Local Structure and Okada’s Empirical Relation for the Internal Mobility of Cations in Molten Alkali Nitrates

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The empirical relation
\[ b_i = (V - V_{0i})^{-1} A_i \exp(-E_i/R\ T) \]
for the internal mobility \( b_i \) of cations \( i \) in mixtures of molten alkali nitrates, where \( V \) is the molar volume of the mixture, is compared with MD simulations. For pure LiNO₃ and NaNO₃ it is found that \( (V - V_{0i})^{-1} \) is proportional to the concentration of oxygens in the first coordination shells of the cations \( i \).

From countercurrent electromigration [1] measurements of internal mobilities \( b_i \) of cations \( i \) in molten binary and ternary alkali nitrate mixtures, the empirical relation
\[ b_i = (V - V_{0i})^{-1} A_i \exp(-E_i/R\ T) \] (1)
has been derived by Okada and coworkers [2–11]. This relation involves the molar volume \( V \) of the mixture and a parameter \( V_{0i} \) which depends on the type of cation \( i \). In such mixtures the number of oxygen atoms per macroscopic unit volume is
\[ n = 3 \ N_N / V, \] (2)
where \( N_N \) is Avogadro’s number.

According to (1), positive (negative) values of \( V_{0i} \) tell us that the concentration of oxygens is greater (smaller) than \( n \) in the microscopic regions which are decisive for the magnitude of \( b_i \). If these regions are considered to be the first oxygen coordination shells around the cation \( i \), the relation
\[ 3 \ N_N / (V - V_{0i}) \approx N_{f1}/v_{f1} \] (3)
should hold, where \( N_{f1} \) is the oxygen atom content of these shells and \( v_{f1} \) their volume.

It is the aim of this note to check the validity of (3) by inserting empirical values of \( V - V_{0i} \) and \( N_{f1}/v_{f1} \). Reprint requests to Dr. Junko Habasaki, Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta 4259, Midori-ku, Yokohama 227, Japan.

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The values \( V - V_{0i} \) were calculated for several molar volumes of the mixtures, as shown in Table 3.

### Table 1. The systems so far studied.

<table>
<thead>
<tr>
<th>( M_i )</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Na, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>[2]</td>
<td>[8]</td>
<td>[2]</td>
<td>[3]</td>
<td>[10]</td>
</tr>
</tbody>
</table>

### Table 2. Parameters \( A_i, E_i, V_{0i} \).

<table>
<thead>
<tr>
<th>( M_i )</th>
<th>( A_i \times 10^{11} ) m³ V⁻¹ s⁻¹ mol⁻¹</th>
<th>( E_i ) kJ mol⁻¹</th>
<th>( V_{0i} ) cm³ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>[2]</td>
<td>2.84</td>
<td>17.80</td>
</tr>
<tr>
<td>Na</td>
<td>[2]</td>
<td>4.94</td>
<td>19.71</td>
</tr>
<tr>
<td>Rb</td>
<td>[10]</td>
<td>3.95</td>
<td>18.00</td>
</tr>
</tbody>
</table>

* The small temperature dependence of \( V_{0i} \) observed for the system is neglected here.

### Table 3. Values of \( V - V_{0i} \) for several \( V \) values of the mixtures. \( V \) and \( V_{0i} \) in cm³ mol⁻¹.

<table>
<thead>
<tr>
<th>( V )</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>20.3</td>
<td>20.8</td>
<td>34.5</td>
</tr>
<tr>
<td>50</td>
<td>25.3</td>
<td>25.8</td>
<td>39.5</td>
</tr>
<tr>
<td>60</td>
<td>35.3</td>
<td>35.8</td>
<td>49.5</td>
</tr>
</tbody>
</table>

* The \( V_{0i} \) value of [3] was used.
The volume of the first oxygen coordination shell was taken to be

$$v_i = \frac{4}{3} \pi (r_2^3 - r_1^3),$$

(4)

where \(r_1\) and \(r_2\) are the distances from the cation where the corresponding \(g(r)\) crosses unity for the first and second time, respectively [14].

An MD simulation of molten LiNO₃ at 550 K [12] gave \(r_{1Li} = 1.65 \text{Å}, \ r_{2Li} = 2.29 \text{Å}\) and \(N_{1Li} = 4.2\). These data coincide well with the data obtained by X-ray diffraction and neutron diffraction. When using these values, \(N_{1Li}/v_{1Li}\) turns out to be \(1.33 \times 10^{23} \text{ cm}^{-3}\). On the other hand, the left hand side of (3) becomes \(1.26 \times 10^{23} \text{ cm}^{-3}\) when using the \(V_{0Li}\) value in Table 2.

An MD simulation of molten NaNO₃ has been carried out at 650 K [15]. The values of \(r_{1Na}, r_{2Na}\) and \(N_{1Na}\) were found to be 2.05 Å, 2.93 Å and 5.40, respectively. With these the value \(7.79 \times 10^{22} \text{ cm}^{-3}\) was obtained for the right hand side of (3), while \(8.36 \times 10^{22} \text{ cm}^{-3}\) was obtained for the left hand side of (3).

This coincidence seems to prove that \(b_i\) is indeed proportional to the concentration of oxygens in the first oxygen coordination shell around the cation \(i\). A definite answer, however, can only be given when (3) has also been checked for mixtures of alkali nitrate melts. This shall be done in a future study.