

terhin sind die Hochfeldspektren und Nullfeldspektren grundsätzlich voneinander verschieden, so daß Linien, die im ersteren aufeinander fallen, im Nullfeldspektrum unter Umständen getrennt aufgezeichnet werden können.

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## The Electrical Conductivity of (Tl-Rb)NO<sub>3</sub> and (Na-Rb)NO<sub>3</sub>

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The electrical conductivity of molten (Na-Rb)NO<sub>3</sub> and (Tl-Rb)NO<sub>3</sub> was determined.

While the equivalent conductivity of the first system shows the usual negative deviation from additivity, that of the second one varies nearly linearly with composition.

After discussing the conductivity isotherms in terms of some proposed models, an excess conductivity isotherm is presented, derived on the basis of simple assumptions about the trend of both cationic mobilities.

In a previous paper<sup>1</sup> dealing with the conductivity of (Na-Tl)NO<sub>3</sub>, it was shown that the equivalent conductivity isotherms of this system could be qualitatively discussed by taking polarization into account. In a subsequent paper<sup>2</sup> the internal mobility variations of the smaller cation (Na<sup>+</sup>) were correlated with the occurrence of the polarized Na<sup>+</sup>-NO<sub>3</sub><sup>-</sup>-Tl<sup>+</sup> triplet.

Polarization occurs because the common anion is subjected in the point-charge approximation, to a net force

$$F \propto 1/\lambda_1^2 - 1/\lambda_2^2 \quad (1)$$

where  $\lambda_1 = r_1 + r_{an}$  and  $\lambda_2 = r_2 + r_{an}$ , by the two opposite cations, the polarization energy being:

$$E_{(p)} = \frac{1}{2} \cdot \alpha_{an} \cdot F^2 \quad (2)$$

where  $\alpha_{an}$  = anion polarizability<sup>3-6</sup>.

In this work we have studied the conductivities of (Tl-Rb)NO<sub>3</sub> and (Na-Rb)NO<sub>3</sub>. Because of the similarity of the Rb<sup>+</sup> and Tl<sup>+</sup> ionic radii<sup>7</sup> the net force  $F$  is bound to be zero for the system

(Tl-Rb)NO<sub>3</sub>. For the same reason the net force  $F$  for the system (Na-Rb)NO<sub>3</sub> is expected to be comparable to that of the (Na-Tl)NO<sub>3</sub> system<sup>1,2</sup>.

The supposition that the same electrical force is exerted on the anion by the cations Rb<sup>+</sup> and Tl<sup>+</sup>, of similar size, but belonging to two different chemical groups, is supported by the circumstance that Tl<sup>+</sup> compounds display many similarities to those of the alkalis<sup>8</sup>. Moreover these two cations have practically equal ionic mobilities in aqueous solution at infinite dilution<sup>9</sup>, thus indicating that comparable electrostatic ion-dipole interactions with the water molecules occur. In addition the lattice energies of pure solid RbNO<sub>3</sub> and TlNO<sub>3</sub> differ only by about 5%<sup>10,11</sup>.

## Experimental

**Apparatus and Material.** The experimental set up is similar to the one previously employed<sup>1</sup>, the sole difference being the substitution of the fused salt thermostatic bath with an Al block, divisible into two pieces,

<sup>1</sup> V. WAGNER and S. FORCHERI, Z. Naturforsch. **22 a**, 891 [1967].

<sup>2</sup> S. FORCHERI and V. WAGNER, Z. Naturforsch. **22 a**, 1171 [1967].

<sup>3</sup> J. LUMSDEN, Discussion Faraday Soc. **32**, 138 [1961].

<sup>4</sup> J. LUMSDEN, Thermodynamics of Molten Salt Mixtures, Academic Press, London 1966, p. 112—114.

<sup>5</sup> S. HAFNER and N. H. NACHTRIEB, J. Chem. Phys. **42**, 631 [1965].

<sup>6</sup> C. T. MOYNIHAN and R. W. LAITY, J. Phys. Chem. **68**, 3312 [1964].

<sup>7</sup> A. J. DEKKER, Solid State Physics, McMillan Co., London 1963, p. 126.

<sup>8</sup> H. REMY, Treatise on Inorganic Chemistry, Elsevier Publ. Co., Amsterdam 1956, p. 381 ff.

<sup>9</sup> See ref. <sup>8</sup>, p. 157 and 382.

<sup>10</sup> M. F. C. LADD and W. H. LEE, J. Inorg. Nucl. Chem. **13**, 218 [1960].

<sup>11</sup> T. C. WADDINGTON, Advan. Inorganic Chemistry and Radiochemistry, Academic Press, New York 1956, p. 157.



apt to contain the U-shaped Vycor glass cells. The thermocouples were standardized by the I.T.I.<sup>1</sup> before and after the measurements. Reagent grade  $\text{RbNO}_3$  and  $\text{NaNO}_3$  were used after several crystallizations, and  $\text{TlNO}_3$  Merck, without further purification.

**Results.** Conductivities as a function of temperature were measured at seven concentrations ( $X_{\text{Rb}} = 0.18; 0.24; 0.48; 0.63; 0.65; 0.85; 1.00$ ) for the system  $(\text{Tl}-\text{Rb})\text{NO}_3$  and at six concentrations ( $X_{\text{Rb}} = 0.05; 0.16; 0.40; 0.60; 0.74; 1.00$ ) for the system  $(\text{Na}-\text{Rb})\text{NO}_3$ .

The experimental results (see Appendix) were treated mathematically in the same way previously reported<sup>1</sup>. The obtained parameters of the linear relationships between specific conductivity,  $\kappa$ , and temperature,  $T$ , °C, are given in Tables 1 and 2. In Fig. 1 specific and equivalent conductivity isotherms at 325 °C are intercompared. The molar volumes  $V$  of the mixtures were calculated by assuming additivity of the pure components for the  $(\text{Tl}-\text{Rb})\text{NO}_3$  system; for  $(\text{Na}-\text{Rb})\text{NO}_3$  the additivity was cor-

$X_{\text{Rb}}$	Conductivity equations	R.M.S.	Temp. Range °C
0.18	$\kappa = -0.2088 + 2.53 \cdot T \cdot 10^{-3}$	$0.80 \cdot 10^{-3}$	304–370
0.24	$\kappa = -0.2060 + 2.48 \cdot T \cdot 10^{-3}$	$1.60 \cdot 10^{-3}$	221–380
0.48	$\kappa = -0.2244 + 2.36 \cdot T \cdot 10^{-3}$	$3.00 \cdot 10^{-3}$	301–389
0.63	$\kappa = -0.2738 + 2.43 \cdot T \cdot 10^{-3}$	$0.70 \cdot 10^{-3}$	268–373
0.65	$\kappa = -0.2265 + 2.29 \cdot T \cdot 10^{-3}$	$2.70 \cdot 10^{-3}$	305–364
0.85	$\kappa = -0.2967 + 2.38 \cdot T \cdot 10^{-3}$	$3.40 \cdot 10^{-3}$	301–372
1.00	$\kappa = -0.3264 + 2.36 \cdot T \cdot 10^{-3}$	$1.80 \cdot 10^{-3}$	327–403

Table 1. Conductivity equations for the  $(\text{Tl}-\text{Rb})\text{NO}_3$  system.

$X_{\text{Rb}}$	Conductivity equations	R.M.S.	Temp. Range °C
0.05	$\kappa = -0.4553 + 4.47 \cdot T \cdot 10^{-3}$	$2.90 \cdot 10^{-3}$	306–400
0.16	$\kappa = -0.4350 + 4.01 \cdot T \cdot 10^{-3}$	$3.30 \cdot 10^{-3}$	289–402
0.40	$\kappa = -0.4161 + 3.33 \cdot T \cdot 10^{-3}$	$2.80 \cdot 10^{-3}$	250–402
0.60	$\kappa = -0.4166 + 3.05 \cdot T \cdot 10^{-3}$	$2.20 \cdot 10^{-3}$	197–396
0.74	$\kappa = -0.3783 + 2.75 \cdot T \cdot 10^{-3}$	$1.20 \cdot 10^{-3}$	227–404
1.00	$\kappa = -0.3615 + 2.43 \cdot T \cdot 10^{-3}$	$0.80 \cdot 10^{-3}$	320–395

Table 2. Conductivity equations for the  $(\text{Na}-\text{Rb})\text{NO}_3$  system.

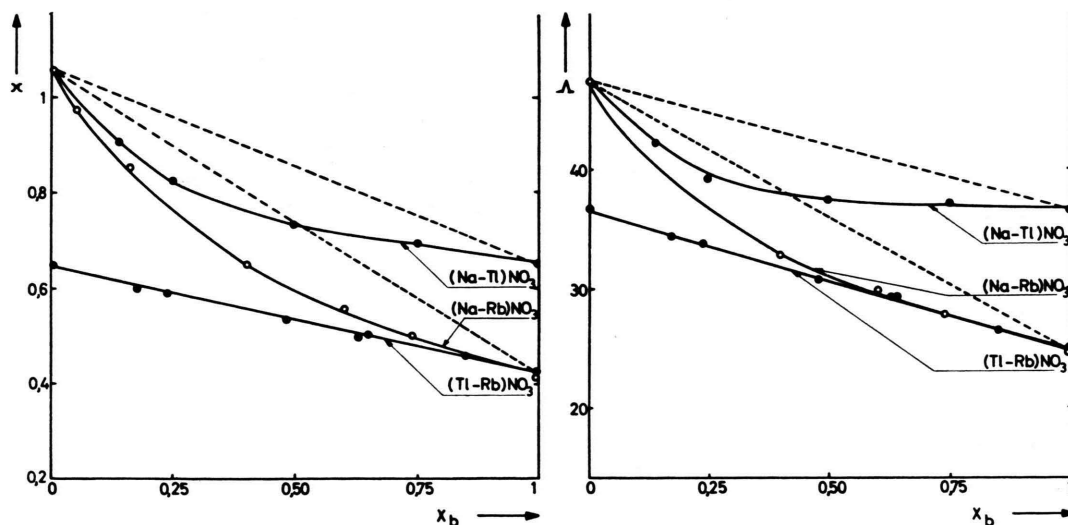


Fig. 1. Specific and equivalent conductivity isotherms for the systems  $(\text{Tl}-\text{Rb})\text{NO}_3$ ,  $(\text{Na}-\text{Rb})\text{NO}_3$  and  $(\text{Na}-\text{Tl})\text{NO}_3$ <sup>1</sup>.  $X_b = X_{\text{RbNO}_3}$  for  $(\text{Tl}-\text{Rb})\text{NO}_3$  and  $(\text{Na}-\text{Rb})\text{NO}_3$ ,  $X_{\text{TlNO}_3}$  for  $(\text{Na}-\text{Tl})\text{NO}_3$ .

rected by taking into account excess volumes<sup>12</sup>. Data for  $V_{\text{RbNO}_3}$  and  $V_{\text{NaNO}_3}$  were taken from reference<sup>13</sup>. For  $\text{TiNO}_3$  the following density equation was employed<sup>14</sup>.

$$d_{\text{TiNO}_3} = 5.8041 - 1.8737 \cdot T_k \cdot 10^{-3}.$$

### Discussion \*

Fig. 1 shows that additivity

$$\Lambda = \Lambda_a X_a + \Lambda_b X_b \quad (3)$$

(where  $X_a$  and  $X_b$  are the mole fractions, and  $\Lambda_a$  and  $\Lambda_b$  are the equivalent conductivities of the pure components) is fulfilled for  $(\text{Ti} - \text{Rb})\text{NO}_3$ , whereas  $(\text{Na} - \text{Rb})\text{NO}_3$  shows negative conductivity excesses which are comparable to those of  $(\text{Na} - \text{Ti})\text{NO}_3$ . These results indicate that the conductivity excesses depend mainly on polarization forces,  $F$  [see Eq. (1)] being  $\cong 0$  for  $(\text{Ti} - \text{Rb})\text{NO}_3$  and taking comparable figures for  $(\text{Na} - \text{Rb})\text{NO}_3$  and  $(\text{Na} - \text{Ti})\text{NO}_3$ .

For the equivalent conductivity of the binary mixtures with a common anion, the following general equation was derived by MARKOW<sup>15</sup>:

$$\Lambda_M = \Lambda_a \cdot e^{-\Delta E_a/RT} \cdot X_a^2 + \Lambda_b \cdot e^{-\Delta E_b/RT} \cdot X_b^2 + \Lambda_{ab} \cdot e^{-\Delta E_{ab}/RT} \cdot 2 X_a X_b \quad (4)$$

$$\text{or} \quad \Lambda_M = \Lambda_a X_a^2 + \Lambda_b X_b^2 + \Lambda_{ab} \cdot 2 X_a X_b. \quad (5)$$

This isotherm was obtained<sup>15</sup> by considering that in a mixture of  $M_a \cdot R$  and  $M_b \cdot R$  (where  $R$  is the common anion) the probabilities of the different arrangements  $M_a R \cdot M_a R$ ,  $M_b R \cdot M_b R$  and  $M_a R \cdot M_b R$  are  $X_a^2$ ,  $X_b^2$  and  $2 X_a X_b$  and by assuming that each of these arrangements will contribute to the total conductivity by terms  $\Lambda_a$ ,  $\Lambda_b$ , and  $\Lambda_{ab}$ , respectively. To evaluate the  $\Lambda_{ab}$  term it is assumed that the rate of interchange of  $M_a$  and  $M_b$  in an environment of  $R$  "will be determined largely by the species having the highest activation energy"<sup>16</sup>.

Therefore if  $\Delta E_a < \Delta E_b$ , then  $\Delta E_{ab} \cong \Delta E_b$ , and putting  $\Lambda_{ab} \cong \Lambda_b$ , Eqs. (4) and (5) simplify to:

$$\Lambda_M = \Lambda_a X_a^2 + \Lambda_b X_b^2 + \Lambda_b \cdot 2 X_a X_b \quad (6)$$

or, being  $X_a^2 + X_b^2 + 2 X_a X_b = 1$ ,

$$\text{to} \quad \Lambda_M = \Lambda_a X_a^2 + \Lambda_b \cdot (1 - X_a^2). \quad (7)$$

Eq. (7) is similar to that derived by KVIST<sup>17</sup> for the conductivity of systems in which  $k$  cations (where  $k$  could take a value different from 2 and is different for different system), are simultaneously involved in the single transport act:

$$\Lambda_K = \Lambda_a X_a^k + \Lambda_b (1 - X_a^k) \quad (8)$$

where  $X_a^k$  represents the probability of a group to contain  $k$  cations, only of  $M_a$  species, in a mixture with a molar fraction  $X_a$ . The contribution of this arrangement to the total conductivity is equal to the conductivity of the pure  $M_a R$ . Conversely, the contribution of the other  $k$ -arrangements, containing the slower  $M_b$  cation, is equal to the pure  $M_b \cdot R$  conductivity. According to this model the conductivity is determined by polycationic arrangements, or groups, of  $k$  cations (as opposite to the dicationic MARKOW arrangements). By analogy to the  $\Lambda_M$  case, in the  $\Lambda_K$  case the  $M_a$  ions rearranging cooperatively with the  $M_b$  ions are slowed down as if the  $M_b$  motion would be the rate determining step of the overall transport process.

In Fig. 2 some experimental data for the  $(\text{Ti} - \text{Rb})\text{NO}_3$  and  $(\text{Na} - \text{Rb})\text{NO}_3$  systems (part a), as well as for the previously studied  $(\text{Na} - \text{Ti})\text{NO}_3$ <sup>1</sup> and  $(\text{Li} - \text{K})\text{SO}_4$  systems<sup>18, 19</sup> (part b), are compared with the corresponding calculated  $\Lambda_M$  isotherms (dotted lines). The agreement for the  $(\text{Na} - \text{Rb})\text{NO}_3$  system is quite good; in this case the condition  $\Delta E_b > \Delta E_a$  seems to be fulfilled ( $\Delta E_{\text{NaNO}_3} = 3.2 \div 3.4$  kcal/mol<sup>1</sup>,  $\Delta E_{\text{RbNO}_3} \cong 4.2$  kcal/mol).

Being  $\Delta E_{\text{TiNO}_3} = 3.2$  kcal/mol<sup>1</sup> the condition  $\Delta E_b > \Delta E_a$  is fulfilled also for the  $(\text{Ti} - \text{Rb})\text{NO}_3$  system. In this case, however, the calculated  $\Lambda_M$  values differ strongly from the experimental ones, as well as in the  $(\text{Li} - \text{K})_2\text{SO}_4$  case, where the difference is larger.

<sup>12</sup> B. F. POWERS, J. L. KATZ, and O. J. KLEPPA, J. Phys. Chem. **66**, 103 [1962].

<sup>13</sup> W. J. MCAULEY, E. RHODES, and A. R. UBBELHODE, Proc. Roy. Soc. London A **289**, 151 [1966].

<sup>14</sup> A. TIMIDEI and G. J. JANZ, Private Communication.

\* In the following the indexes a and b always refer to the component whose cationic internal mobility,  $u$ , in the pure state is greater and smaller respectively. The mobility isotherms of the two cations are considered to have, in general, at least one common value.

<sup>15</sup> I. K. DELIMARSKII and B. F. MARKOW, Electrochemistry of Fused Salt, The Sigma Press, Washington 1961, p. 32 ff.

<sup>16</sup> A. T. WARD and G. J. JANZ, Electrochim. Acta **10**, 849 [1965].

<sup>17</sup> A. KVIST, Z. Naturforsch. **22a**, 208 [1967].

<sup>18</sup> A. KVIST, Z. Naturforsch. **21a**, 1221 [1966].

<sup>19</sup> A. KVIST, Z. Naturforsch. **21a**, 1601 [1966].

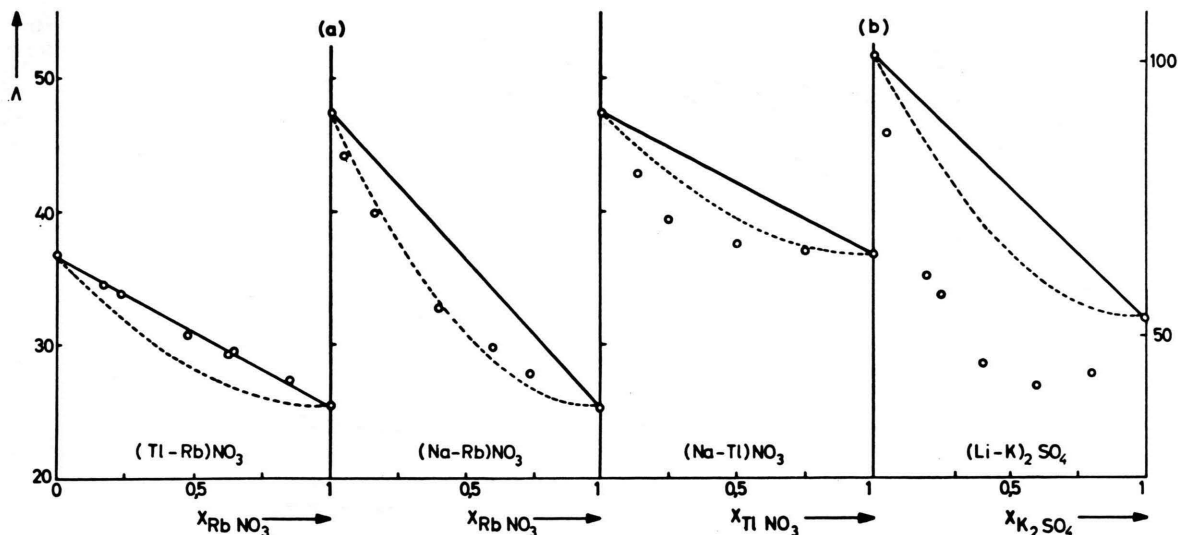


Fig. 2. Comparison between the experimental conductivity values and those calculated by means of Eq. (7) (dotted lines).

It is worth to note that, all the  $\Delta E$  values being rather similar for molten nitrates<sup>20</sup> (contrary to the molten halides<sup>21</sup>), the use of  $\Delta_M$  is seldom justified for these systems.

The agreement with the experimental data for the  $(\text{Tl}-\text{Rb})\text{NO}_3$  and  $(\text{Na}-\text{Tl})\text{NO}_3$  systems could be *formally* improved by using Kvist's equation (8), that is by lowering the Markow original exponent towards unity ( $k=1$ ), in the  $(\text{Tl}-\text{Rb})\text{NO}_3$ , or by suitably increasing it in the  $(\text{Na}-\text{Tl})\text{NO}_3$  case.

As the author<sup>17</sup> states that "his model cannot explain the minimum of the  $\Delta$  curves" [as in the  $(\text{Li}-\text{K})_2\text{SO}_4$  case], it seems to be interesting to obtain a more general equation valid for different cases [for example the linear trend of  $(\text{Rb}-\text{Tl})\text{NO}_3$ , the negative deviations in systems like  $(\text{Na}-\text{Tl})\text{NO}_3$ , and the minima of systems like  $(\text{Li}-\text{K})_2\text{SO}_4$ ].

### The Equivalent Conductivity as a Function of the Internal Mobilities

It is assumed that, at each composition, the following relationships for the internal mobilities,  $u$ , are fulfilled (see Fig. 3):

$$u_a = u_{a,1} X_a + u_{a,0} X_b + \Delta u_{a,0.5} P, \quad (9a)$$

$$u_b = u_{b,1} X_b + u_{b,0} X_a + \Delta u_{b,0.5} P, \quad (9b)$$

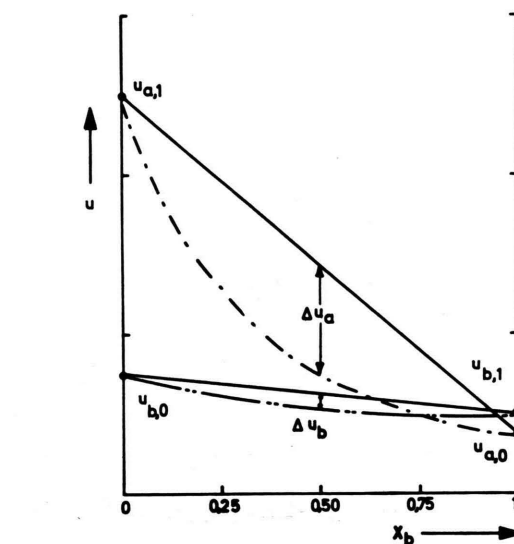


Fig. 3. Ionic parameters of the conductivity Eq. (11).

where the alphabetic subscript refers to the cationic species and the numerical one to the relative concentration;  $P$ , as previously indicated<sup>2</sup>, (see ref. <sup>22</sup>), is defined as  $X_a X_b / 0.25$ , and

$$\begin{aligned} \Delta u_{a,0.5} &\equiv u_{a,0.5}(\text{exp.}) - u_{a,0.5}(\text{linear}) < 0, \\ \Delta u_{b,0.5} &\equiv u_{b,0.5}(\text{exp.}) - u_{b,0.5}(\text{linear}) < 0. \end{aligned} \quad (10)$$

As

$$\Delta/F = u_a \cdot X_a + u_b \cdot X_b$$

<sup>20</sup> J. JANZ, A. T. WARD, and R. D. REEVES, Molten Salt Data, US-AFOSRN 64-0039, Rensselaer Polytech. Inst., Troy N. Y.

<sup>21</sup> E. KORTÜM, Lehrbuch der Elektrochemie, Verlag Chemie, Weinheim 1966, p. 257.

<sup>22</sup> If the negative mobility excess is mainly due to the polarization of the common anion, it rises up to the maximum value around 50 mole per cent, if the solution is considered as an array of ions randomly distributed.

it results that

$$\Delta A/F = u_{a,1} X_a^2 + u_{b,1} X_b^2 + [u_{ab} + 2(\Delta u_a \cdot X_a + \Delta u_b \cdot X_b)] \cdot 2 X_a X_b \quad (11)$$

where  $u_{ab} \equiv (u_{a,0} + u_{b,0})/2$  and the 0.5 subscript (as in the following) is omitted. The condition

$$\Delta u_a \equiv \Delta u_b = 0 \quad (12a)$$

is a necessary condition but not a sufficient one for having  $\Delta A = 0$  [as in (Tl-Rb)NO<sub>3</sub>]. In fact it is also necessary that

$$u_{ab} \equiv (u_{a,0} + u_{b,0})/2 = (u_{a,1} + u_{b,1})/2 \quad (12b)$$

as only in this case we have from relation (11):

$$\Delta A/F = u_{a,1} X_a^2 + u_{b,1} X_b^2 + (u_{a,1} + u_{b,1}) X_a X_b \quad (13a)$$

$$= u_{a,1} X_a (X_a + X_b) + u_{b,1} X_b (X_a + X_b) \quad (13b)$$

$$= u_{a,1} X_a + u_{b,1} X_b.$$

Equation (12b) is fulfilled when

$$u_{a,0} = u_{a,1} \quad \text{and} \quad u_{b,0} = u_{b,1} \quad (14a)$$

as well as when

$$u_{a,0} = u_{b,1} \quad \text{and} \quad u_{b,0} = u_{a,1}. \quad (14b)$$

An excess isotherm is easily calculated from Eqs. (11) and (13a). One obtains the relation

$$\Delta A/F = [\frac{1}{2}(u_{a,0} + u_{b,0} - u_{a,1} - u_{b,1}) + 2\Delta u_a X_a + 2\Delta u_b X_b] \cdot 2 X_a X_b \quad (15)$$

that is symmetrical only if  $\Delta u_a = \Delta u_b$ .

An useful form of Eq. (15) is obtained if it is assumed that: 1)  $\Delta u_b \cong 0$ , and, 2)  $u_{a,0} = u_{b,1}$ , i. e., that the excess term for the larger, slower, cation is  $\cong 0$  and that the tracer mobility  $u_{a,0}$  of the smaller cation in the pure M<sub>b</sub>R is nearly equal to the  $u_{b,1}$  term. Under these assumptions we obtain

$$\Delta A/F = [\frac{1}{2}(u_{b,0} - u_{a,1}) + 2\Delta u_a X_a] \cdot 2 X_a X_b. \quad (16)$$

If  $\Delta A = 0$  in the whole concentration range, the parameters  $(u_{b,0} - u_{a,1})/2$  and  $\Delta u_a$  in brackets (16) must be zero, and therefore:

$$u_{b,0} = u_{a,1}. \quad (17)$$

This last condition is accounted for by Eqs. (14b). When the  $\Delta A$  values for the mixtures are known, the plot  $\Delta A/2 X_a X_b$  vs.  $X_a$  gives a straight-line, whose intercept and slope are related to the ionic parameters  $u_{b,0}$  and  $\Delta u_a$  respectively<sup>23</sup>.

<sup>23</sup> The trend of the internal mobility isotherms as in Fig. 3 is rather general in nitrates<sup>24</sup>. If the two simplifying assumptions on Eq. (15) leading to the Eq. (16) are erroneous to a large extent it is impossible to determine the

The plots  $\Delta A/2 X_a X_b$  vs.  $X_a$  for the systems (Na-Tl)NO<sub>3</sub><sup>1</sup>, (Na-Rb)NO<sub>3</sub> and (Li-K)<sub>2</sub>SO<sub>4</sub><sup>19</sup> are presented in Fig. 4. Due to the larger error percentage for the dilute solutions the corresponding points are not reported. By means of  $u_{b,0}$  and  $\Delta u_a$  parameters, so obtained, together with the  $u_{a,1}$  and  $u_{b,1}$ , an approximate evaluation of both mobility trends can be inferred, as in the simpler (Rb-Tl)NO<sub>3</sub> case [see Eqs. (14b) and (17)].

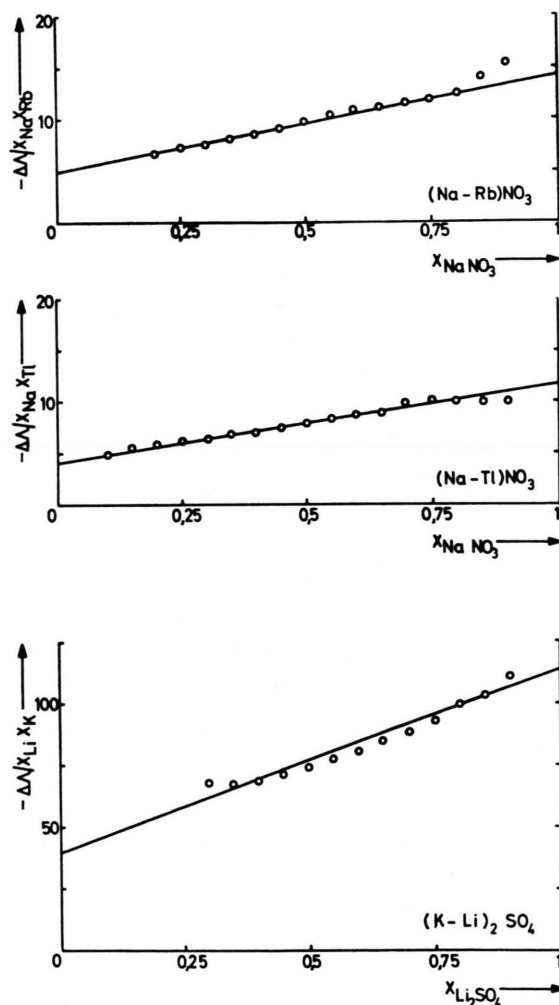


Fig. 4.  $\Delta A/2 X_a X_b$  vs.  $X_a$  plots for the systems (Na-Rb)NO<sub>3</sub>, (Na-Tl)NO<sub>3</sub> and (Li-K)<sub>2</sub>SO<sub>4</sub>.

The calculated mobility isotherms for the systems (Rb-Tl)NO<sub>3</sub> and (Rb-Na)NO<sub>3</sub>, whose experimental data are unknown so far (part a), as well

ion parameters in such a simple way; but the conductivity equations [Eqs. (11) and (15)] are always valid.

<sup>24</sup> See ref. <sup>2</sup>, p. 1173.



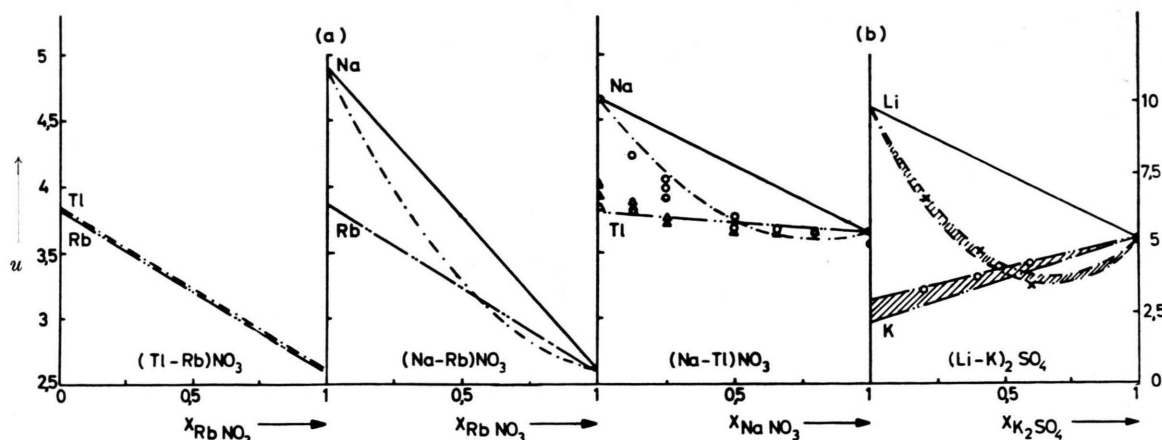


Fig. 5. a) Internal mobility isotherms for (Tl-Rb)NO<sub>3</sub> and (Na-Rb)NO<sub>3</sub> at 325 °C calculated by Eqs. (12 a), (14 b), and (9 a), (9 b) (with  $\Delta u_b=0$ ). b) Internal mobility isotherms for (Na-Tl)NO<sub>3</sub> at 316 °C and (Li-K)<sub>2</sub>SO<sub>4</sub> at 750 °C calculated by Eqs. (9 a), (9 b) (with  $\Delta u_b=0$ ) and compared with experimental results<sup>2, 18</sup>.

for the systems (Na-Tl)NO<sub>3</sub> and (Li-K)<sub>2</sub>SO<sub>4</sub>, whose mobility data are available<sup>2, 12</sup> (part b), are presented in Fig. 5 (see also Fig. 3). The agreement for (Na-Tl)NO<sub>3</sub> and (Li-K)<sub>2</sub>SO<sub>4</sub> is fairly good.

To confirm the usefulness of this procedure for binary nitrates systems, internal mobility measure-

ments in the (Na-Rb)NO<sub>3</sub> and (Tl-Rb)NO<sub>3</sub> mixtures could be of interest. The previous treatment is not applicable to systems in which complexions are present (e. g. MgCl<sub>2</sub>-KCl<sup>25, 26</sup>), because in this case the assumption of a random distribution is no longer fulfilled.

## Appendix

System (Tl-Rb)NO<sub>3</sub>

<i>T</i>	<i>x</i>	<i>T</i>	<i>x</i>	<i>T</i>	<i>x</i>	<i>T</i>	<i>x</i>
<i>X<sub>Rb</sub></i> = 0.18		<i>X<sub>Rb</sub></i> = 0.24		<i>X<sub>Rb</sub></i> = 0.63		<i>X<sub>Rb</sub></i> = 0.85	
360.2	0.7028	272.9	0.4716	372.8	0.6297	344.6	0.5249
360.0	0.7023	272.9	0.4716	372.8	0.6297	344.3	0.5247
370.8	0.7269	256.0	0.4296	361.6	0.6036	332.3	0.4953
369.7	0.7264	256.2	0.4294	361.6	0.6036	332.3	0.4953
345.5	0.6640	235.0	0.3761	341.3	0.5551	321.2	0.4797
345.5	0.6640	235.2	0.3761	341.3	0.5551	311.7	0.4443
330.0	0.6253	221.0	0.3405	327.6	0.5213	311.7	0.4443
330.0	0.6253	221.0	0.3405	327.7	0.5213	311.5	0.4439
329.5	0.6241			296.4	0.4443	301.2	0.4191
304.7	0.5615			296.3	0.4441	301.2	0.4189
304.2	0.5606			267.7	0.3758	300.9	0.4185
		<i>X<sub>Rb</sub></i> = 0.48		267.7	0.3758		
		388.6	0.6865			<i>X<sub>Rb</sub></i> = 1.00	
		388.3	0.6899	<i>X<sub>Rb</sub></i> = 0.65		403.0	0.6217
		388.3	0.6904	363.7	0.6058	403.0	0.6217
379.7	0.7335	388.3	0.6909	363.7	0.6055	402.7	0.6217
379.7	0.7329	378.2	0.6681	337.7	0.5529	376.7	0.5648
369.2	0.7089	378.1	0.6686	337.7	0.5529	376.4	0.5644
369.2	0.7084	338.8	0.5775	320.4	0.5085	376.4	0.5638
351.7	0.6672	330.7	0.5583	320.4	0.5085	370.8	0.5492
351.7	0.6672	330.7	0.5583	317.2	0.4999	370.8	0.5492
343.4	0.6477	320.3	0.5315	317.2	0.4999	352.5	0.5061
343.4	0.6477	320.7	0.5312	305.2	0.4727	352.6	0.5061
327.3	0.6081	316.7	0.5232	305.2	0.4727	352.4	0.5061
327.3	0.6077	316.5	0.5230			341.3	0.4778
321.3	0.5922	309.3	0.5067	<i>X<sub>Rb</sub></i> = 0.85		341.3	0.4778
320.9	0.5922	309.3	0.5067	372.3	0.5883	341.3	0.4778
290.7	0.5169	303.4	0.4886	372.3	0.5883	334.8	0.4631
290.6	0.5168	303.4	0.4886	364.7	0.5721	335.2	0.4631
290.3	0.5158	303.4	0.4826	364.6	0.5717	327.1	0.4439
290.3	0.5158	301.4	0.4857			327.2	0.4439

<sup>25</sup> W. K. BEHL and J. J. EGAN, J. Phys. Chem. **71**, 1764 [1967].

<sup>26</sup> K. BALASUBRAMANYAN, J. Chem. Phys. **44**, 3270 [1966].

System (Na—Rb)NO<sub>3</sub>

$T$	$x$	$T$	$x$	$T$	$x$	$T$	$x$	$T$	$x$	$T$	$x$
$X_{\text{Rb}} = 0.05$		$X_{\text{Rb}} = 0.16$		$X_{\text{Rb}} = 0.40$		$X_{\text{Rb}} = 0.60$		$X_{\text{Rb}} = 0.74$		$X_{\text{Rb}} = 1.00$	
400.0	1.3411	352.1	0.9804	313.1	0.6363	397.6	0.7944	403.8	0.7306	395.1	0.5995
372.1	1.2003	352.6	0.9820	411.7	0.9618	397.5	0.7941	401.5	0.7245	393.2	0.5956
368.5	1.1900	390.2	1.1306	409.7	0.9558	394.0	0.7820	393.2	0.7024	392.9	0.5947
368.3	1.1843	390.2	1.1307	407.7	0.9490	370.5	0.7120	375.3	0.6522	388.4	0.5838
360.4	1.1545	402.3	1.1758	407.5	0.9482	350.9	0.6550	375.2	0.6520	387.6	0.5816
355.8	1.1359	402.1	1.1743	395.7	0.9089	350.8	0.6547	375.3	0.6519	379.3	0.5615
355.3	1.1348	401.6	1.1713	395.3	0.9074	327.7	0.5826	370.0	0.6338	378.6	0.5597
344.6	1.0876	400.5	1.1688	395.5	0.9067	319.7	0.5595	368.2	0.6336	378.2	0.5586
344.4	1.0861	374.4	1.0699	395.3	0.9056	319.8	0.5595	365.6	0.6215	372.5	0.5441
337.0	1.0509	374.4	1.0700	395.4	0.9046	300.0	0.4984	365.4	0.6248	372.4	0.5418
336.9	1.0506	374.5	1.0706	391.8	0.8854	284.1	0.4488	365.4	0.6247	367.9	0.5347
336.7	1.0496	331.4	0.8999	372.5	0.8331	283.8	0.4477	358.8	0.6074	366.0	0.5288
335.5	1.0443	331.4	0.8997	372.8	0.8327	257.7	0.3741	356.3	0.6012	363.3	0.5224
335.2	1.0419	311.5	0.8168	357.8	0.7838	251.3	0.3464	355.8	0.5976	362.7	0.5206
334.1	1.0374	311.0	0.8141	357.7	0.7832	248.6	0.3392	351.0	0.5873	359.3	0.5120
333.4	1.0372	310.7	0.8128	351.4	0.7551	247.6	0.3367	340.0	0.5578	356.6	0.5057
333.3	1.0337	310.4	0.8112	372.8	0.6924	231.8	0.2855	334.0	0.5398	355.0	0.5016
331.8	1.0299	299.0	0.7641	320.1	0.6514	227.0	0.2750	290.6	0.4190	350.4	0.4912
329.0	1.0172	299.1	0.7642	320.1	0.6513	214.7	0.2370	321.9	0.5057	347.8	0.4816
324.1	0.9954	299.0	0.7641	320.0	0.6512	213.8	0.2364	311.9	0.4782	344.9	0.4776
324.2	0.9933	289.6	0.7221	301.4	0.5915	197.4	0.1875	291.8	0.4221	340.7	0.4675
324.3	0.9936	289.6	0.7221	301.4	0.5915			285.6	0.4044	336.6	0.4568
321.9	0.9842	289.5	0.7220	269.6	0.4820			253.2	0.3161	330.7	0.4428
315.7	0.9558	353.3	0.9855	269.5	0.4819			251.1	0.3103	329.8	0.4408
306.4	0.9148	353.3	0.9862	269.5	0.4818			244.1	0.2923	327.6	0.4360
306.5	0.9144			250.0	0.4124			235.2	0.2673	327.1	0.4345
306.4	0.9137							228.4	0.2508	326.1	0.4316
306.3	0.9136							226.9	0.2449	322.7	0.4239
										322.5	0.4229
										320.3	0.4178
										320.0	0.4170

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