The Effect of the Anion Polarization on the Cationic Mobilities in Nitrate Binary Mixtures

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The electrical perturbation induced by the simultaneous presence of two different cations near the anion (which is the frame of reference) is indicated as main factor influencing the internal mobilities in dilute solutions of monovalent nitrates in NaNO₃.

By extending the mobility isotherm derived on the basis of the previous assumptions to a larger concentration range, an equivalent conductivity isotherm is proposed.

In a systematic investigation of the effect on the conductivity, of small additions of foreign sulphates to molten Li₂SO₄, KVIST found that the decrease of the conductivity is greater the greater is the size of the foreign cation ¹.

We have extended this type of measurements to nitrate systems, in order to find possible correlations with the anion polarization.

### Results

A series of measurements of the specific conductivity, , as function of the temperature , °C, of solutions of NaNO₃ "doped" with small quantities of KNO₃, RbNO₃, CsNO₃, AgNO₃, TlNO₃ is summarized in Table 1.

Literature data for the molar volumes of TlNO₃, AgNO₃, NaNO₃, KNO₃, RbNO₃ and CsNO₃ were employed to compute the equivalent conductivities.

The values at °C are reported in Fig. 1. The straight lines corresponding to the equivalent conductivity of each binary dilute solution calculated by conventional methods are reported in Table 2.

In binary systems of the type (Ma — Mb) • R, where Ma = Na⁺ and Mb = Ag⁺, K⁺, Tl⁺, Rb⁺ and Cs⁺, the dependency of the equivalent conductivity on the concentration, , (mole fraction of Ma: R) is

\[ \frac{A}{F} = u_a + (u_b - u_a) \cdot x_b \]

(1)

where uₐ and uₐ, the internal mobilities of Ma and Mb, are both functions of xₐ. By expansion of Eq. (1), in the linear approximation, the equivalent conductivity \( A \) of a dilute solution of M₁NO₃ in NaNO₃ is

\[ \frac{A}{F} = (u_b)_{x_b=0} + \left( \frac{dA}{dx_b} \right)_{x_b=0} + (u_b - u_a)_{x_b=0} \cdot x_b \]

(2)

and therefore

\[ \frac{dA}{dx_b} = \frac{(A_{NaNO₃} - A)}{x_b} + \frac{F}{(u_b - u_a)_{x_b=0}} \]

(3)

### Table 1. Conductivity equations for dilute solutions of monovalent nitrates M₁NO₃ in NaNO₃

<table>
<thead>
<tr>
<th>Added salt</th>
<th>Molar fraction x₀</th>
<th>Conductivity equations</th>
<th>Temp. Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>0.00</td>
<td>( x = 0.9993 + 4.695 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>0.05(0)</td>
<td>( x = 0.9970 + 4.705 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>KNO₃</td>
<td>0.04(9)</td>
<td>( x = 0.9510 + 4.725 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>RbNO₃</td>
<td>0.03(2)</td>
<td>( x = 0.9780 + 4.220 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>CsNO₃</td>
<td>0.03(8)</td>
<td>( x = 0.9290 + 4.500 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>TlNO₃</td>
<td>0.03(1)</td>
<td>( x = 0.9340 + 4.370 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>TlNO₃*</td>
<td>0.03(4)</td>
<td>( x = 0.9510 + 3.870 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>TlNO₃′</td>
<td>0.04(0)</td>
<td>( x = 0.9570 + 4.520 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
<tr>
<td>TlNO₃‡</td>
<td>0.15(1)</td>
<td>( x = 0.8514 + 4.059 \times (T - 321) \times 10^{-3} )</td>
<td>312—400</td>
</tr>
</tbody>
</table>

where $\chi_{an}$ = anionic polarizability and $F$, the net electrical force acting on the anion, is

$$F \propto (1/\chi_{a}^2 - 1/\chi_{b}^2) = F_{(p)}$$

(5)

where $\chi_{a}$, $\chi_{b}$ = anionic radius + cationic radius of $M_a$ and $M_b$ respectively.

For nitrate systems the relationship (5) may be conveniently substituted by

$$F' \propto (1/V_{a}^{2/3} - 1/V_{b}^{2/3}) = F'_{(p)}$$

(6)

where $V_{a}$ and $V_{b}$ are the molar volumes of the two pure salts respectively.

The value of $F'_{(p)}$ calculated by the reported molar volume data are given in Table 3. In order to check the linear correspondence between the two formulations also $F_{(p)}$ values were calculated and compared with the $F'_{(p)}$ values (see Fig. 2).

The ionic radii employed for calculating $F_{(p)}$ are reported in ref. 7 of the previous work 3. The only apparent disagreement is presented by the $F_{(p)}$ values for TlNO$_3$ and RbNO$_3$ which differ by more than 20% while the difference between the $F'_{(p)}$ values is smaller than 10%. From the $F_{(p)}$ values one may foresee comparable polarization effects for the (Na – Rb)NO$_3$ and (Na – Tl)NO$_3$ mixtures as previously reported 3, but this is probably not true if the $F'_{(p)}$ values are considered.

In Fig. 3 (left) the values

$$(A_{NaNO_3} - A)/X_b$$

Table 2. Equivalent conductivity isotherms ($T=350\degree C$) for dilute solutions of monovalent nitrates (MbNO$_3$) in NaN$_3$.

Table 3. $F^2_{(p)}$ polarization factors for the salt couples $M_a$NO$_3$–$M_b$NO$_3$ with $M_a$NO$_3$=NaN$_3$ and $M_b$NO$_3$=added salt.

* Data from Ref. 5; ** from Ref. 4; *** from Ref. 3.


Discussion

According to Frenkel in a binary system with a common cation M, of the type $M-(R_p - R_q)$, where $X_p$ and $X_q = 1 - X_p$ are the molar fractions of the two salts, the activation energy $\Delta E$ for the migration of $M$ with respect to the nearest neighbour anions $R_p$ and $R_q$, is the weighted sum of the energies involved in the pure $MR_p$ and $MR_q$ salts, $\Delta E_p$ and $\Delta E_q$ respectively, i. e.:

$$\Delta E = \Delta E_p \cdot X_p + \Delta E_q \cdot X_q.$$  \hspace{1cm} (7)

In systems with a common anion, as those considered in this work, each carrier is surrounded by the same n. n. (the anions) in the pure state and in the mixture. Therefore, if the activation energy for the internal mobility is due to the interactions with the anions, and if the simultaneous presence of different cations does not introduce new energetic terms, the $\Delta E$ term is constant in the mixtures. On the contrary, if the anion becomes polarized, a variation of $\Delta E$ in the mixture is to be expected, following the polarization direction. Because each cation $M_a$ in a mixture $(M_a - M_b) \cdot R$ participates in some polarized and unpolarized triplet $(M_a \cdot R \cdot M_b$ and $M_a \cdot R \cdot M_a$ respectively), by analogy with Eq. (7) the actual value for $\Delta E$ is assumed to be the weighted sum:

$$\Delta E_a,_{\text{mix}} = \Delta E_a \cdot X_a + (\Delta E_a + \Delta W_a) \cdot X_b$$  \hspace{1cm} (8)

or

$$\Delta E_a,_{\text{mix}} = \Delta E_a + \Delta W_a \cdot X_b$$  \hspace{1cm} (9)

where $\Delta E_a = $ activation energy for the $M_a \cdot R \cdot M_a$ triplet, $\Delta E_a + \Delta W_a = id$, for the $M_a \cdot R \cdot M_b$ triplet and

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8 The $F \cdot (u_b - u_a)X_b = 0$ values for K+, Tl+, Rb+ and Cs+ in NaNOS at $T=350$ °C are derived respectively from Molten Salts Handbook p. 355; S. Forcheri and V. Wagner, Z. Naturforsch. 22a, 1171 [1967]; S. Forcheri and V. Wagner, work in preparation; S. Forcheri and V. Wagner, unpublished results.

\( \Delta W_a \) = polarization contribution (\( \cong 0 \) depending on the polarization direction).

The mean cation (drift) mobility, neglecting the dependence of \( \Delta E_{a, \text{mix}} \) on temperature due to the thermal expansion, is 10:

\[
\begin{align*}
  u_a &= u' \cdot \exp \left( - \frac{\Delta E_{a, \text{mix}}}{RT} \right) \\
  &= u' \cdot \exp \left( - \frac{\Delta E_a}{RT} \right) \cdot \exp \left( - \frac{\Delta W_a \cdot X_b}{RT} \right)
\end{align*}
\]

where \( \Delta E_{a, \text{mix}} \) is given by Eq. (9) and \( u' = e a^2 v/kT \) with \( e \) = electronic charge, \( a \) = distance between adjacent potential energy minima (\( \sim \) the \( \text{NO}_3^- \) diameter), \( v \) = “lattice-like” anion-cation vibration frequency (\( \sim 10^{13} \text{ sec}^{-1} \)). All the parameters of \( u' \), except \( v \), are concentration independent terms. However, \( v \), a mass dependent term, does not vary considerably with composition. Consequently \( u' \) is expected to be rather insensitive towards changes of the composition, if \( \Delta W_a \cdot X_b \ll RT \). Under these conditions from Eq. (10) we have:

\[
\begin{align*}
  \left( \frac{d u_a}{d X_b} \right) \bigg|_{X_b=0} &= u' \cdot \exp \left( - \frac{\Delta E_a}{RT} \right) \cdot \left( - \frac{\Delta W_a}{RT} \right) \\
  &= (u_a)_{X_b=0} \cdot \left( - \frac{\Delta W_a}{RT} \right) .
\end{align*}
\]

Because of the Eq. (11) an increase of \( \left( \frac{d u_a}{d X_b} \right) \bigg|_{X_b=0} \) proportional to the activation energy excess \( \Delta W_a \) is demanded. On the other hand, as we suppose

\[
\Delta W_a \propto F_{(0)}^2
\]

we have, at constant \( T \), and in dilute solution (remembering that \( a \) indicates Na):

\[
- \left( \frac{d u_a}{d X_b} \right) \bigg|_{X_b=0} = \text{const} \cdot F_{(0)}^2 .
\]

The experimental results reported in Fig. 3 can be interpreted at least on a qualitative basis, by means of the linear relationships (12) and (13). The decrease of the conductivity as a consequence of small additions of foreign sulphates to molten Li\(_2\)SO\(_4\) could be temptatively explained in the same framework. As a further remark one must point out that the most striking effects are observed when \( \Delta W_a > RT \) (where \( a \) is the lighter cation). In this case both \( \Delta E_{a, \text{mix}} \) and \( u_a \) are strongly affected (in the opposite sense) by changes of the composition. This is elucidated by the (Li – K) – Cl system 17 and by (Li – K)\(_2\)SO\(_4\) 18, even if for this last system the \( \Delta E_{a, \text{mix}} \) values are lacking. If \( \Delta W_a < RT \), as in the case of (Na – Rb) – NO\(_3\), one must expect a weaker dependence of the mobilities 3, 19 and \( \Delta E_{a, \text{mix}} \) on the composition 21. It is noteworthy that HAENER and NACHTRIEB in N.M.R. studies on halide binary systems, interpreted the chemical shift changes in mixture in terms of a polarizing field \( F \) acting on the anion, given by 22, 23

\[
F = 2 e \cdot \Delta \varepsilon / \varepsilon_a^2
\]

corresponding to the first term in Eq. (5), from which the \( F_{(0)}^2 \) parameters (see Figs. 2, 3) are calculated, subjected to a Taylor series expansion.

By applying Eq. (10) with the second exponential expanded into a series, to the two cationic internal mobilities in a binary system, we have for addition of \( M_i R \) to the \( M_i R \) salt and of \( M_i R \) to the \( M_i R \) salt respectively:

\[
\begin{align*}
  u_{a,x} &= u_{a,1} - u_{a,1} \cdot \Delta W_a \cdot X_b / RT \\
  &+ \frac{1}{2} u_{a,1} \cdot (\Delta W_a \cdot X_b / RT)^2 - \ldots
\end{align*}
\]

and

\[
\begin{align*}
  u_{b,x} &= u_{b,1} - u_{b,1} \cdot \Delta W_b \cdot X_a / RT \\
  &+ \frac{1}{2} u_{b,1} \cdot (\Delta W_b \cdot X_a / RT)^2 - \ldots
\end{align*}
\]

where the alphabetic subscripts refer to the cationic species and the numerical ones to the respective mole fraction (see Fig. 3, ref. 3).

10 N. F. MOTT and R. W. GURNEY, Electronic Processes in Ionic Crystals, Oxford Clarendon Press, 2nd Edn., p. 43. In the text \( u \), instead of \( r \), is employed for the ionic mobility, as in the previous papers.
12 This situation exactly corresponds to the assumed invariance of \( r \), after the application of an external electrical field \( F_{Ext} \) varying the height of the potential energy barriers by \( \pm e \) a. e. \( F_{Ext} \perp \parallel T \) 13–15
16 In these systems the increase of the restoring force on the lighter cation due to strong polarization, may cause an increase of \( r \) and \( u' \) in mixture: consequently the treatment becomes more complicated (see also ref. 15).
20 S. FORCHERI and V. WAGNER, work in preparation.
21 In this system the \( u' \) values for both cations are effectively independent of the composition.
If the negative deviation $\Delta A = A - A_{\text{add}}$ from the additivity value $A_{\text{add}}/\mathcal{F} = u_a,1 \cdot X_a + u_b,1 \cdot X_b$ is calculated by means of the Eqs. (15 a) and (15 b) including cubic terms, then it is easy to demonstrate that the excess conductivity function $\Delta A_x/\mathcal{F} \cdot X_a X_b$ may be represented as:

$$\Delta A_x/\mathcal{F} \cdot X_a X_b = l + m'X_b + n'X_b^2 + \ldots.$$  \hspace{1cm} (16)

Neglecting in the mobility isotherms [(15 a) and (15 b)] terms higher than the quadratic ones, Eq. (16) reduces to an expression which presents the same analytical form of the previously reported excess isotherm, i.e.:

$$\Delta A_x/\mathcal{F} \cdot X_a X_b = l' + m'X_b + \ldots$$  \hspace{1cm} (17)

where now the parameters of the straight line have the following meaning:

24 The Eqs. (15 a) and (15 b) are less correct for higher values of $X_b$ and $X_a$, respectively, but at the same time the influence on the conductivity decreases [see Eq. (1)].

25 The cation and anion motions (influencing respectively the conductivity and the viscosity) are strictly intercorrelated in molten nitrates, because of the cation-anion pair rotation, as one can infer from the close constancy of the ratio between the activation energy for the conductivity and the viscosity for the pure alkali nitrates (but not for TINO₃) \(^{28, 27}\). Therefore, the stabilization of the pair due to the polarization slows down the Na⁺ mobility and, reducing the NO₃⁻ mobility, increases the viscosity. Viscosity data are available only for (NaNO₃—RbNO₃) \(^{28}\) and (NaNO₃—TINO₃) \(^{29}\). Effectively, in the first case, after the Rb⁺ introduction, we observe a viscosity increase while for the latter case the contrary is observed.

26 See ref. \(^{9}\), p. 441.


29 See ref. \(^{19}\), p. 127.

The most serious limitation of the present treatment is inherent in the simplicity of the assumptions and in particular in the tacit supposition that in the whole concentration range only one phenomenon (the polarization) is predominant.

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