MIXING ENTHALPY AND STRUCTURE OF
THE MOLTEN NaCl-DyCl₃ SYSTEM

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ABSTRACT

The enthalpy of mixing \( \Delta_{\text{mix}} H_m \) of the NaCl-DyCl₃ system was measured at 1100K by direct calorimetry in the whole composition range. The enthalpies of mixing values are negative with a minimum value at DyCl₃ ≈ 0.4.

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 was investigated.

In the simulated systems the coordination number of the Cl⁻ ions around the Dy³⁺ ion is 6. The complex ions Dy₂Cl₁₁⁻ and Dy₃Cl₁₆⁻ were observed as well as DyCl₆⁻. Although most of these polymers share apex Cl⁻ ions, an edge sharing polymers were found around xDyCl₃ ≈ 0.4.

INTRODUCTION

Spent metallic fuels in fast nuclear reactors contain significant amount of fissile lanthanide elements. In the Integral Fast Reactor (IFR) program proposed by Argonne National Laboratory in the United States, fissile lanthanide elements as well as other elements are transferred into a molten salt (an eutectic mixture of LiCl and KCl) by anodic dissolution since a spent metallic fuel acts as an anode (1).
Depending on standard decomposition potentials, some elements among those 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:

\[ E = E_0 + \frac{RT}{nF} \ln \left( \frac{a_{Mn^+}}{a_M} \right) \]

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

\[ RT \ln \gamma_i = \Delta_{mix}^{G^{xs}}_{m,i} = \Delta_{mix}^{H^{m}}_{m,i} - T \Delta_{mix}^{S^{xs}}_{m,i} \]

where \( \Delta_{mix}^{G^{xs}}_{m,i} \), \( \Delta_{mix}^{H^{m}}_{m,i} \) and \( \Delta_{mix}^{S^{xs}}_{m,i} \) are the partial molar excess Gibbs free energy, mixing enthalpy and excess entropy of the component i.

The thermodynamic properties and the phase diagrams of lanthanide halides in molten alkali chloride solvents show that the lanthanide ions are much stabilized (2-11), i.e. that their activities become much smaller than in their pure melts. The structure of structure of the molten lanthanide halides or of halides containing a trivalent cation is not accurately known so far since most structural investigations, by X-ray or neutron diffraction, were performed on monovalent and divalent molten salts (12-15).

Although structure of the molten lanthanide halides and their mixtures have been scarcely revealed, Mochinaga et al. (16) suggested complexes more complicated than \( MX_6^{3-} \) ( M: lanthanide ion and X: halide ion ) which is determined by X-ray diffraction.

In the present work the mixing enthalpy of the molten NaCl-DyCl\(_3\) system was measured by direct calorimetry and the stabilization of the Dy\(^{3+}\) ion in this system was interpreted in terms of complexes by molecular dynamics (MD) simulation.

**EXPERIMENTAL**

Mixing enthalpy at 1100K was measured in the molten NaCl-DyCl\(_3\) system by direct calorimetry.

**A. Chemicals**

DyCl\(_3\) was synthesized from Dy\(_2\)O\(_3\) (99.9 %) produced by Hydromet Co. (Kowary, Poland). The main steps of this synthesis are the same as for NdCl\(_3\) preparation and have been described in detail previously (17): DyCl\(_3\) obtained after successive distillations, was of high grade (min. 99.9 %).
NaCl was a Merck Suprapur reagent (min. 99.9%). Before its use in the calorimeter it was purified and treated by progressive heating up to fusion under gaseous HCl atmosphere. Excess HCl was removed from the melt by argon. All the salts were kept and handled in the glove-box.

B. Procedures.

The mixing experiments were all of the simple liquid-liquid type under argon at atmospheric pressure. The calorimetric apparatus, a Calvet-type high temperature microcalorimeter, the mixing devices used and the experimental methods adopted have all been described in some detail elsewhere (18). Mixing of the two salts was obtained by the break-off ampoule technique.

Calibration of the calorimeter was performed with NIST α-alumina (19); known amounts of alumina were dropped directly in the melt. Integration of the surface of thermograms was made automatically by computer. The experimental uncertainty on calibration is about 3%; the experimental uncertainty on enthalpy of mixing data is estimated to be 6% since they are obtained from independent experiments.

**COMPUTATION**

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

$$u_{ij}(r) = z_i z_j e^2 / 4 \pi \varepsilon_0 r + b A_{ij} \exp[(r_1^\circ + r_2^\circ - r) / \rho]$$  \[3\]

where $r$, $z$, $e$, $\varepsilon_0$, $b$, $A$, $r^\circ$ and $\rho$ are the 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 $r^\circ$ and $\rho$ of Dy$^{3+}$ ion are not available, they were adjusted to reproduce experimental structure factors (20) of the molten DyCl$_3$ and the molten NaCl-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 973K and the other one for the equimolar NaCl-DyCl$_3$ (50/50 mol%) mixture. The basic cells contained 108 Dy and 324 Cl ions for the pure DyCl$_3$, and 80 Dy, 80 Na and 320 Cl ions for the NaCl-DyCl$_3$ (50/50 mol%) mixture. The softness parameter $\rho$ for NaCl is given by Fumi and Tosi (21) and $\rho$ in the mixture was evaluated according to Larsen and Forland (22). The simulated systems were well annealed (more than 10 time steps: $\Delta t = 0.5$fs) by the Velret method, then the isothermal MD simulation proposed by Nose (20) was adopted. The structure factors were estimated in the basic cells by the Debye
equation.

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

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 1100K to obtain the enthalpy of mixing in this system. Potential energy $\Phi$ was estimated according to Eq. [1], where the Coulomb energy was evaluated by the Ewald method, and the internal energy $U$ was calculated by

$$U = \Phi + E_k$$

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

$$H = U + pV$$

where $p$ and $V$ are pressure and molar volume, respectively, it is usually difficult to estimate $p$, because $p$ is small and results from the 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. Accordingly, in this work the enthalpy was assimilated to internal energy.

RESULTS

Figure 1 shows the molar mixing enthalpy $\Delta_{\text{mix}} H_m$ measured by calorimetry. The interaction parameter, $\lambda$, defined by

$$\Delta_{\text{mix}} H_m = -\lambda x_{\text{DyCl}}^3 (1 - x_{\text{DyCl}})$$

is obtained by least square fitting of calorimetric data (in kJ/mol):

$$\lambda = 48.74 \times_{\text{DyCl}}^3 - 20.90 \times_{\text{DyCl}}^2 - 62.92 \times_{\text{DyCl}} + 56.44$$

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%) separately. We concluded that the adjusted parameter ($r_{\text{Dy}} = 0.173$ nm and $r = 0.025$ nm) give reasonable agreement between experimental and computational structure factors.

The mixing enthalpy in the simulated system was calculated by the following equation and depicted in Fig.3.

$$\Delta_{\text{mix}} H_m = H_m(x_{\text{NaCl}}, x_{\text{DyCl}}^3) - x_{\text{NaCl}} H_m(\text{NaCl}) - x_{\text{DyCl}} H_m(\text{DyCl}_3)$$

where $H_m(\text{NaCl})$ and $H_m(\text{DyCl}_3)$ are the enthalpies of the pure components.

DISCUSSION

Although there are some discrepancies between Fig. 1 and Fig. 3 as follows, an
interaction around \( x_{\text{DyCl}_3} = 0.35 \) is realized by the MD simulation.

i) In Fig. 3, one can see two peaks at \( x_{\text{DyCl}_3} = 0.35 \) and \( x_{\text{DyCl}_3} = 0.50 \), while in Fig. 1, one peak at \( x_{\text{DyCl}_3} = 0.30 \) and one shoulder around \( x_{\text{DyCl}_3} = 0.80 \) are observed. The peak implies a preferential interaction between ions. In this MD simulation, only ionic sizes and charges are taken into account. An orientational interaction of orbital electrons cannot be included. Then the peaks shown in Fig. 3 correspond to a geometrical preferential arrangement.

ii) The magnitude of the enthalpy of mixing 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 \( \rho \).

Then in this work we try to interpret the interaction at \( x_{\text{DyCl}_3} = 0.35 \) by the MD simulation.

The pair correlation functions between Dy and Cl are depicted in Figs. 4a, 4b and 4c for the systems with \( x_{\text{DyCl}_3} = 1.0 \) and 0.2. While interaction distance between Cl-Cl does not significantly depend on composition, interaction distance between Dy and Cl increases with an increase of \( x_{\text{DyCl}_3} \), and that between Dy and Dy drastically increases at \( x_{\text{DyCl}_3} = 0.4 \). 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 Dy\(^{3+}\) ion is 6. As shown in Fig. 4b, the first peak of \( g_{\text{DyCl}} \) is isolated, which means that the complex \( \text{DyCl}_6^{3-} \) 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 Dy\(^{3+}\) ions selected arbitrarily in a group of Dy\(^{3+}\) ions is within this extinction distance, we considered a group of these Dy\(^{3+}\) ions as a complex. Most Dy ions exist as \( \text{DyCl}_6^{3-} \) and most polymers as \( \text{Dy}_n\text{Cl}_{5n+1} \) (\( n = 2 \) or 3). Polymers which are different from \( \text{Dy}_n\text{Cl}_{5n+1} \) appear between \( x_{\text{DyCl}_3} = 0.1 \) 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 \( g_{\text{DyDy}} \), as shown in Fig. 5. This peak is remarkable at \( x_{\text{DyCl}_3} = 0.4 \) 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 at \( x_{\text{DyCl}_3} = 0.4 \) instead of \( x_{\text{DyCl}_3} = 0.35 \).

Although we repeated the MD simulation with a different initial configuration at \( x_{\text{DyCl}_3} = 0.4 \), we failed to obtain the minimum of the mixing enthalpy at \( x_{\text{DyCl}_3} = 0.4 \). It is difficult to say what shifts the minimum of the mixing enthalpy at present. However, it may be concluded that the decrease of interaction distance between opposite sign ions with decrease of \( x_{\text{DyCl}_3} \) and appearance of the edge sharing complexes decreases the mixing enthalpy.

The partial molar mixing enthalpy of DyCl\(_3\) in the molten NaCl-DyCl\(_3\) can be
estimated by the following equation.

\[ \Delta_{\text{mix}}H_m^{\text{DyCl}_3} = \Delta_{\text{mix}}H_m + (1 - x_{\text{DyCl}_3}) \left[ \frac{d\Delta_{\text{mix}}H_m}{dx_{\text{DyCl}_3}} \right] \]  

Then at the limit \( x_{\text{DyCl}_3} \rightarrow 0 \), we obtain \( \Delta_{\text{mix}}H_m^{\text{DyCl}_3} = -56.44 \text{ kJ mol}^{-1} \), which means that the \( \text{Dy}^{3+} \) ion is stabilized in the dilute solution of \( \text{DyCl}_3 \).

CONCLUSION

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

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