].

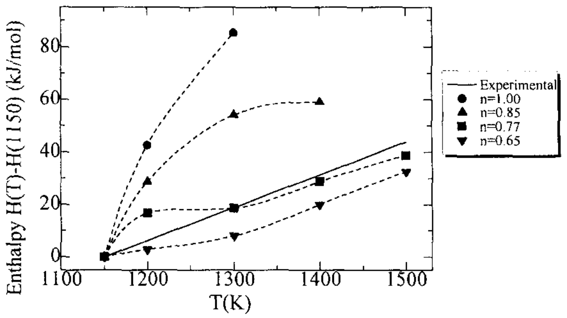

Fig. 5. Enthalpy $H(T) - H(1150)$ of molten $LaCl_3$ by NPT simulation.

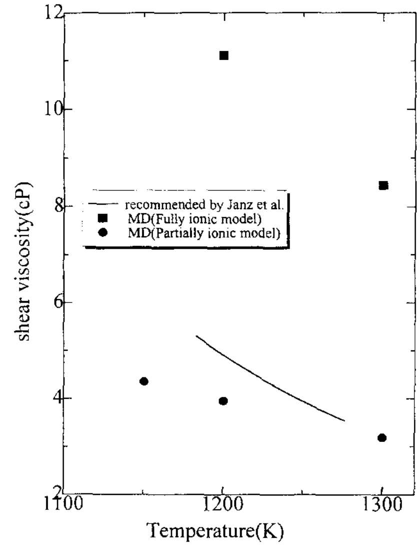

Fig. 6. Shear viscosity of molten $LaCl_3$ by NVT simulation.

The shear viscosity of molten $LaCl_3$ calculated by the NVT simulation was shown in Fig. 6. The calculated value from the fully ionic model was extraordinarily greater than the experimental data recommended by Janz [11]. On the other hand, the result from the partially ionic model $n = 0.77$ was smaller, especially at a lower temperature, than the recommended data. Evidently, the best model concerning the shear viscosity of molten $LaCl_3$ is not $n = 0.77$. There is no unique model also in molten $LaCl_3$ similar to molten YCl_3.

4. Conclusion

The applicability of the partially ionic model, in which covalent contribution was considered in the nearest correlation between cation and anion, was investigated for molten rare earth trichlorides. In the present study, thermodynamic properties calculated from the NPT simulation were used to examine the models in addition to the properties calculated from the NVT simulation [3].

The partially ionic models gave a better agreement in all physical properties than the fully ionic model. This proved that the partially ionic models, $n = 0.67$ for molten YCl_3 and $n = 0.77$ for molten $LaCl_3$, were better models in fitting to the experimental data of the molar volume and the structure than the fully ionic model. The model $n = 0.80$ for molten YCl_3, however, also matched with the experimental data of the enthalpy changes. The model

$n = 0.77$ in molten $LaCl_3$ showed considerably lower shear viscosity than the recommended data. It can be concluded that the partially ionic model may be better than the fully ionic model, though a unique model could not be obtained in the simulations.

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