Mixing Enthalpy and Structure of the Molten NaCl-DyCl₃ System

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Mixing enthalpy (H_{mix}) at 1100 K was measured in the molten NaCl–DyCl₃ system by calorimetry. The interaction parameter (λ : $H_{\text{mix}} = -\lambda x_1 x_2$) of this system is given in kJ mol⁻¹ by

$$\lambda = 48.74x_2^3 - 20.90x_2^2 - 62.92x_2 + 56.44$$

where x_1 and x_2 are mole fractions of NaCl and DyCl₃, respectively. Isothermal molecular dynamics (MD) simulations of the molten DyCl₃ and NaCl–DyCl₃ systems were carried out to calculate the mixing enthalpy, and then the structure in these systems were investigated. In the simulated systems the coordination number of Cl⁻ ions around Dy³⁺ ion is 6, and Dy₂Cl₁₁¹⁵⁻ and Dy₃Cl₁₆⁷⁻ were observed as well as DyCl₆³⁻. Although most of these polymers share apex Cl⁻ ions, an edge sharing polymers were found around $x_2 = 0.4$. Experimental mixing enthalpy is discussed in terms of polymers in the simulated systems.

1 INTRODUCTION

Spent metallic fuels in fast nuclear reactors contain significant amount of fission lanthanide elements. In the Integral Fast Reactor (IFR) program¹⁾ proposed by Argonne National Laboratory in the United States, fission lanthanide elements as well as other elements are transferred into a molten salt (an eutectic mixture of LiCl and KCl) by anodic dissolution: a spent metallic fuel is an anode. Depending on standard decomposition potentials, some elements among elements transferred from the anode to the melt may be recovered by electrolysis. As well known, a decomposition potential (E) is determined by the Nernst equation,

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

where E_0 , R , T , F , n , a_{Mn^+} and a_{M} are a standard decomposition potential, the gas constant, temperature, the Faraday constant, an electron transfer number and activities of an ion Mn^+ and a product M . The activity coefficient ($\gamma_i = a_i/x_i$) of a component i is related to the mixing enthalpy as follows.

$$RT \ln \gamma_i = G^e_i = H^i_{\text{mix}} - TS^e_i \quad (2)$$

where G^e_i , H^i_{mix} and S^e_i are partial molar quantities of excess Gibbs energy, mixing enthalpy and excess entropy of a component i . Thermodynamic properties of lanthanide halides in molten salt solvents show that lanthanide ions are much stabilized²⁾, which means that their activities become much smaller than in their pure melts. Although structure of the molten lanthanide halides and their mixture have been scarcely revealed, Mochinaga and Igarashi³⁾ suggested more complicated complexes than MX_6^{3-} (M : lanthanide ion and X : halide ion), which is determined by X-ray diffraction. In this paper, mixing enthalpy was estimated experimentally in the molten NaCl–DyCl₃ and stabilization of Dy³⁺ ion in this system was interpreted in terms

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of complexes by molecular dynamics (MD) simulation.

2 COMPUTATIONAL AND EXPERIMENTAL

In order to carry out MD simulations, the following pair potential (u_{ij}) between ions i and j was employed.

$$u_{ij}(r) = z_i z_j e^2 / 4\pi\epsilon_0 r + b A_{ij} \exp((r_i^0 + r_j^0 - r) / \rho) \quad (3)$$

where r , z , e , ϵ_0 , b , A , r^0 and ρ are a separation distance between ions i and j , the valence number, the elementary charge of electron, the dielectric constant of vacuum, the pre-exponential term, the Pauling factor, an ionic radius and a softness parameter, respectively. Since the values of r^0 and ρ of Dy^{3+} ion are not available, they were adjusted to reproduce experimental structure factors⁴⁾ of the molten DyCl_3 and the molten $\text{NaCl}-\text{DyCl}_3$ systems. In order to compare the experimental and computational structure factors, MD simulations of two systems were carried out, i. e., one is for the pure molten DyCl_3 at 973 K and the other is for the equimolar $\text{NaCl}-\text{DyCl}_3$ system at 743 K. The basic cells contain 108 Dy and 324 Cl ions for the pure DyCl_3 , and 80 Dy, 80 Na and 320 Cl ions for the $\text{NaCl}-\text{DyCl}_3$ (50/50 mol%) mixture. The softness parameter ρ for NaCl is given by Fumi and Tosi⁵⁾ and ρ in the mixture was evaluated according to Larsen and Førlund⁶⁾. The simulated systems were well annealed (more than 10^4 time steps: $\Delta t = 0.5$ fs) by the Verlet method, then the isothermal MD simulation proposed by Nose⁷⁾ was adopted. The structure factors were estimated in the basic cells by the Debye equation.

$$Q_i(Q) = \sum \sum f_i f_j \sin(Qr_{ij}) / r_{ij} \quad (4)$$

where Q and f_i are the wave number and the atomic structure factor of a component i , respectively.

Then we made MD simulations at 1100 K to obtain mixing enthalpy in this system. Potential energy ϕ was estimated according to Eq. (1), where the coulomb energy was evaluated by the

Ewald method, and the internal energy U was calculated by

$$U = \phi + K.E. \quad (5)$$

where $K.E.$ is the kinetic energy. Although one can obtain enthalpy by

$$H = U + pV \quad (6)$$

where p and V are pressure and molar volume, respectively, it is usually difficult to estimate p , because p is small difference between two large quantities (coulombic and repulsive). In condensed phases pV is so small that it can be neglected: in this work pV is less than 0.1 kJ/mol. Thus in this work the internal energy is employed as enthalpy.

Mixing enthalpy at 1100 K was measured in the molten $\text{NaCl}-\text{DyCl}_3$ system by calorimetry. Experimental procedure is described elsewhere in detail^{2,8)}.

3 RESULTS

Figure 1 shows the molar mixing enthalpy (H_{mix}) measured by calorimetry. The interaction parameter, λ , is defined by

$$H_{mix} = -\lambda x_1 x_2 \quad (7)$$

where x is a mole fraction (x_1 : NaCl and x_2 : DyCl_3), and obtained by the least square fitting of calorimetric data.

$$\lambda = 48.74x_2^3 - 20.90x_2^2 - 62.92x_2 + 56.44 \quad (8)$$

Fig. 1 Experimental mixing enthalpy in the molten $\text{NaCl}-\text{DyCl}_3$ system at 1100 K.

The solid line in Fig. 1 indicates the mixing enthalpy estimated with Eqs. (7) and (8).

Figures 2a and 2b are the experimental and computational structure factors for the molten systems DyCl_3 and NaCl-DyCl_3 (50/50 mol%), respectively. We concluded that the adjusted parameter ($r^0_{\text{Dy}} = 0.113$ nm and $\rho = 0.025$ nm) give reasonable agreement between experimental and computational structure factors.

Conditions of the simulated systems to estimate the mixing enthalpy are listed in Table 1 as well as the estimated internal energy. The mixing enthalpy in the simulated system was calculated by the following equation and depicted in Fig. 3.

$$H_{\text{mix}} = H(x_1, x_2) - x_1 H_1 - x_2 H_2 \quad (9)$$

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

Fig. 2 Experimental and computational structure factors.
a: DyCl_3 and b: equimolar NaCl-DyCl_3
○: X-ray⁴⁾ and —: MD simulation

Table 1 Conditions of MD simulation and estimated internal energy of the molten NaCl-DyCl_3 system.

x_2	Number of ions			Internal energy/kJ mol ⁻¹
	Dy	Na	Cl	
0	0	108	108	-695.5 ± 1.7
0.20	40	160	280	-1398.3 ± 1.7
0.30	45	105	240	-1747.7 ± 1.7
0.35	35	65	170	-1919.5 ± 2.5
0.40	60	90	270	-2087.5 ± 2.0
0.40	40	60	180	-2089.1 ± 2.0
0.45	45	55	190	-2261.6 ± 2.5
0.50	80	80	320	-2436.5 ± 1.9
0.60	60	40	220	-2765.8 ± 2.3
0.70	70	30	240	-3102.5 ± 2.5
1.0	108	0	324	-4119.8 ± 2.7

Fig. 3 Computational mixing enthalpy in the molten NaCl-DyCl_3 system at 1100 K.

4 DISCUSSION

Although there are some discrepancies between Fig. 1 and Fig. 3 as follows, an interaction around $x_2 = 0.35$ is realized by the MD simulation.

(1) In Fig. 3, one can see two peaks at $x_2 = 0.35$ and 0.50 of DyCl_3 , while in Fig. 1, one peak at $x_2 = 0.30$ and one shoulder around $x_2 = 0.80$ are observed. The peak implies a preferential interaction between ions. In this MD simulation, ionic sizes and charges alone are taken into account. An orientational interaction of orbital electrons can not be included. Then the peaks shown in Fig. 3 correspond to a geometrical preferential arrangement.

Fig. 4 Pair correlation functions in the molten NaCl-DyCl₃ system.

(a) g_{DyDy} , (b) g_{DyCl} and (c) g_{ClCl}
solid line: DyCl₃ and broken line: $x_2 = 0.2$

(2) The magnitude of the mixing enthalpy in the simulated system is about 4 times larger than that in the experimental system. The pair potential given by Eq. (1) excludes dispersion terms, which may affect the repulsion parameter ρ . We should discuss an inclination of the mixing enthalpy.

Then in this work we try to interpret the interaction at $x_2 = 0.35$ by the MD simulation.

Table 2 First peak position of the pair correlation functions.

x_2	First peak positions/nm		
	Dy-Dy	Dy-Cl	Cl-Cl
0.20	0.507	0.253	0.363
0.30	0.507	0.255	0.363
0.35	0.511	0.255	0.361
0.40	0.515	0.257	0.363
0.45	0.507	0.257	0.363
0.50	0.507	0.255	0.361
0.60	0.507	0.259	0.359
0.70	0.507	0.261	0.359
1.00	0.509	0.265	0.363

The pair correlation functions between Dy and Cl are depicted in Figs. 4a, 4b and 4c for the systems with $x_2 = 1.0$ and 0.2 and their first peak positions of the interactions are listed in Table 2. While interaction distance between Cl-Cl does not significantly depend on composition, interaction distance between Dy and Cl increases with an increase of x_2 , and that between Dy and Dy drastically increases at $x_2 = 0.4$. An increase in separation distance between opposite sign ions will bring increase of the internal energy and vice versa. In all compositions, a coordination number of Cl⁻ ions around Dy³⁺ ion is 6. As shown in Fig. 4b, the first peak of g_{DyCl} is isolated, which means that the complex DyCl₆³⁻ is rigid. Figure 4a shows that the first interaction between Dy and Dy is extinct at 0.58 nm. When separation distance between any two Dy³⁺ ions selected arbitrarily in a group of Dy³⁺ ions is within this extinction distance, we considered a group of these Dy³⁺ ions as a complex. Size distribution of

Table 3 Size distribution of complex ions in the molten NaCl-DyCl₃ system.

x_2	monomer ^{a)}	dimer ^{b)}	trimer ^{c)}	tetramer ^{d)}
	%			
0.20	79	21	0	0
0.30	87	10	3	0
0.35	70	30	0	0
0.40	81	12	4	0
0.40	78	19	3	0
0.50	79	15	5	1
0.60	82	14	4	0

a) DyCl₆³⁻, b) Dy₂Cl₁₁⁵⁻ and Dy₂Cl₁₀⁴⁻, c) Dy₃Cl₁₆⁷⁻ and Dy₃Cl₁₅⁶⁻ and d) Dy₄Cl₂₁⁹⁻.

Fig. 5 Pair correlation functions between Dy and Dy around $r=0.5$ nm.

---: $x_2=0.2$, $\bullet$: $x_2=0.3$, $\circ$: $x_2=0.4$ and $\square$: $x_2=0.5$.

complex ions is listed in Table 3. At $x_2=1.0$ and 0.7 , more complicated networks were found, so that these results were excluded in Table 3. Most Dy ions exist as DyCl_6^{3-} and most polymers as $\text{Dy}_n\text{Cl}_{5n+1}$ ($n=2$ or 3). Polymers which is different from $\text{Dy}_n\text{Cl}_{5n+1}$ appear between $x_2=0.4$ and 0.6 . For example, stereoscopic views of $\text{Dy}_2\text{Cl}_{10}^{4-}$ and $\text{Dy}_3\text{Cl}_{15}^{6-}$ are depicted in Figs. 6a and 6b, respectively.

We observed a small hump before the first main peak of g_{DyDy} , as shown in Fig. 5. This peak is remarkable at $x_2=0.4$ and corresponds to a separation distance between Dy and Dy in the edge shared complex, which is shown in Fig. 6a. Formation of this kind of complex decreases the enthalpy. Thus we should find the minimum of the of the mixing enthalpy as $x_2=0.4$ instead of $x_2=0.35$. Although we repeated the MD simulation with a different initial configuration at $x_2=0.4$, we failed to obtain the minimum of the mixing enthalpy at $x_2=0.4$. It is difficult to say what sifts the minimum of the mixing enthalpy at present. However, it may be concluded that decrease of interaction distance between opposite sign ions with decrease of x_2 and appearance of the edge sharing complexes decreases the mixing enthalpy.

Partial molar mixing enthalpy of DyCl_3 in the molten $\text{NaCl}-\text{DyCl}_3$ can be estimated by the following equation.

Fig. 6 Stereoscopic view of complex ions. (a) $\text{Dy}_2\text{Cl}_{10}^{4-}$ and (b) $\text{Dy}_3\text{Cl}_{15}^{6-}$.

$$H_2 = H_{\text{mix}} + x_1 \frac{dH_{\text{mix}}}{dx_2} \quad (10)$$

Then at the limit $x_2 \rightarrow 0$, we obtain $H_2 = -56.44 \text{ kJ mol}^{-1}$, which means that Dy^{3+} ion is stabilized in the dilute solution of DyCl_3 .

5 CONCLUSIONS

Mixing enthalpy in the molten $\text{NaCl}-\text{DyCl}_3$ was measured at 1100 K by calorimetry. As shown in Fig. 1, the molar mixing enthalpy of this system has a minimum at $x_2=0.3$. Isothermal MD simulation of this system was carried out to estimate the mixing enthalpy. Although the experimental and computational mixing enthalpies show some discrepancies, they have minimums around $x_2=0.3$. This minimum is attributed to formation of the edge sharing polymers.

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