A Molecular Dynamics Simulation of the Electric and Thermodynamic Properties in Molten ($Nd_{1/3}$, Na or K)Cl Mixtures

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Molecular dynamics simulations have been carried out on molten ($Nd_{1/3}$, K)Cl at 1065 and 1073 K and ($Nd_{1/3}$, Na)Cl at 1124 K for various compositions. The calculated self-exchange velocity (v), self-diffusion coefficient (D), electrical conductivity (κ) and enthalpy of mixing (ΔH_{mix}) were compared with the corresponding experimental values. The calculated results revealed that v and D of potassium decrease with increasing anmount of neodymium, as expected from the experimental internal mobility (b). The decrease of b_K, v_K, and D_K are attributed to the tranquilization effect by Nd^{3+} which strongly interacts with Cl^- as well as Dy^{3+}. On the contrary, b_{Nd}, v_{Nd}, and D_{Nd} increase with increasing concentration of Nd^{3+}. This might be ascribed to the stronger association of Nd^{3+} with Cl^- due to the enhanced charge asymmetry of the two cations neighboring Cl^-. In addition, the sequences of the calculated v's, D's and κ's for the various compositions were consistent with those of the known experimental results. The experimental enthalpy of mixing with its negative dependence on the cation size was qualitatively reproduced.

Key words: Electric Conductivity, Enthalpy of Mixing; Internal Mobility; Molten $NdCl_3$-Alkali Chloride; Molecular Dynamics Simulation; Self-exchange Velocity; Self-diffusion Coefficient.

1. Introduction

Spent metallic nuclear fuels are to be reprocessed in a molten salt in the Integral Fast Reactor (IFR) program proposed by the Argonne National Laboratory (ANL) [1]. Since fission products (FPs) consist of many elements, and knowledge of the thermodynamic properties of their salts is needed to recover them, it is of interest to see if such properties can be estimated computationally. On the other hand, for this purpose, our laboratory has already examined the alloy formation of electronegative elements at liquid metal cathodes in chloride and fluoride melts by means of electrochemical techniques [2 - 6] and has proposed to apply the countercurrent electromigration method [7, 8] in order to enrich the FPs containing rare earth elements. Moreover, we have estimated the limitation of the enrichment degree in alkali chloride and fluoride ternary [9, 10] and quaternary [11] melts by MD simulation. Countercurrent electromigration has shown a significant possibility to recover La^{3+} [12], Dy^{3+} [13], and Nd^{3+} [14] in a chloride bath. Recently we have demonstrated that the orders of self-exchange velocities (SEVs) obtained from MD simulations are in good agreement with the experimental internal mobilities in molten ($Dy_{1/3}$, K)Cl [15]. The molar enthalpies of mixing of molten ($Dy_{1/3}$, A)Cl (A = Na, K, Rb and Cs) mixtures [16] display interesting tendencies: the enthalpy of mixing of binary molten rare earth-alkali chlorides is negative, and its minimum becomes deeper as the size of the alkali metal ion increases and that of the rare earth metal ion decreases. In the present work we compared the relationship between the computed electrical and thermodynamic properties with the corresponding experimental results and the structure of molten ($Nd_{1/3}$, K)Cl and ($Nd_{1/3}$, Na)Cl.

2. The Molecular Dynamics Simulation

In order to obtain a canonical ensemble, we made the MD simulation proposed by Nose [17] with the

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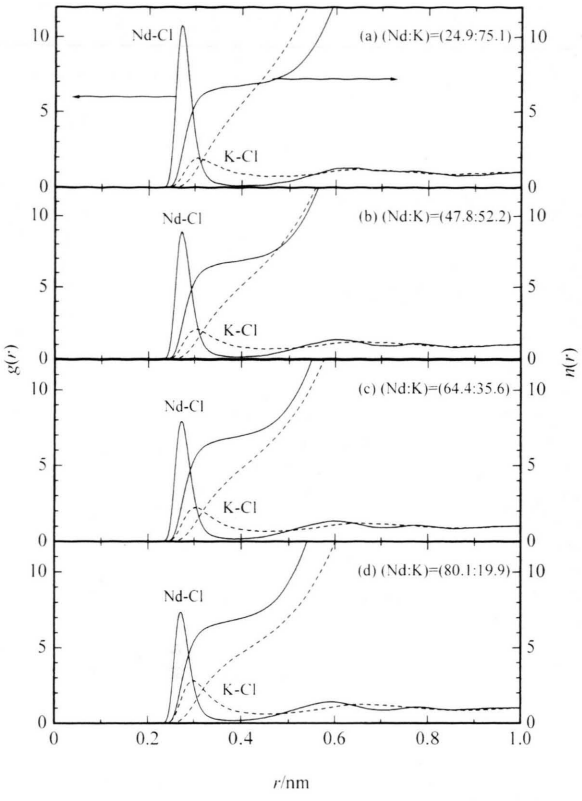

Fig. 1. The pair correlation functions $g(r)$ and the running coordination numbers $n(r)$ of molten ($Nd_{1/3}$,K)Cl for four compositions. $g_{Nd\text{-}Cl}(r)$ and $n_{Nd\text{-}Cl}(r)$; solid lines, $g_{KzCl}(r)$ and $n_{K\text{-}Cl}(r)$; broken lines.

7 points predictor-corrector method, using periodic boundaries. We employed the Born-Mayer-Huggins pair potential, excluding the dipole-quadrupole term for $NdCl_3$ and alkali chloride mixtures,

$$\Phi_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r} + A_{ij} b \exp\left[(\sigma_i + \sigma_j - r)/\rho\right] - \frac{c_{ij}}{r^6}, \quad (1)$$

$$A_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}, \quad (2)$$

where r, z, e, ε_0, b, A, σ, and ρ are the distance between the ions i and j, the valency, the elementary charge, the dielectric constant of vacuum, the pre-exponential factor, the ionic radius and a softness parameter, respectively. The Coulomb potential was evaluated by the Ewald method [18]. The potential parameters of Na^+, K^+ and Cl^-, given by Tosi and Fumi [19], were employed. The parameter c_{ij} was estimated from the ionic polarizability [20]. The side length of the periodic cell corresponded to the available density [21]. The corresponding parameters for the mixtures were determined by the combination rule given by Larsen et al. [22]. The initial cell, in which the ions were arranged in crystalline structure, was first annealed at constant temperature, following Woodcock [23]. After thousand steps, constant energy runs were started. From runs of more than 10^4 time steps, using Verlet's Algorithm by isothermal-choric (NVT) MD simulations after attainment of equilibrium, the structural and the dynamical properties were obtained. The electric conductivity was calculated by the Kubo formula [24] using 10^6 MD steps data. Isothermal-isobaric (NPT) simulations were performed in order to obtain the thermodynamic properties.

Table 1. Characteristic values of the $g_{ij}(r)$'s for cation-anion and anion-anion pairs in molten ($Nd_{1/3}$, K)Cl at 1073 K. R_1 and R_2 are the distances where $g_{ij}(r)$ crosses unity for the first and second time, respectively. R_M and R_m are the distances at the first maximum and minimum, respectively. $n_{eq}(R_2 - R_m)$ is the partial equivalent coordination number within $R_2 - R_m$ of a cation, which is equal to the coordination number of Cl^- around the cation.

System (Nd:K)	Ion Pair	R_1 /nm	R_M /nm	$g(R_M)$	R_2 /nm	R_m /nm	n_{eq} $(R_2 - R_m)$
(24.9:75.1)	Nd-Cl	0.240	0.270	10.77	0.319	0.406	6.37-6.87
	K-Cl	0.274	0.305	1.98	0.384	0.465	5.01-8.00
(47.8:52.2)	Nd-Cl	0.244	0.272	8.93	0.318	0.398	6.23-6.91
	K-Cl	0.272	0.304	2.11	0.374	0.475	4.30-7.83
(64.4:35.6)	Nd-Cl	0.246	0.272	7.95	0.318	0.387	6.22-6.91
	K-Cl	0.271	0.302	2.30	0.374	0.463	4.11-6.70
(80.1:19.9)	Nd-Cl	0.246	0.269	7.38	0.316	0.390	6.16-6.93
	K-Cl	0.264	0.299	2.85	0.371	0.460	3.99-6.07
(100.0:0.0)	Nd-Cl	0.244	0.271	6.38	0.318	0.384	6.28-7.14

3. Results and Discussion

The pair correlation functions $g(r)$ and the running coordination numbers $n(r)$ for increasing Nd/K-ratio in ($Nd_{1/3}$, K)Cl are represented in Figure 1. Some characteristic properties of $g(r)$ and $n(r)$ are tabulated in Table 1. Comparison of the pair correlation functions of pure $NdCl_3$ and KCl with those of the binary mixtures ($Nd_{1/3}$, K)Cl for various compositions shows that the position R_M of the first peak of $g_{Nd\text{-}Cl}$ remains much the same. As for the peak heights, $g_{Nd\text{-}Cl}$ is larger in the binary mixtures than in the pure $NdCl_3$ and is decreasing with increasing mole fraction of neodimium. On the contrary, $g_{K\text{-}Cl}$ is increasing with increasing contents of neodymium. These behaviors are similar to those of ($Dy_{1/3}$, K)Cl [15].

Table 2. Main experimental results and characteristic parameters obtained from MD simulation in molten ($Nd_{1/3}$, K)Cl system at 1073 K.

x_{Nd}	κ_{exp} [26] (Sm^{-1})	κ_{cal} (Sm^{-1})	$b_{Nd,exp}$ [14] ($10^{-8}m^2V^{-1}s^{-1}$)	$b_{K,exp}$ [14] ($10^{-8}m^2V^{-1}s^{-1}$)	SEV_{Nd} (ms^{-1})	SEV_K (ms^{-1})	$D_{Nd,cal}$ ($10^{-9}m^2s^{-1}$)	$D_{K,cal}$ ($10^{-9}m^2s^{-1}$)
0	224	167.6	–	–	–	–	–	2.81
0.066	206	136.2	0.95±1.67	10.7±0.1	4.589	78.343	0.45	2.23
0.249	166	102.3	–0.29±0.36	9.85±0.13	4.948	72.161	0.52	2.16
0.279	160	118.1	0.07±0.17	9.63±0.08	5.519	69.675	0.58	1.93
0.370	144	102.3	0.51±0.13	9.12±0.09	8.960	63.345	0.65	1.86
0.450	132	93.7	0.61±0.07	8.89±0.06	10.235	58.558	0.74	1.72
0.478	128	82.4	0.31±0.17	9.19±0.16	11.568	52.619	0.82	1.56
0.644	109	71.8	1.27±0.14	8.26±0.25	15.162	49.252	0.91	1.31
0.801	97.2	62.6	2.05±0.03	6.67±0.08	16.964	44.196	1.08	1.16
1.000	69.2	52.3	–	–	–	–	1.17	–

The sign ± for b indicates the errors due to the chemical analysis.

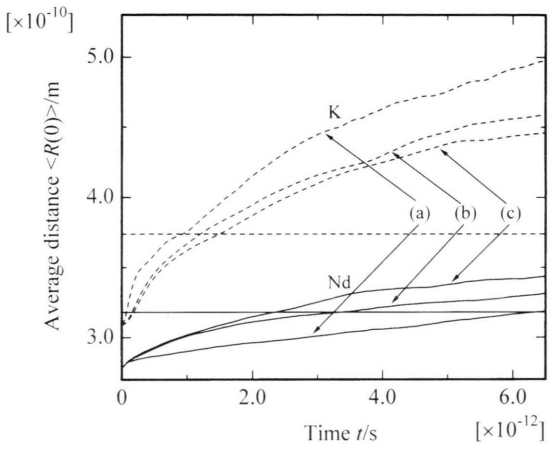

Fig. 2. Evolution for molten ($Nd_{1/3}$, K)Cl of the average distance of a marked cation from Cl^-. solid lines: Nd^{3+}, broken lines: K^+, (a) $x_{Nd} = 0.279$, (b) $x_{Nd} = 0.478$, (c) $x_{Nd} = 0.801$.

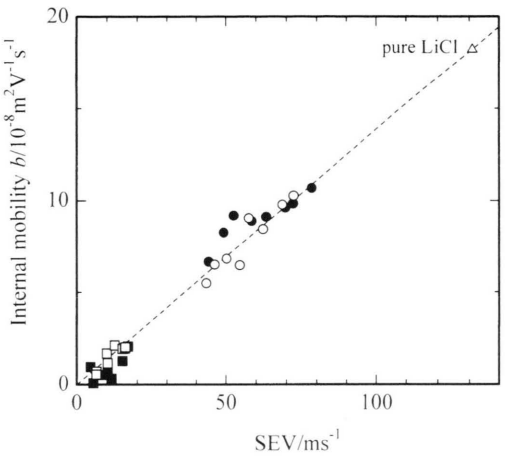

Fig. 3. Relationship between the internal cation mobility and self-exchange velocity (SEV) in molten ($Nd_{1/3}$, K)Cl at 1073 K and ($Dy_{1/3}$, K)Cl [15] at 1093 K. Nd^{3+}: black squares, K^+ in ($Nd_{1/3}$, K)Cl: black circles, Dy^{3+} [15]: white squares, K^+ [15] in ($Dy_{1/3}$, K)Cl: white circles, Li^+ in pure LiCl [25]: white triangle.

The separating motion of a cation-anion pair can be obtained in terms of the self-exchange velocity (SEV) by the molecular dynamics method. The evolution of the average distance of marked Nd^{3+} and K^+ ions from a Cl^- ion for three compositions is displayed in Figure 2. The SEV, v, which is correlated with internal mobility [25], is defined by

$$v = \frac{(R_2 - \langle R(0)\rangle)}{\tau}, \tag{3}$$

where R_2 is the distance where $g(r)$ between cation and anion reaches unity after the first peak, R_1, and $\langle R(0)\rangle$ is the average distance of cations located within R_2 from a reference anion at $t = 0$. $t = \tau$ is the average time in which the mean distance of such particles becomes R_2. Thus, the SEV is the velocity of the separating motion of two neighboring unlike ions and can be calculated with good accuracy from quite short MD simulation steps, since each anion has several neighboring cations. For the present system the SEV was calculated from 150 origins for molten binary mixtures. The solid and broken lines exhibited in Fig. 2 indicated R_2 for Nd and K, respectively. The obtained SEVs for Nd and K are summarized in Table 2, which shows that the SEV of Nd is smaller than that of K at all compositions. The strong correlation between internal mobilities and SEVs for some alkali chlorides has already been reported in [25]. The re-

Table 3. Molar enthalpy of mixing and electric parameters obtained from MD simulation in molten ($Nd_{1/3}$, A)Cl (where A = Na, K).

($Nd_{1/3}$, K)Cl, T = 1065 K			($Nd_{1/3}$, Na)Cl, T = 1124 K			($Nd_{1/3}$, Na)Cl, T = 1124 K		
x_{Nd}	$-\Delta H_{mix,exp}$ [16] ($kJmol^{-1}$)	$-\Delta H_{mix,cal}$ ($kJmol^{-1}$)	x_{Nd}	$-\Delta H_{mix,exp}$ [16] ($kJmol^{-1}$)	$-\Delta H_{mix,cal}$ ($kJmol^{-1}$)	x_{Nd} (Sm^{-1})	κ_{exp} [26] (Sm^{-1})	κ_{cal}
0.000	0.00	–	0.000	0.00	–	0.000	371.5	308.3
0.090	5.87	7.68	0.099	2.92	5.57	0.125	283.3	252.4
0.204	10.76	12.52	0.200	5.79	8.64	0.249	228.0	197.6
0.251	13.80	15.38	0.275	6.06	9.23	0.350	199.3	165.3
0.307	16.30	20.64	0.350	6.32	10.42	0.500	163.5	143.8
0.350	16.00	22.61	0.499	6.74	10.74	0.624	147.3	124.9
0.478	16.13	19.24	0.576	6.15	10.56	0.760	116.4	101.7
0.650	13.24	16.18	0.651	5.56	8.24	0.874	114.2	97.6
0.749	9.69	12.47	0.751	4.24	6.65	1.000	81.9	77.3
0.829	6.57	8.87	0.899	1.65	4.87			
1.000	0.00	–	1.000	0.00	–			

lationship between the internal cation mobility [14], b, and SEV, v, in ($Nd_{1/3}$, K)Cl and ($Dy_{1/3}$, K)Cl is shown in Figure 3. The experimentally obtained b values of K^+ and Nd^{3+} are calculated from (4), using the ε values [14] and data available on the electrical conductivities κ [26] and equivalent volumes V_e [27] of the mixtures:

$$b_K = (\kappa V_e/F)(1 + \varepsilon x_{Nd}),$$
$$b_{Nd} = (\kappa V_e/F)(1 + \varepsilon x_K), \quad (4)$$

where x is the equivalent fraction. The value of b_{Nd} increases with x_{Nd}. Cl^- ions associate with Nd^{3+} ions and form the complexes of $[NdCl_6]^{3-}$, such as $[DyCl_6]^{3-}$ in the system ($Dy_{1/3}$, K)Cl [14, 15]. The species $[NdCl_6]^{3-}$ is at high composition of Nd^{3+} less stable than at low composition of Nd^{3+} due to a shortage of Cl^- ions. b_{Nd} may be almost zero at low composition of Nd^{3+} owing to the stabilization of $[NdCl_6]^{3-}$, although it has not been confirmed yet whether b_{Nd} for $x_{Nd} < 0.4$ is negative or positive. On the contrary, b_K decreases with increasing concentration of Nd^{3+}. We believe that this is due to the tranquilization effect [28], i. e., Cl^- in $[NdCl_6]^{3-}$ approaches slowly to the K^+ ion because $[NdCl_6]^{3-}$ is very massive. Therefore the separating motion of K^+ from the neighboring Cl^- ion is slow and b_K decreases. The decrease of b_{Nd} and SEV_{Nd} with decreasing concentration of Nd^{3+} would be caused mainly by the charge-asymmetry stated below rather than by the increase in the equivalent volume. Owing to the charge asymmetry of the coordinating cations about the Cl^- ions, associates such as $[NdCl_6]^{3-}$ will have a longer life time. X-ray diffraction studies [29] of pure $NdCl_3$ melts also indicate that even in the pure melts octahedra exist, which are connected to other ones by edge- or corner-sharing. The formation with increasing x_K of such species as $[NdCl_6]^{3-}$ could be explained based on the coulombic interaction. Consequently, it seems that there is an approximately linear relation between two entities, and the ionic behavior is reproduced by SEVs obtained from the simulation.

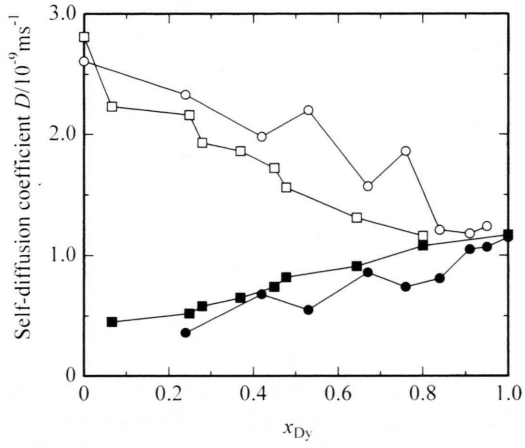

Fig. 4. Relationship between the self-diffusion coefficient and the mole fraction of Nd in molten ($Nd_{1/3}$, K)Cl at 1073K and ($Dy_{1/3}$, K)Cl at 1093 K. Nd^{3+}: black squares, K^+ in ($Nd_{1/3}$, K)Cl: white squares, Dy^{3+}: black circles, K^+ in ($Dy_{1/3}$, K)Cl: white circles.

The self-diffusion coefficients of Nd and K in molten ($Nd_{1/3}$, K)Cl were calculated from the mean squares displacements according to the Einstein expression [30]

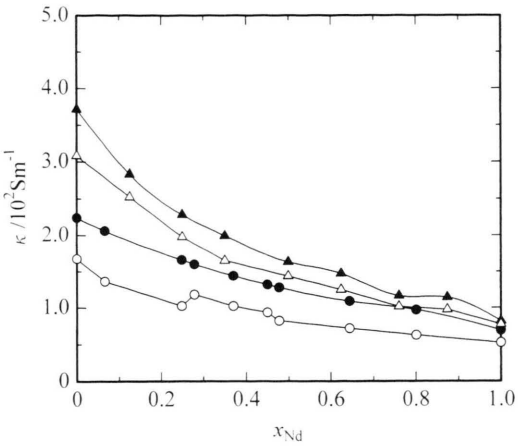

Fig. 5. Relationship between the electrical conductivity and the mole fraction of Nd in molten ($Nd_{1/3}$, K)Cl at 1073 K and ($Nd_{1/3}$, Na)Cl at 1124 K. Experimental results in ($Nd_{1/3}$, K)Cl at 1073 K [26]: black circles, MD simulation in ($Nd_{1/3}$, K)Cl at 1073 K: white circles, experimental results in ($Nd_{1/3}$, Na)Cl at 1124 K [26]: black triangles, MD simulation in ($Nd_{1/3}$, Na)Cl at 1124 K: white triangles.

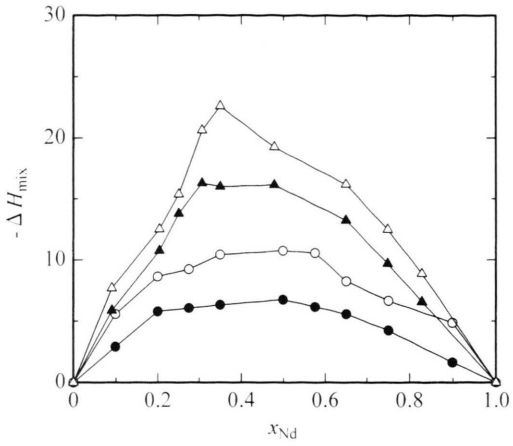

Fig. 6. Relationship between the enthalpy of mixing of molten ($Nd_{1/3}$, K)Cl at 1065 K and ($Nd_{1/3}$, Na)Cl at 1124 K. Experimental results in ($Nd_{1/3}$, K)Cl at 1065 K [26]: black triangles, MD simulation in ($Nd_{1/3}$, K)Cl at 1065 K: white triangles, experimental results in ($Nd_{1/3}$, Na)Cl at 1124 K [26]: black circles, MD simulation in ($Nd_{1/3}$, Na)Cl at 1124K: white circles.

$$D = \frac{1}{6}\frac{1}{\mathrm{d}\tau}\left\langle \{r_i(t+\tau) - r_i(t)\}^2 \right\rangle, \tag{5}$$

as given in Fig. 4 together with the results of ($Dy_{1/3}$, K)Cl [15] and Table 3, which shows that the self-diffusion coefficient of Nd^{3+} increases with increasing the concentration of Nd, and the self-diffusion coefficient of K^+ decreases with decreasing concentration of K. This is consistent with observations on our calculated self-exchange velocities and the experimental internal cation mobilities. The tendency of the self-diffusion coefficient of Nd^{3+} and K^+ is consistent with the results onf Dy^{3+} and K^+ in ($Dy_{1/3}$, K)Cl melts [15].

In addition, the electric conductivity is calculated from the integral of the current autocorrelation function $j(t)$ according to Kubo's linear response theory [24] using

$$\kappa = \frac{1}{kT}\int_0^\infty [j(0)\cdot j(t)], \tag{6}$$

where the MD contained up to 10^6 steps, because the Nernst-Einstein equation could not be applied for molten salts conventionally. The electric conductivity, calculated from the MD simulation by comparison with the experimental results, is expressed in Figure 5. The tendency could be reproduced by the MD simulation, i. e., the electric conductivity is decreasing with increasing concentration of Nd, although the values calculated from the MD simulation are smaller than the experimental one [26].

The enthalpy H was defined as internal energy U at zero pressure. U was deduced from the sum of the kinetic and potential energy:

$$U = \frac{3}{2}NkT + \sum_{i>j}\sum \phi(r_{ij}), \tag{7}$$

where N is the number of ions of the calculated system. The enthalpy of mixing was calculated by the equation [31]

$$\Delta H_{mix} = H[x\cdot NdCl_3 + (1-x)\cdot ACl] - xH[NdCl_3] - (1-x)H[ACl],\ A = Na,\ K, \tag{8}$$

where x means the mole fraction of the $NdCl_3$. In the present work, 10^6 steps were used to obtain the enthalpy. The calculated molar enthalpies of mixing of molten ($Nd_{1/3}$, A)Cl (A = Na, K) at 1065 K, 1125 K are shown in Figure 6. The calculations resulted in deeper minima for the two mixtures than found experimentally. The calculated minimum for ($Nd_{1/3}$, K)Cl is deeper than the reported value of ca. –16.30 kJ/mol [16]. There is, however, qualitative reproducibility: negative deviation, increasing with the size of the alkali ion.

The following sentence describes the correlation between the enthalpy of mixing and the molten structure. The stability of the octahedron in molten $NdCl_3$ may change by adding KCl, though the fundamental structure around the Nd ion does not change. Addition of alkali chlorides stabilizes the octahedron in both mixtures. In the single salt, the number of Cl^- ions is not sufficient to build an octahedrally-coordinated network. On the other hand, the octahedron becomes stable by supplying Cl^- ions from alkali chloride. The octahedron $[NdCl_6]^{3-}$ is more strongly stabilized by the larger K^+ ion compared with the smaller Na^+ ion. This stability of the octahedron and the medium range structural order are strongly affected by the ionic size. In the simulation, a combination of larger alkali and smaller rare-earth ions was found to produce more negative values of the enthalpy of mixing. The quantitative discrepancy between the experimental and calculated values, remains unexplained. Papatheodorou et al. [32] explained the behavior of the enthalpy of mixing of rare earth-alkali chloride binary systems by electrostatic interactions with polarization between the octahedron and the alkali ions. Better precision will be obtained by considering the polarization effect in further simulations.

4. Conclusion

This electromigration method could be used for effective separation of rare earth ions from alkali ions, because b_K and v_K are much greater than b_{Nd} and v_{Nd} in the whole concentration range, as expected. As the concentration of Nd^{3+} increases, b_K, v_K, and D_K considerably decrease. This decrease is caused by the tranquilization effect of Nd^{3+} which strongly interacts with common Cl^- ions. As the composition of K^+ increases, b_{Nd}, v_{Nd} and D_{Nd} gradually decrease and become very small at concentrations rich in KCl. This decrease could lead to a promoted association of species containing Nd^{3+} and the generation of the long-lived species $[NdCl_6]^{3-}$. In addition, the self-exchange velocity, self-diffusion coefficient and electrical conductivity of molten rare earth-alkalichloride mixtures by MD simulation were estimated and found consistent with the experimental results. The enthalpy of mixing of molten rare earth-alkali chloride mixtures has been correlated to their structural features by a molecular dynamics method. In the simulations, the dependence of the enthalpy of mixing on the ionic sizes and composition of the mixtures was qualitatively reproduced.

[1] Y. I. Chang, L. C. Walters, J. E. Battles, D. C. Wade, and M. J. Lineberry, ANL-IFR-125 (1990).
[2] M. Matsumiya and R. Takagi, Z. Naturforsch. **55a**, 673 (2000).
[3] M. Matsumiya, R. Takagi, and R. Fujita, J. Nucl. Sci. Technol. **34**, 310 (1997).
[4] M. Matsumiya, M. Takano, R. Takagi, and R. Fujita, J. Nucl. Sci. Technol. **35**, 836 (1998).
[5] M. Matsumiya, M. Takano, R. Takagi, and R. Fujita, Z. Naturforsch. **54a**, 739 (1999).
[6] M. Matsumiya, R. Takagi, and R. Fujita, J. Nucl. Sci. Technol. **35**, 137 (1998).
[7] M. Matsumiya, H. Matsuura, R. Takagi, and R. Fujita, J. Alloys Compd. **306**, 87 (2000).
[8] M. Matsumiya, H. Matsuura, R. Takagi, and R. Fujita, J. Electrochem. Soc. **147**, 11 (2000).
[9] M. Matsumiya and R. Takagi, Z. Naturforsch. **55a**, 856 (2000).
[10] M. Matsumiya and R. Takagi, Z. Naturforsch. **56a**, 279 (2001).
[11] M. Matsumiya and R. Takagi, Electrochim. Acta, to be submitted.
[12] M. Iwasaki and R. Takagi, J. Nucl. Sci. Technol. **31** [7], 751 (1994).
[13] H. Matsuura, I. Okada, R. Takagi, and Y. Iwadate, Z. Naturforsch. **53a**, 45 (1998).
[14] R. Ohashi, M. Matsumiya, H. Matsuura, and R. Takagi, Electrochemistry **67**, 550 (1999).
[15] M. Matsumiya and R. Takagi, Z. Naturforsch. **56a**, 273 (2001).
[16] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, Thermochimica **236**, 67 (1994).
[17] S. Nose, Mol. Phys. **52**, 255 (1984).
[18] P. P. Ewald, Ann. Phys. **64**, 253 (1921).
[19] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 45 (1964).
[20] Y. Iwadate, J. Mochinaga, and K. Kawamura, J. Phys. Chem. **85**, 3708 (1981).
[21] G. J. Janz, J. Phys. Chem. Ref. Data **17**, 1 (1988).
[22] B. Larsen, T. Forland, and K. Singer, Mol. Phys. **26**, 1521 (1973).
[23] L. V. Woodcock, Chem. Phys. Lett. **10**, 257 (1971).
[24] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, Academic Press, London 1986.
[25] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **35a**, 493 (1980).
[26] J. Mochinaga, Y. Iwadate, and K. Igarashi, J. Electrochem. Soc. **138**, 3588 (1991).

[27] J. Mochinaga, K. Igarashi, H. Kuroda, and H. Iwasaki, Bull. Chem. Soc. Japan. **49**, 2625 (1976).
[28] T. Koura, H. Matsuura, and I. Okada, J. Mol. Liquids **73,74** 195 (1997).
[29] K. Igarashi, M. Kosaka, M. Ikeda, and J. Mochinaga, Z. Naturforsch. **45a**, 623 (1990).
[30] N. Wax, Selected Papers on Noise and Stochastic Processes, Dover 1954.
[31] R. Takagi, L. Rycerz, and M. Gaune-Escard, Proceedings of the 9th International Symposium on Molten Salts (1994), p. 99.
[32] G. N. Papatheodorou, Inorg. Nucl. Chem. Lett. **11**, 483 (1975).