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

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Z. Naturforsch. 56 a, 466–472 (2001); received May 3, 2001

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 ($v_s$), self-diffusion coefficient ($D_s$), electrical conductivity ($\kappa$) and enthalpy of mixing ($\Delta H_{\text{mix}}$) were compared with the corresponding experimental values. The calculated results revealed that $v_s$ and $D_s$ of potassium decrease with increasing amount of neodymium, as expected from the experimental internal mobility ($b$). The decrease of $b_d$, $v_K$, 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 $v_s$, $D_s$'s and $\kappa$'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 ions increases and that of the rare earth metal ions 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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7 points predictor-corrector method, using periodic boundaries. We employed the Born-Mayer-Huggins pair potential, excluding the dipole-quadrupole term for NdCl₃ and alkali chloride mixtures,

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

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

where \( r, z, e, \varepsilon_0, b, A, \sigma, \) and \( \rho \) 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 pair correlation functions \( g(r) \) and the running coordination numbers \( n(r) \) for molten (Nd₁/₃, K)Cl for four compositions, \( g_{Nd-Cl}(r) \) and \( n_{Nd-Cl}(r) \); solid lines, \( g_{K-Cl}(r) \) and \( n_{K-Cl}(r) \); broken lines.

Table 1. Characteristic values of the \( g_{ij}(r) \)'s for cation-anion and anion-anion pairs in molten (Nd₁/₃, 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.

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

3. Results and Discussion

The pair correlation functions \( g(r) \) and the running coordination numbers \( n(r) \) for increasing Nd/K-ratio in (Nd₁/₃, 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 NdCl₃ and KCl with those of the binary mixtures (Nd₁/₃, K)Cl for various compositions shows that the position \( R_M \) of the first peak of \( g_{Nd-Cl} \) remains much the same. As for the peak heights, \( g_{Nd-Cl} \) is larger in the binary mixtures than in the pure NdCl₃ and is decreasing with increasing mole fraction of neodimium. On the contrary, \( g_{K-Cl} \) is increasing with increasing contents of neodymium. These behaviors are similar to those of (Dy₁/₃, K)Cl [15].
Table 2. Main experimental results and characteristic parameters obtained from MD simulation in molten (Nd₁/₃, K)Cl system at 1073 K.

<table>
<thead>
<tr>
<th>xNd</th>
<th>κexp [26] (Sm⁻¹)</th>
<th>κcal (Sm⁻¹)</th>
<th>bNd,exp [14] (10⁻⁵m²V⁻¹s⁻¹)</th>
<th>bK,exp [14] (10⁻⁵m²V⁻¹s⁻¹)</th>
<th>SEVNd (ms⁻¹)</th>
<th>SEVK (ms⁻¹)</th>
<th>DNd,cal (10⁻⁸m²s⁻¹)</th>
<th>DK,cal (10⁻⁸m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>224</td>
<td>167.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.81</td>
</tr>
<tr>
<td>0.066</td>
<td>206</td>
<td>136.2</td>
<td>0.95±0.16</td>
<td>10.7±0.1</td>
<td>4.589</td>
<td>78.343</td>
<td>0.45</td>
<td>2.23</td>
</tr>
<tr>
<td>0.249</td>
<td>166</td>
<td>102.3</td>
<td>-0.29±0.36</td>
<td>9.85±0.13</td>
<td>4.948</td>
<td>72.161</td>
<td>0.52</td>
<td>2.16</td>
</tr>
<tr>
<td>0.279</td>
<td>160</td>
<td>118.1</td>
<td>0.07±0.17</td>
<td>9.63±0.08</td>
<td>5.519</td>
<td>69.675</td>
<td>0.58</td>
<td>1.93</td>
</tr>
<tr>
<td>0.370</td>
<td>144</td>
<td>102.3</td>
<td>0.51±0.13</td>
<td>9.12±0.09</td>
<td>8.960</td>
<td>63.345</td>
<td>0.65</td>
<td>1.86</td>
</tr>
<tr>
<td>0.450</td>
<td>132</td>
<td>93.7</td>
<td>0.61±0.07</td>
<td>8.89±0.06</td>
<td>10.235</td>
<td>58.558</td>
<td>0.74</td>
<td>1.72</td>
</tr>
<tr>
<td>0.478</td>
<td>128</td>
<td>82.4</td>
<td>0.31±0.17</td>
<td>9.19±0.16</td>
<td>11.568</td>
<td>52.619</td>
<td>0.82</td>
<td>1.56</td>
</tr>
<tr>
<td>0.644</td>
<td>109</td>
<td>71.8</td>
<td>1.27±0.14</td>
<td>8.26±0.25</td>
<td>15.162</td>
<td>49.252</td>
<td>0.91</td>
<td>1.31</td>
</tr>
<tr>
<td>0.801</td>
<td>97.2</td>
<td>62.6</td>
<td>2.05±0.03</td>
<td>6.67±0.08</td>
<td>16.964</td>
<td>44.196</td>
<td>1.08</td>
<td>1.16</td>
</tr>
<tr>
<td>1.000</td>
<td>69.2</td>
<td>52.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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

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 Nd³⁺ 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

\[
v = \frac{(R_2 - \langle R(0) \rangle)}{\tau},
\]

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).

<table>
<thead>
<tr>
<th>$x_{\text{Nd}}$</th>
<th>(Nd_{1/3}, K)Cl, T = 1065 K</th>
<th>$-\Delta H_{\text{mix,exp}}$ [16] (kJ mol$^{-1}$)</th>
<th>$-\Delta H_{\text{mix,cal}}$ (kJ mol$^{-1}$)</th>
<th>$x_{\text{Nd}}$</th>
<th>(Nd_{1/3}, Na)Cl, T = 1124 K</th>
<th>$-\Delta H_{\text{mix,exp}}$ [16] (kJ mol$^{-1}$)</th>
<th>$-\Delta H_{\text{mix,cal}}$ (kJ mol$^{-1}$)</th>
<th>$x_{\text{Nd}}$</th>
<th>(Nd_{1/3}, K)Cl, T = 1124 K</th>
<th>$\kappa_{\text{exp}}$ [26] (Sm$^{-1}$)</th>
<th>$\kappa_{\text{cal}}$ (Sm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.00</td>
<td>–</td>
<td>0.000</td>
<td>0.00</td>
<td>–</td>
<td>0.000</td>
<td>371.5</td>
<td>308.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.090</td>
<td>5.87</td>
<td>7.68</td>
<td>0.099</td>
<td>2.92</td>
<td>5.57</td>
<td>0.125</td>
<td>283.3</td>
<td>252.4</td>
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<tr>
<td>0.204</td>
<td>10.76</td>
<td>12.52</td>
<td>0.200</td>
<td>5.79</td>
<td>8.64</td>
<td>0.249</td>
<td>228.0</td>
<td>197.6</td>
<td></td>
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</tr>
<tr>
<td>0.251</td>
<td>13.80</td>
<td>15.38</td>
<td>0.275</td>
<td>6.06</td>
<td>9.23</td>
<td>0.350</td>
<td>199.3</td>
<td>165.3</td>
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<tr>
<td>0.307</td>
<td>16.30</td>
<td>20.64</td>
<td>0.350</td>
<td>6.32</td>
<td>10.42</td>
<td>1.000</td>
<td>81.9</td>
<td>77.3</td>
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</tr>
<tr>
<td>0.350</td>
<td>16.00</td>
<td>22.61</td>
<td>0.499</td>
<td>6.74</td>
<td>10.74</td>
<td>0.624</td>
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<td>124.9</td>
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</tr>
<tr>
<td>0.478</td>
<td>16.13</td>
<td>19.24</td>
<td>0.576</td>
<td>6.15</td>
<td>10.56</td>
<td>0.760</td>
<td>116.4</td>
<td>101.7</td>
<td></td>
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</tr>
<tr>
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<td>16.18</td>
<td>0.651</td>
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<td>8.24</td>
<td>0.874</td>
<td>114.2</td>
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<td>0.751</td>
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<td>6.65</td>
<td>1.000</td>
<td>81.9</td>
<td>77.3</td>
<td></td>
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<tr>
<td>0.829</td>
<td>6.57</td>
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<td>0.899</td>
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<td>4.87</td>
<td>0.651</td>
<td>5.56</td>
<td>8.24</td>
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<tr>
<td>1.000</td>
<td>0.00</td>
<td>–</td>
<td>1.000</td>
<td>0.00</td>
<td>–</td>
<td>0.760</td>
<td>116.4</td>
<td>101.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relationship 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 $\varepsilon$ values [14] and data available on the electrical conductivities $\kappa$ [26] and equivalent volumes $V_e$ [27] of the mixtures:

$$ b_K = \left( \frac{\kappa V_e}{F} \right) (1 + \varepsilon x_{\text{Nd}}) \quad \text{(4)} $$

$$ b_{\text{Nd}} = \left( \frac{\kappa V_e}{F} \right) (1 + \varepsilon x_K) $$

where $x$ is the equivalent fraction. The value of $b_{\text{Nd}}$ increases with $x_{\text{Nd}}$. 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. $b_{\text{Nd}}$ 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 $b_{\text{Nd}}$ for $x_{\text{Nd}} < 0.4$ 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 $b_{\text{Nd}}$ and SEV$_{\text{Nd}}$ 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.

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\textsubscript{1/3}, K)Cl at 1073 K and (Nd\textsubscript{1/3}, Na)Cl at 1124 K. Experimental results in (Nd\textsubscript{1/3}, K)Cl at 1073 K [26]: black circles, MD simulation in (Nd\textsubscript{1/3}, K)Cl at 1073 K: white circles, experimental results in (Nd\textsubscript{1/3}, Na)Cl at 1124 K [26]: black triangles, MD simulation in (Nd\textsubscript{1/3}, Na)Cl at 1124 K: white triangles.

\[ D = \frac{1}{6} \frac{1}{\tau} \langle \{ r_i(t + \tau) - r_i(t) \}^2 \rangle, \]  

(5)

as given in Fig. 4 together with the results of (Dy\textsubscript{1/3}, K)Cl [15] and Table 3, which shows that the self-diffusion coefficient of Nd\textsuperscript{3+} increases with increasing the concentration of Nd, and the self-diffusion coefficient of K\textsuperscript{+} 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\textsuperscript{3+} and K\textsuperscript{+} is consistent with the results on Dy\textsuperscript{3+} and K\textsuperscript{+} in (Dy\textsubscript{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

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

(6)

where the MD contained up to 10\textsuperscript{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:

\[ U = \frac{3}{2} N kT + \sum_{i>j} \sum \phi(r_{ij}), \]  

(7)

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

\[ \Delta H_{\text{mix}} = H[x \cdot \text{NdCl}_3 + (1-x) \cdot \text{ACl}] - xH[\text{NdCl}_3] 
- (1-x)H[\text{ACl}], \ A = \text{Na}, \ K, \]  

(8)

where \( x \) means the mole fraction of the NdCl\textsubscript{3}. In the present work, 10\textsuperscript{6} steps were used to obtain the enthalpy. The calculated molar enthalpies of mixing of molten (Nd\textsubscript{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\textsubscript{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 NdCl₃ 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 [NdCl₆]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 Nd³⁺ increases, \(b_K\), \(v_K\), and \(D_K\) considerably decrease. This decrease is caused by the tranquilization effect of Nd³⁺ 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 Nd³⁺ and the generation of the long-lived species [NdCl₆]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.