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 $NaNO_3$.

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 Li_2SO_4, 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, $\varkappa$, as function of the temperature T, °C, of solutions of $NaNO_3$ "doped" with small quantities of KNO_3, $RbNO_3$, $CsNO_3$, $AgNO_3$, $TlNO_3$ is summarized in Table 1.

Literature data for the molar volumes of $TlNO_3$ [3], $AgNO_3$ [4], $NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$ [5] were employed to compute the equivalent conductivities. The values at $T = 350$ °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 $(M_a - M_b)\cdot R$, where $M_a = Na^+$ and $M_b = Ag^+, K^+, Tl^+, Rb^+$ and Cs^+, the dependency of the equivalent conductivity on the concentration, X_b (mole fraction of $M_b \cdot R$) is

$$\Lambda/\mathcal{F} = u_a + (u_b - u_a)\cdot X_b \tag{1}$$

where u_a and u_b, the internal mobilities of M_a and M_b, are both functions of X_b. By expansion of Eq. (1), in the linear approximation, the equivalent conductivity Λ of a dilute solution of M_bNO_3 in $NaNO_3$ is

$$\Lambda/\mathcal{F} = (u_a)_{X_b=0} + \left[\left(\frac{\mathrm{d}u_a}{\mathrm{d}X_b}\right)_{X_b=0} + (u_b - u_a)_{X_b=0}\right]\cdot X_b \tag{2}$$

and therefore

$$-\mathcal{F}\cdot\left(\frac{\mathrm{d}u_a}{\mathrm{d}X_b}\right)_{X_b=0} = (\Lambda_{NaNO_3} - \Lambda)/X_b + \mathcal{F}\cdot(u_b - u_a)_{X_b=0} \tag{3}$$

Added salt M_bNO_3	Molar fraction X_b	Conductivity equations	Temp. Range °C
— *	0.000	$\varkappa = 0.9938 + 4.695\ (T - 312)\cdot 10^{-3}$	312—400
$AgNO_3$	0.05(0)	$\varkappa = 0.9970 + 4.705\ (T - 312)\cdot 10^{-3}$	312—400
KNO_3	0.04(9)	$\varkappa = 0.9510 + 4.725\ (T - 312)\cdot 10^{-3}$	312—400
KNO_3	0.09(1)	$\varkappa = 0.9310 + 4.510\ (T - 312)\cdot 10^{-3}$	312—400
$RbNO_3$	0.03(2)	$\varkappa = 0.9780 + 4.220\ (T - 312)\cdot 10^{-3}$	312—400
$RbNO_3$	0.05(8)	$\varkappa = 0.9290 + 4.480\ (T - 312)\cdot 10^{-3}$	312—400
$CsNO_3$	0.03(1)	$\varkappa = 0.9340 + 4.370\ (T - 312)\cdot 10^{-3}$	312—400
$CsNO_3$	0.03(4)	$\varkappa = 0.9510 + 3.870\ (T - 312)\cdot 10^{-3}$	312—400
$TlNO_3$	0.04(0)	$\varkappa = 0.9570 + 4.520\ (T - 312)\cdot 10^{-3}$	312—400
$TlNO_3$ *	0.15(1)	$\varkappa = 0.8514 + 4.059\ (T - 312)\cdot 10^{-3}$	312—400

Table 1. Conductivity equations for dilute solutions of monovalent nitrates M_bNO_3 in $NaNO_3$. * Data from Ref. [2].

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[1] A. KVIST, Z. Naturforsch. **21 a**, 1601 [1966].

[2] V. WAGNER and S. FORCHERI, Z. Naturforsch. **22 a**, 891 [1967].

[3] V. WAGNER and S. FORCHERI, Z. Naturforsch. **23 a**, 926 [1968].

[4] J. JANZ, A.T. WARD, and R. D. REEVES, Molten Salts Data, US-AFOSRN 64-0039, Rensselear Polytech. Inst. Troy, N.Y.

[5] W. J. MCAULEY, E. RHODES, and A. R. UBBELHODE, Proc. Roy. Soc. London A **289**, 151 [1966].

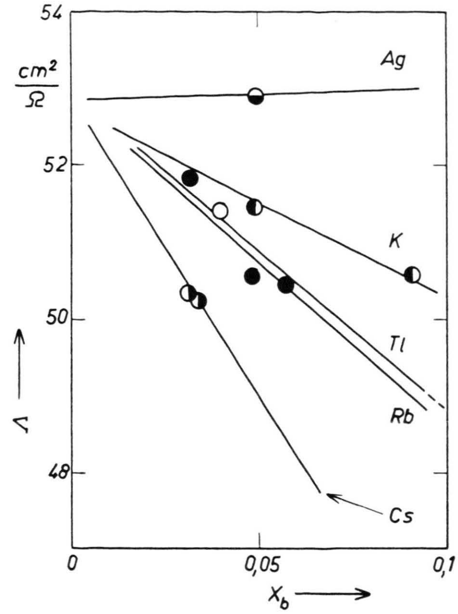

Fig. 1. Equivalent conductivity isotherms for dilute solutions of monovalent nitrates in $NaNO_3$ at $T=350$ °C. X_b=Molar fraction of the solute.

where $\Lambda_{NaNO_3} = \mathcal{F} \cdot (u_a)_{X_b=0}$ = equivalent conductivity of pure $NaNO_3$.

As previously reported [3], the polarization energy [6] is

$$E_p = -\tfrac{1}{2} \cdot \alpha_{an} \cdot F^2 \qquad (4)$$

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

$$F \propto (1/\lambda_a^2 - 1/\lambda_b^2) = F_{(p)} \qquad (5)$$

where λ_a, λ_b = anionic radius + cationic radius of M_a and M_b respectively.

For nitrate systems the relationship (5) may be conveniently substituted by [7]

$$F' \propto (1/V_a^{2/3} - 1/V_b^{2/3}) = F'_{(p)} \qquad (6)$$

where V_a and V_b are the molar volumes of the two pure salts respectively.

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

The ionic radii employed for calculating $F^2_{(p)}$ are reported in ref. [7] of the previous work [3]. The only apparent disagreement is presented by the $F'^2_{(p)}$ values for $TlNO_3$ and $RbNO_3$ which differ by more than 20% while the difference between the $F^2_{(p)}$ values is smaller than 10%. From the $F^2_{(p)}$ 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 $F'^2_{(p)}$ values are considered.

In Fig. 3 (left) the values

$$(\Lambda_{NaNO_3} - \Lambda)/X_b$$

Added salt M_bNO_3	Equivalent conductivity isotherm	RMS	Concentration range (X_b)
$AgNO_3$	$\Lambda = 52.82 + 2.62 \cdot X_b$	—	0.00–0.05(0)
KNO_3	$\Lambda = 52.77 - 24.37 \cdot X_b$	0.14	0.00–0.09(1)
$RbNO_3$	$\Lambda = 52.91 - 43.28 \cdot X_b$	0.26	0.00–0.05(8)
$CsNO_3$	$\Lambda = 52.81 - 75.98 \cdot X_b$	0.15	0.00–0.03(4)
$TlNO_3$	$\Lambda = 52.92 - 41.21 \cdot X_b$	0.18	0.00–0.14(1)

Table 2. Equivalent conductivity isotherms ($T=350$ °C) for dilute solutions of monovalent nitrates (M_bNO_3) in $NaNO_3$.

Salt	Molar Volume $T = 350$ °C	$1/V^{2/3}_{M_aNO_3} - 1/V^{2/3}_{M_bNO_3} = F'_{(p)}$	$F'^2_{(p)}$
$NaNO_3$	45.06 *	—	—
$AgNO_3$	44.49 **	$-6.7 \cdot 10^{-4}$	$\sim 0.00 \cdot 10^{-4}$
KNO_3	54.40 *	$93.22 \cdot 10^{-4}$	$0.87 \cdot 10^{-4}$
$RbNO_3$	59.68 *	$134.91 \cdot 10^{-4}$	$1.82 \cdot 10^{-4}$
$CsNO_3$	67.78 *	$188.18 \cdot 10^{-4}$	$3.54 \cdot 10^{-4}$
$TlNO_3$	57.45 ***	$118.10 \cdot 10^{-4}$	$1.39 \cdot 10^{-4}$

Table 3. $F'^2_{(p)}$ polarization factors for the salt couples $M_aNO_3-M_bNO_3$ with M_aNO_3=$NaNO_3$ and M_bNO_3=added salt. * Data from Ref. [5]; ** from Ref. [4]; *** from Ref. [3].

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[6] J. LUMSDEN, Discussions Faraday Soc. **32**, 138 [1961].

[7] J. LUMSDEN, Thermodynamics of Molten Salt Mixtures, Academic Press, London 1966, p. 112–114.

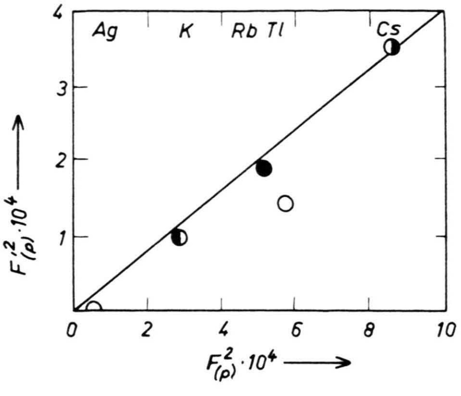

Fig. 2. Comparison between the trend of the $F'^2_{(p)}$ and $F^2_{(p)}$ values [see Eqs. (5) and (6)].

obtained from the straight lines of Table 2 are plotted as functions of $F'^2_{(p)}$. The corresponding values of $\mathcal{F} \cdot (u_b - u_a)_{X_b=0}$ are also reported[8].

In Fig. 3 (right) the $-\mathcal{F} \cdot (du_{Na}/dX_b)_{X_b=0}$ values [according to Eq. (3)], for each added cation, are presented. Plots with only slight differences may be traced for temperatures higher or lower than 350 °C.

Discussion

According to FRENKEL[9] in a binary system with a common cation M, of the type $M \cdot (R_p - R_q)$, where X_p and $X_q = 1 - X_p$ are the molar fractions of the two salts, the activation energy ΔE for the migration of M with respect to the nearest neighbour anions R_p and R_q, is the weighed sum of the energies involved in the pure MR_p and MR_q salts, ΔE_p and ΔE_q respectively, i. e.:

$$\Delta E = \Delta E_p \cdot X_p + \Delta E_q \cdot X_q\,. \tag{7}$$

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 ΔE term is constant in the mixtures. On the contrary, if the anion becomes polarized, a variation of ΔE 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 ΔE is assumed to be the weighed sum:

$$\Delta E_{a,\,mix} = \Delta E_a \cdot X_a + (\Delta E_a + \Delta W_a) \cdot X_b \tag{8}$$

or

$$\Delta E_{a,\,mix} = \Delta E_a + \Delta W_a \cdot X_b \tag{9}$$

where ΔE_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

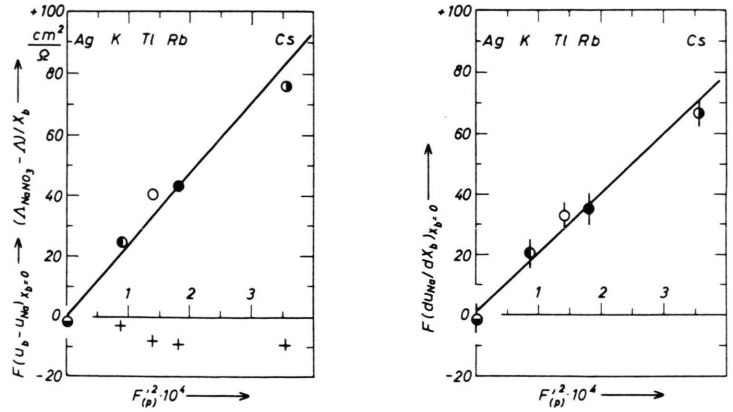

Fig. 3. Left part: $(\Lambda_{NaNO_3} - \Lambda)/X_b$ vs. $F'^2_{(p)}$ plot for the dilute solutions of Fig. 1 [in the lower part the $\mathcal{F} \cdot (u_b - u_a)_{X_b=0}$ values are also reported for comparison]. Right part: $-(du_{Na}/dX_b)_{X_b=0}$ vs. $F'^2_{(p)}$ plot. The $(du_{Na}/dX_b)_{X_b=0}$ values are obtained according to the Eq. (3).

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[8] The $\mathcal{F} \cdot (u_b - u_{Na})_{X_b=0}$ values for K^+, Tl^+, Rb^+ and Cs^+ in $NaNO_3$ at $T = 350$ °C are derived respectively from Molten Salts Handbook p. 355; S. FORCHERI and V. WAGNER, Z. Naturforsch. **22 a**, 1171 [1967]; S. FORCHERI and V. WAGNER, work in preparation; S. FORCHERI and V. WAGNER, unpublished results.

[9] J. FRENKEL, Kinetic Theory of Liquids, University Press, New York 1947, p. 442.

ΔW_a = polarization contribution ($\lesseqgtr 0$ depending on the polarization direction).

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

$$\begin{aligned} u_a &= u' \cdot \exp\{-\Delta E_{a,\,\mathrm{mix}}/R\,T\} \qquad (10)\\ &= u' \cdot \exp\{-\Delta E_a/R\,T\} \cdot \exp\{-\Delta W_a \cdot X_b/R\,T\} \end{aligned}$$

where $\Delta E_{a,\,\mathrm{mix}}$ is given by Eq. (9) and $u' = e\,a^2\,\nu/k\,T$ with e = electronic charge, a = distance between adjacent potential energy minima ($\sim$ the NO_3^- diameter), ν = "lattice-like" anion-cation vibration frequency ($\sim 10^{13}\ \mathrm{sec}^{-1}$) [11]. All the parameters of u', except ν, are concentration independent terms. However, ν, a mass dependent term, does not vary considerably with composition [11]. Consequently u' is expected to be rather insensitive towards changes of the composition, if $\Delta W_a \cdot X_b \ll R\,T$ [12]. Under these conditions from Eq. (10) we have:

$$\begin{aligned} \left(\frac{\mathrm{d}u_a}{\mathrm{d}X_b}\right)_{X_b=0} &= u' \cdot \exp\{-\Delta E_a/R\,T\} \cdot (-\Delta W_a/R\,T)\\ &= (u_a)_{X_b=0} \cdot (-\Delta W_a/R\,T). \qquad (11) \end{aligned}$$

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

$$\Delta W_a \propto F'^2_{(\mathrm{p})} \qquad (12)$$

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

$$-(\mathrm{d}u_{\mathrm{Na}}/\mathrm{d}X_b)_{X_b=0} = \mathrm{const} \cdot F'^2_{(\mathrm{p})}. \qquad (13)$$

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_2SO_4 [1] could be temptatively explained in the same framework [16]. As a further remark one must point out that the most striking effects are observed when $\Delta W_a > R\,T$ (where a is the lighter cation). In this case both $\Delta E_{a,\,\mathrm{mix}}$ and u_a are strongly affected (in the opposite sense) by changes of the composition. This is elucidated by the $(Li-K) \cdot Cl$ system [17] and by $(Li-K)_2 \cdot SO_4$ [18], even if for this last system the $\Delta E_{a,\,\mathrm{mix}}$ values are lacking. If $\Delta W_a < R\,T$, as in the case of $(Na-Rb) \cdot NO_3$, one must expect a weaker dependence of the mobilities [3, 19] and $\Delta E_{a,\,\mathrm{mix}}$ [20] on the composition [21]. It is noteworthy that HAFNER 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]

$$F = 2\,e \cdot \Delta\lambda/\lambda_a^3 \qquad (14)$$

corresponding to the first term in Eq. (5), from which the $F^2_{(\mathrm{p})}$ 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_bR to the M_aR salt and of M_aR to the M_bR salt respectively:

$$\begin{aligned} u_{a,\,x} &= u_{a,\,1} - u_{a,\,1} \cdot \Delta W_a \cdot X_b/R\,T\\ &\quad + \tfrac{1}{2}\,u_{a,\,1} \cdot (\Delta W_a \cdot X_b/R\,T)^2 - \dots \qquad (15\,a) \end{aligned}$$

and

$$\begin{aligned} u_{b,\,x} &= u_{b,\,1} - u_{b,\,1} \cdot \Delta W_b \cdot X_a/R\,T\\ &\quad + \tfrac{1}{2}\,u_{b,\,1} \cdot (\Delta W_b \cdot X_a/R\,T)^2 - \dots \qquad (15\,b) \end{aligned}$$

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

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[10] N. F. MOTT and R. W. GURNEY, Electronic Processes in Ionic Crystals, Oxford Clarendon Press, 2nd Edit., p. 43. In the text u, instead of v, is employed for the ionic mobility, as in the previous papers.

[11] J. K. WILMSHURST, J. Chem. Phys. **36,** 2415 [1962]; **39,** 1779 [1963]; J. K. WILMSHURST and S. SENDEROFF, ibid. **35,** 1078 [1961].

[12] This situation exactly corresponds to the assumed invariance of ν, after the application of an *external* electrical field F_{ext} varying the height of the potential energy barriers by $\pm\frac{1}{2}$ e. a. $F_{\mathrm{ext}} \ll k\,T$ [13−15].

[13] G. KORTÜM, Treatise on Electrochemistry, Elsevier Publishing Company, Amsterdam 1965, p. 267.

[14] R. W. LAITY, Molten Salts, Ann. New York Acad. Sci. **79,** 997 [1960].

[15] A. DEKKER, Solid State Physics, Prentice-Hall Technical Books, U.S.A. Englewood Cliffs, N.J., March 1965, p. 150.

[16] In these systems the increase of the restoring force on the lighter cation due to strong polarization, may cause an increase of ν, and u' in mixture: consequently the treatment becomes more complicated (see also ref. [12]).

[17] C. T. MOYNIHAN and R. W. LAITY, J. Phys. Chem. **68,** 3312 [1964].

[18] A. KVIST, Z. Naturforsch. **21 a,** 1601 [1966].

[19] S. FORCHERI, V. WAGNER, and E. BERRA, Electrochim. Metall. **3,** 123 [1968].

[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.

[22] S. HAFNER and N. H. NACHTRIEB, J. Chem. Phys. **42,** 631 [1965].

[23] S. FORCHERI and V. WAGNER, Z. Naturforsch. **22 a,** 1171 [1967].

If the negative deviation $\Delta\Lambda = \Lambda - \Lambda_{\text{lin}}$ from the additivity value $\Lambda_{\text{lin}}/\mathcal{F} = u_{\text{a},1} \cdot X_{\text{a}} + u_{\text{b},1} \cdot X_{\text{b}}$ is calculated by means of the Eqs. (15 a) and (15 b) including cubic terms [24], then it is easy to demonstrate that the excess conductivity function $\Delta\Lambda_{\text{x}}/\mathcal{F} \cdot X_{\text{a}} X_{\text{b}}$ may be represented as:

$$\Delta\Lambda_{\text{x}}/\mathcal{F} \cdot X_{\text{a}} X_{\text{b}} = l + m \cdot X_{\text{b}} + n \cdot X_{\text{b}}^2 + \dots . \tag{16}$$

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 [3], i. e.:

$$\Delta\Lambda_{\text{x}}/\mathcal{F} \cdot X_{\text{a}} X_{\text{b}} = l' + m' \cdot X_{\text{b}} + \dots \tag{17}$$

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

$$l' = -u_{\text{a},1} \cdot \Delta W_{\text{a}}/R\,T - u_{\text{b},1} \cdot \Delta W_{\text{b}}/R\,T + \tfrac{1}{2}\, u_{\text{b},1} \cdot (\Delta W_{\text{b}}/R\,T)^2, \tag{18 a}$$

$$m' = \tfrac{1}{2}\, u_{\text{a},1} \cdot (\Delta W_{\text{a}}/R\,T)^2 - \tfrac{1}{2}\, u_{\text{b},1} \cdot (\Delta W_{\text{b}}/R\,T)^2. \tag{18 b}$$

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 [25].

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[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 $TlNO_3$) [26, 27]. Therefore, the stabilization of the pair due to the polarization slowes down the Na^+ mobility and, reducing the NO_3^- mobility, increases the viscosity. Viscosity data are available only for ($NaNO_3-RbNO_3$) [28] and ($NaNO_3-TlNO_3$) [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.

[27] A. TIMIDEI and G. J. JANZ, Trans. Faraday Soc. **64**, 202 [1967].

[28] J. G. MURGULESCU and S. ZUCA, Electrochim. Acta **11**, 1383 [1966].

[29] See ref. [19], p. 127.