

## Electrical Mobilities and Tracer-diffusion Coefficients of the Na and Tl Ions in the Molten (Na—Tl)NO<sub>3</sub> System

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The ionic mobilities and the diffusion coefficients of Na and Tl in the (Na—Tl)NO<sub>3</sub> system have been determined by means of a zone electrophoresis and diffusion technique. The most significant feature of the Na mobility isotherm is its rapid variation with composition in the NaNO<sub>3</sub> rich region.

The diffusion coefficients of both cations have been found to depend rather weakly on composition. The electrical and diffusional mobilities of both cations show trends opposite to that of the fluidity.

These results are discussed in terms of the anion polarization model.

Equilibrium properties of molten binary mixtures with a common anion have been successfully correlated to the anion polarization effect<sup>1–3</sup>. A straightforward test of this effect has been given for molten chloride binary mixtures by means of N.M.R. measurements<sup>4</sup>. Concerning transport processes, recently LAITY<sup>5</sup> observed that some electrical properties (conductivity and ion mobilities) of the (Li—K)Cl system are consistent with the anion polarization model.

In molten alkali nitrate binary mixtures, systematic deviations of the conductivity isotherms from additivity<sup>6</sup>, together with positive deviations of the corresponding activation energies, have been considered as a consequence of the anionic polarization due to the difference of the cationic fields<sup>7</sup>.

More detailed information on the factors affecting the transport properties can be obtained by determining the electrical and diffusional ion mobilities. In this work the (Na—Tl)NO<sub>3</sub> system is investigated by means of tracer zone electrophoresis and tracer diffusion measurements (Na<sup>22</sup> and Tl<sup>204</sup>).

After their first application to molten salts by ARNIKAR<sup>8</sup>, who used asbestos paper as a support, zone electrophoresis methods have been frequently

used in this field<sup>9, 10</sup>. Recently the accuracy of the measurements on glass fiber paper has been greatly improved<sup>11</sup>. The method we have used in this work is based on the utilization of porous ceramic thin layers, in powder or in fritted form, as a support for the molten electrolyte in the electromigration and diffusion experiments. The electrical conductivity and density of the (Na—Tl)NO<sub>3</sub> system have been recently determined<sup>7</sup>. The present experimental results of ionic mobilities and of tracer diffusion coefficients are compared to some viscosity data which became lately available<sup>12</sup>.

### Experimental

Reagent grade NaNO<sub>3</sub> and TlNO<sub>3</sub> were purified by recrystallization from aqueous solutions. Na<sup>22</sup> and Tl<sup>204</sup> were supplied by the Radiochemical Center Amersham, Buckinghamshire, England.

Although with zone electrophoresis it is possible to determine the ionic mobility and the diffusion coefficient simultaneously, from the displacement and the widening of the labelled zone, nevertheless separate experiments are more suitable.

The preparation of the porous layers, the assembly and the procedure of the electromigration experiments were previously described<sup>13–15</sup>. The mobility of the

<sup>1</sup> C. D. THURMOND, J. Am. Chem. Soc. **75**, 3928 [1953].

<sup>2</sup> J. LUMSDEN, Discussions Faraday Soc. **32**, 138 [1961].

<sup>3</sup> J. LUMSDEN, Thermodynamics of Molten Salt Mixtures, Academic Press, London 1966, p. 112—114.

<sup>4</sup> S. HAFNER and N. H. NACHTRIEB, J. Chem. Phys. **42**, 631 [1965].

<sup>5</sup> C. T. MOYNIHAN and R. W. LAITY, J. Phys. Chem. **68**, 3312 [1964].

<sup>6</sup> B. DE NOOJER and J. A. A. KETELAAR, Rec. Trav. Chim., Pays Bas **83**, 573 [1964].

<sup>7</sup> V. WAGNER and S. FORCHERI, I. Congresso di Chimica-Fisica, Trieste Dec. 19—21 (1966). Z. Naturforsch. **22 a**, 891 [1967].

<sup>8</sup> H. ARNIKAR, C. R. Acad. Sci. Paris **244**, 2241 [1957].

<sup>9</sup> R. A. BAILEY and A. STEGER, J. Chromatogr. **11**, 122 [1963].

<sup>10</sup> G. ALBERTI, S. ALLULLI, and G. MODUGNO, J. Chromatogr. **15**, 420 [1964].

<sup>11</sup> E. P. HONIG and J. A. A. KETELAAR, Trans. Faraday Soc. **62**, 190 [1966].

<sup>12</sup> G. FRIZ, unpublished results.

<sup>13</sup> S. FORCHERI, Quaderni Ric. Sci. Rome **35**, 50 [1965].

<sup>14</sup> S. FORCHERI and V. WAGNER, Ann. Chim. Rome **56**, 213 [1966].

<sup>15</sup> S. FORCHERI and A. BERLIN, J. Chromatogr. **26**, 239 [1967].



two cations was determined simultaneously at each composition by labelling two or more points of the strip (length  $\sim 15$  cm, width  $\sim 0.6$  cm) with a small quantity (several tenths of mg) of  $\text{Na}^{22}\text{NO}_3$  and of  $\text{Tl}^{204}\text{NO}_3$ .

The ionic mobility  $u_w$  of a cation is proportional to its zone mobility  $u_z$ ,

$$u_w = K u_z \quad (K > 1) \quad (1)$$

where  $u_z$  is the rate of the displacement of the labelled zone in unit apparent electrical field ( $\Delta V/\text{length of the strip}$ ), and the factor  $K$  accounts for the obstruction of the particles of the porous support to the ionic migration. If this correction factor is defined as the inverse of the obstruction factor derived by CRAWFORD and EDWARD<sup>16</sup> for paper electrophoresis:

$$K = R_p \chi p/d \quad (2)$$

where  $R_p$  = resistance of the strip per unit length,  $\chi$  = specific conductivity of the melt,  $p$  = salt weight per unit length,  $d$  = density of the melt, then

$$u_w = (\chi/d) (p/l/q) \quad (3)$$

where  $l$  = the measured displacement of the labelled zone,  $q$  = ionic charge passed through the strip.

The precision of the measurement of  $u_w$  depends essentially on the accuracy ( $\pm 2\%$ ) of the determination of the displacement  $l$ , (usually several centimeters)<sup>14</sup>.

According to formula (3)  $u_w$  can be determined without any knowledge of the  $K$  factor. On the contrary to measure diffusion coefficients from the gaussian activity distribution on the strip<sup>15</sup> this parameter must be determined by means of a measurement of  $R_p$  [see Eq. (2)]. The assembly used in the diffusion experiments is shown in Fig. 1.  $R_p$  is measured by means of two platinum electrodes placed in contact with the porous layer. The diffusion coefficient was calculated by the formula:

$$D = - (1/2,3) (K/4 S t) \quad (4)$$

where  $S$  = slope of the plots log activity vs. the squared distance from the gaussian centre (Fig. 2),  $t$  = time of the diffusion experiment.

The accuracy in the measurement of  $D$  depends mainly on the precision of the determination of the  $K$

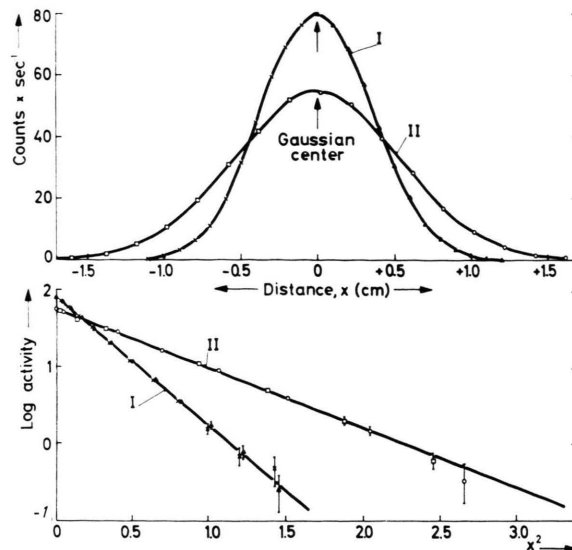


Fig. 2. Gaussian diffusion profiles of  $\text{Tl}^{204}$  in 0.2 mole fraction of  $\text{NaNO}_3$  mixture, determined at two different times at  $219.0^\circ\text{C}$ . — According to Eq. (4) the slopes of the straight lines reported in the lower part of the figure are inversely proportional to the respective diffusion times.

factor and of the slope  $S$ .  $K$  was usually determined at  $\sim \pm 1.5\%$ ; in the case of the  $\text{Tl}^{204}$  ( $\beta$  emitting isotope)  $S$  was determined at  $\sim \pm 2\%$ ; in the case of the  $\text{Na}^{22}$  ( $\beta$ - $\gamma$  emitting isotope)  $S$  was determined at  $\sim \pm 4\%$ .

The scanning of the strip was performed according to a method previously described<sup>17</sup>.

The temperature during the experiments was measured by means of a calibrated Cr—Al thermocouple, placed very near to the strip. After each experiment the composition of the molten mixtures was controlled by analysis.

In a preliminary investigation conductivity determinations of alumina porous thin layers impregnated with various molten nitrates (alkali as well Tl and Ag nitrates) were carried out. The results obtained showed that  $K$  (usual value  $1.3 \div 1.9$ ) is only a function of the absorbance of the system (salt volume/weight of support)<sup>18</sup> (for more general informations on this topic see Ref. 19),

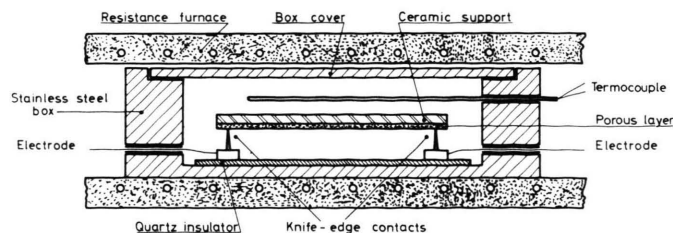


Fig. 1. Cell for diffusion measurements. The strip is in the reverse position, for conductivity determination.

<sup>16</sup> R. CRAWFORD and J. EDWARD, *Anal. Chem.* **29**, 1543 [1957].

<sup>17</sup> V. WAGNER and S. FORCHERI, *Energia Nucl. Milan* **14**, 380 [1967].

<sup>18</sup> S. FORCHERI and V. WAGNER, EUR Report, in preparation.

<sup>19</sup> R. A. BAILEY and L. YAFFE, *Can. J. Chem.* **37**, 1527 [1959].

## Results and Discussion

### Ionic mobilities

Equation (1) expresses external mobilities (frame of reference = the wall). When discussing ion mobility isotherms of binary systems with a common anion, it seems more suitable to consider internal quantities<sup>20</sup> (frame of reference = the anion).

To obtain the internal mobility,  $u$ , the following equation must be employed:

$$u = u_w + u_{w, \text{NO}_3} \quad (5)$$

in which:

$$u_{w, \text{NO}_3} = \Delta/F - X_{\text{Tl}} \cdot u_{\text{Tl}, w} - X_{\text{Na}} \cdot u_{\text{Na}, w} \quad (6)$$

where  $X_{\text{Na}}$  and  $X_{\text{Tl}}$  are the molar fractions of the  $\text{NaNO}_3$  and  $\text{TlNO}_3$ .

In Table 1 the internal mobilities and equivalent conductivities at 316 °C are reported. Fig. 3 is a plot of  $u_{\text{Na}}$ ,  $u_{\text{Tl}}$  and  $\Delta$  vs. the composition of the mixture.

The most striking feature of the mobility diagram is the rapid decrease of the mobility of the smaller ion, (Na), at increasing concentrations of the larger cation. From the data reported in the literature on  $(\text{Na} - \text{K})\text{NO}_3$ <sup>11, 21</sup>,  $(\text{Li} - \text{K})\text{NO}_3$ <sup>22, 23</sup>,  $(\text{Li} - \text{K})\text{Cl}$ <sup>5</sup>, and  $(\text{Li} - \text{K})\text{SO}_4$ <sup>24</sup>, it can be inferred that this behaviour is not unusual in molten systems (if internal quantities are considered). In the  $(\text{Na} - \text{Tl})\text{NO}_3$  system the variation of the mobility of the larger cation with composition is smaller than in the cases quoted above.

As was pointed out in a previous paper<sup>7</sup> the trend of the electrical conductivity and of the Na mobility could be well accounted for, at least quali-

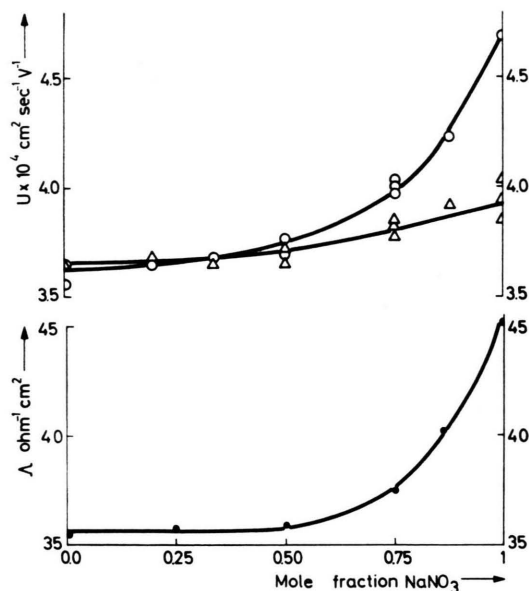


Fig. 3. Ionic internal mobilities and equivalent conductivity of the  $(\text{Na} - \text{Tl})\text{NO}_3$  system at 316 °C.  $\circ = \text{Na}$ ,  $\triangle = \text{Tl}$ .

tatively, by the LUMSDEN polarization model. Moreover, in agreement with LAITY's<sup>5</sup> results in chloride melts, the mobility of the larger cation rises only slowly at increasing concentrations of the smaller cation.

Let us define the function

$$P = \frac{pX}{p_{0.5}} = \frac{X_{\text{Na}} \cdot (1 - X_{\text{Na}})}{0.25}$$

(where  $X_{\text{Na}}$  is the molar fraction of  $\text{NaNO}_3$ ) as the ratio between the chance of finding the ion triplet  $\text{Na} \cdot \text{NO}_3 \cdot \text{Tl}$  at  $0.5 < X_{\text{Na}} < 1$  and the chance of finding it at  $X_{\text{Na}} = 0.5$  (the ions being supposed randomly distributed<sup>25</sup>). The increase of the sodium

$X_{\text{Na}}$	0,00	0,20	0,34	0,50	0,75	0,875	1,00
$\Delta$ *	35,268	35,525	35,340	35,439	37,482	40,454	45,214
$u_{\text{Na}, \text{NO}_3} \cdot 10^4$	3,56 3,65	3,66	3,68	3,69 3,77	3,92 3,99 3,96 4,06	4,23	4,68
$u_{\text{Tl}, \text{NO}_3} \cdot 10^4$	3,65	3,68	3,65	3,65	3,77 3,73	3,92 3,85 3,82 3,91	3,95 4,04 3,85

\* Data taken from ref. 7.

Table 1. Equivalent conductivity and internal mobilities at 316 °C.

<sup>20</sup> A. KLEMM, Molten Salt Chemistry, Ed. by M. BLANDER, John Wiley & Sons, New York 1964, p. 537.

<sup>21</sup> F. LANTELME and M. CHEMLA, Bull. Soc. Chim. France **1963**, 2200.

<sup>22</sup> F. LANTELME and M. CHEMLA, Electrochim. Acta **10**, 663 [1965].

<sup>23</sup> F. LANTELME and M. CHEMLA, Electrochim. Acta **11**, 1023 [1966].

<sup>24</sup> A. KVIST, Z. Naturforsch. **21 a**, 1601 [1966].

mobility,  $u_{\text{Na}, X}$ , in the range  $0.5 < X_{\text{Na}} < 1$ , may be related to the decrease of the function  $P$ , by means of a relationship of the type

$$u_{\text{Na}, X} = u_{\text{Na}, 1} - (u_{\text{Na}, 1} - u_{\text{Na}, 0.5}) P$$

where  $u_{\text{Na}, 1}$  is the sodium mobility in pure  $\text{NaNO}_3$  and  $u_{\text{Na}, 0.5}$  the mobility in the equimolecular mixture.

The sodium mobility and the fluidity  $\Phi = 1/\eta$  ( $\eta$  = viscosity) vary in an opposite way (see Figs. 3 and 4).

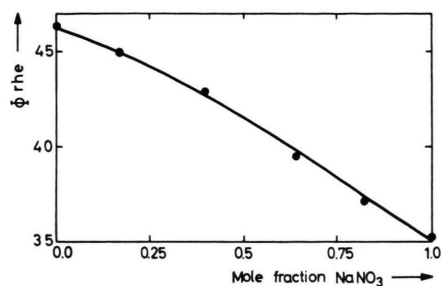


Fig. 4. Fluidity isotherm of the (Na—Tl)  $\text{NO}_3$  system at 316 °C.

#### Tracer diffusion coefficients

The cationic tracer diffusion coefficients of the (Na—Tl)  $\text{NO}_3$  system at 316 °C are reported in Table 2. In Fig. 5 the diffusion isotherms at this temperature in the whole composition range and at 219 °C in the range from 0.0 to 0.3 mole fraction of  $\text{NaNO}_3$  are presented.

Table 3 lists some diffusional results on pure  $\text{TlNO}_3$  and on a mixture containing 20%  $\text{NaNO}_3$  at

$X_{\text{Na}}$	0,00	0,20	0,40	0,44	0,50	0,73	1,00
$D_{\text{Na}} \cdot 10^5$	1,98 1,92 1,78	2,13	2,11 2,02	2,03	2,17	2,02	2,15 2,04 1,98
$D_{\text{Tl}} \cdot 10^5$	1,64 1,64 1,62	1,74	1,81	—	1,86	1,85	1,85 1,81

Table 2. Tracer diffusion coefficients at 316 °C.

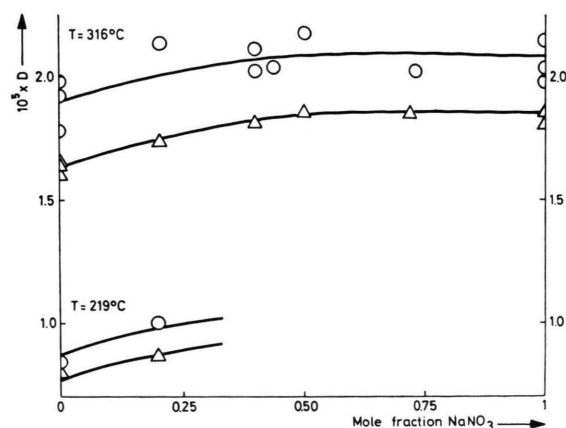


Fig. 5. Cationic tracer-diffusion coefficients of the (NaTl)  $\text{NO}_3$  system at 316 °C and at 219 °C.  $\circ$  = Na,  $\triangle$  = Tl.

different temperatures. Fig. 6 presents these results in the form of *ARRHENIUS* plots.

The possibility of comparing the obtained diffusion coefficients with those obtained by other workers is limited to the  $\text{Na}^{22}$  diffusion in pure  $\text{NaNO}_3$ . In the range of our measurements (316 ÷ 358 °C), the obtained values show deviations from literature data<sup>26-29</sup> not larger than 15% (Fig. 7, Table 4).

$T$ °C	214,5	219,0	225,7	233,0	267,0	278,2	282,0	316,0
$X_{\text{Na}} = 0,00$								
$D_{\text{Na}} \cdot 10^5$	0,86	0,87	—	—	—	1,44	1,43	1,98 1,92 1,78
$D_{\text{Tl}} \cdot 10^5$	0,76	0,80	—	—	—	—	1,36	1,64 1,64 1,62
$X_{\text{Na}} = 0,20$								
$D_{\text{Na}} \cdot 10^5$	—	1,00	1,00 1,04 1,04	—	—	—	—	2,13
$D_{\text{Tl}} \cdot 10^5$	—	—	0,91 0,90 0,89	0,94	1,22	—	—	1,74

Table 3. Tracer diffusion coefficients at different temperatures.

<sup>25</sup> J. C. SLATER, Introduction to the Chemical Physics, Mc-Graw-Hill Co., New York 1939, p. 275.

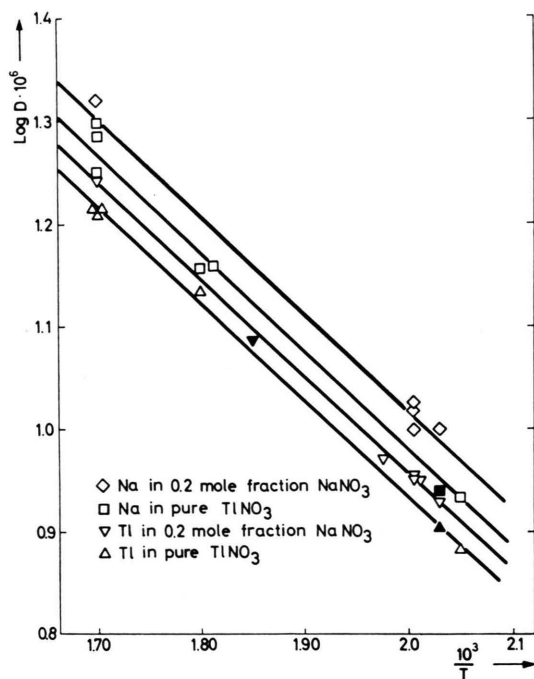


Fig. 6. ARRHENIUS plots of the cationic tracer-diffusion coefficients in pure  $\text{TiNO}_3$  and in a mixture 0.2 mole fraction of  $\text{NaNO}_3$ . Open points — zone diffusion on thin layers of alumina powder<sup>14</sup>. Full points — zone diffusion on thin layers of fritted alumina<sup>15</sup>.

The trend of the diffusion isotherms (Fig. 5), is similar to that in  $(\text{Na}-\text{K})\text{NO}_3$ <sup>11, 27</sup>, and in  $(\text{Li}-\text{K})\text{NO}_3$ <sup>23</sup>. The small positive deviations shown in our case are present also in  $(\text{Li}-\text{K})\text{NO}_3$ <sup>23</sup>, and, more markedly, in  $(\text{Li}-\text{Na})\text{CO}_3$ <sup>30</sup>.

$T$ °C	325	349	358
$D_{\text{Na}} \cdot 10^5$	2,22	2,73 2,69	2,90 2,70

Table 4. Tracer diffusion coefficients of Na in  $\text{NaNO}_3$  at different temperatures.

From the ARRHENIUS plots of Fig. 6, it can be observed that the tracer diffusion activation energies of both cations are nearly equal ( $4.3 \div 4.4$  kcal/mole) in pure  $\text{TiNO}_3$  as well as in a mixture containing 20%  $\text{NaNO}_3$ . A similar situation was found

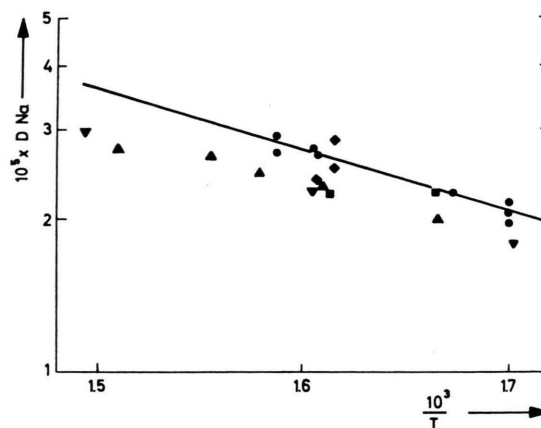


Fig. 7. Sodium tracer diffusion coefficients in pure molten Na nitrate as a function of the temperature.  $\blacktriangle$  Ref. 28,  $\blacktriangledown$  Ref. 27,  $\blacklozenge$  Ref. 28,  $\blacksquare$  Ref. 29,  $\bullet$  This work.

for the system  $(\text{Na}-\text{K})\text{NO}_3$  by LANTELME and CHEMLA<sup>27</sup>.

Activation energies for interdiffusion of a number of cations and anions in nitrate environments [ $(\text{Na}-\text{K})\text{NO}_3$  and  $(\text{Li}-\text{Na}-\text{K})\text{NO}_3$  eutectic], measured polarographically by FRANCINI and MARTINI<sup>31, 32</sup>, were found equal among them. For Na diffusion in pure  $\text{NaNO}_3$  the calculated activation energy is 5.3 kcal/mole. The corresponding value of VAN ARTSDALEN<sup>26</sup> is 4.97 kcal/mole. It has been observed<sup>5</sup> that the polarization of the common anion, which causes an increased (or reduced) hindrance in the relative cation-anion motion, should have a smaller influence on diffusion than on electromigration. The present results are in agreement with these arguments.

Tracer diffusion coefficients have been usually correlated to the fluidity  $\Phi$  through the SUTHERLAND-(STOKES)-EINSTEIN relationship:

$$D = (K/a) (\Phi T / r_{\text{Me}}') \quad (7)$$

where  $r_{\text{Me}}'$  is the radius of the diffusing particle and the numerical factor  $a$  is  $6\pi$  for large diffusing particles, and  $4\pi$  for small ones, in the classical formulation, or even smaller according to other theories<sup>33, 34</sup>.

<sup>26</sup> S. DWORKIN, R. B. ESCUE, and E. R. VAN ARTSDALEN, *J. Phys. Chem.* **64**, 872 [1960].

<sup>27</sup> F. LANTELME and M. CHEMLA, *Bull. Soc. Chim. France* **1963**, 969.

<sup>28</sup> S. DJORDJEVIC and G. J. HILLS, *Trans. Faraday Soc.* **56**, 269 [1960].

<sup>29</sup> C. A. ANGELL and J. W. TOMLINSON, *Discussions Faraday Soc.* **32**, 237 [1961].

<sup>30</sup> P. L. SPEDDING and R. MILLS, *J. Electrochem. Soc.* **113**, 599 [1966].

<sup>31</sup> M. FRANCINI and S. MARTINI, *EUR Report 1908 e* [1964].

<sup>32</sup> M. FRANCINI, S. MARTINI, and C. MONFRINI, *Elettrochimica Metallorum*, in press.

<sup>33</sup> H. J. TYRRELL, *Diffusion and Heat Flow in Liquids*, Butterworths, London 1961, p. 126.

<sup>34</sup> W. SUTHERLAND, *Phil. Mag.* **9**, 781 [1905].



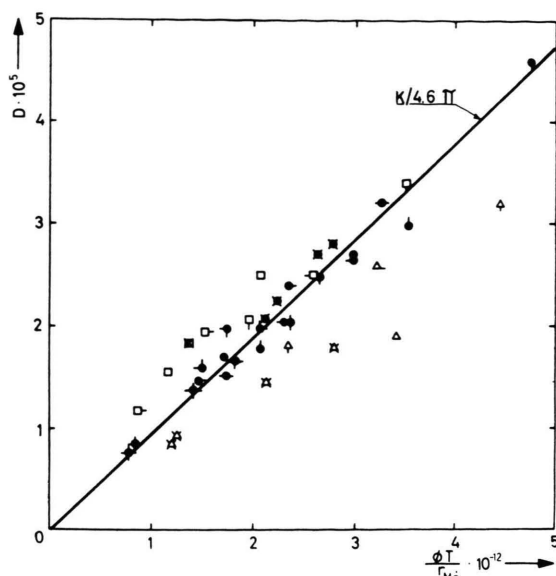


Fig. 8. Tracer diffusion of univalent cations,  $Me'$ , in molten univalent nitrate,  $MeNO_3$ , as a function of  $\Phi T / r_{Me'}$  [Eq. (7)]. Circular full points:  $r_{Me'} = r_{Me}$ , Square open points:  $r_{Me'} > r_{Me}$ , Triangle open points:  $r_{Me'} < r_{Me}$ , GOLDSCHMIDT ionic radii,  $r_{Me'}$  and  $r_{Me}$  were used<sup>35</sup>.

$r_{Me'} = r_{Me}$		
●	Li in $LiNO_3$	diffusion data from ref. <sup>36</sup>
●	Li in $LiNO_3$	diffusion data from ref. <sup>26</sup>
●	Na in $NaNO_3$	diffusion data from ref. <sup>11</sup>
●	Na in $NaNO_3$	diffusion data from ref. <sup>26</sup>
●	Na in $NaNO_3$	diffusion data from this work
●	Na in $NaNO_3$	diffusion data from ref. <sup>27</sup>
●	K in $KNO_3$	diffusion data from ref. <sup>11</sup>
●	K in $KNO_3$	diffusion data from ref. <sup>27</sup>
●	K in $KNO_3$	diffusion data from ref. <sup>26</sup>
●	Cs in $CsNO_3$	diffusion data from ref. <sup>26</sup>
●	Tl in $TlNO_3$	diffusion data from this work
●	Ag in $AgNO_3$	diffusion data from ref. <sup>26</sup>
$r_{Me'} > r_{Me}$		
□	Na in $LiNO_3$	diffusion data from ref. <sup>36</sup>
□	K in $LiNO_3$	diffusion data from ref. <sup>36</sup>
□	K in $NaNO_3$	diffusion data from ref. <sup>11</sup>
□	K in $NaNO_3$	diffusion data from ref. <sup>27</sup>
⋈	Tl in $NaNO_3$	diffusion data from this work
$r_{Me'} < r_{Me}$		
△	Li in $KNO_3$	diffusion data from ref. <sup>23</sup>
△	Na in $KNO_3$	diffusion data from ref. <sup>27</sup>
△	Na in $KNO_3$	diffusion data from ref. <sup>11</sup>
⋈	Na in $TlNO_3$	diffusion data from this work

Viscosity data of  $LiNO_3$  and of  $CsNO_3$  were taken from ref. <sup>37</sup>. Viscosity data of  $NaNO_3$  and  $TlNO_3$  were taken from ref. <sup>12</sup>. Viscosity data of  $KNO_3$  and  $AgNO_3$  were taken from ref. <sup>38</sup>.

Fig. 8 ( $D$  vs.  $\Phi T / r_{Me'}$ ) shows that Eq. (7) accounts fairly well for the diffusion of Na in  $NaNO_3$  and of Tl in  $TlNO_3$  as well as for cation diffusion in other pure univalent nitrates, if an  $\alpha$  value of about  $4.6\pi$  is chosen. The tracer diffusion coefficients of foreign ions deviate the more from this behaviour the larger the difference in size between foreign and proper cation. The diffusion coefficients of foreign ions smaller (larger) than the proper ions are below (above), the straight line in Fig. 8 ( $\alpha$  values of about  $7\pi$  for Na in  $TlNO_3$  and Li in  $KNO_3$ ;  $\alpha$  values of about  $3.5\pi$  for Tl in  $NaNO_3$  and K in  $LiNO_3$ ).

The dependence on composition of the tracer diffusion coefficients of Na and Tl (Fig. 5), as well as that of mobilities, differs in sign from that of the fluidity (Fig. 4).

From RAMAN spectroscopy evidences, in pure molten univalent nitrates, JANZ<sup>39</sup> pointed out that the metal ion-nitrate interaction, may cause "the time of residence of the cation near the anion to be long compared with the time of the molecular vibration". It can be expected that in mixtures this effect for a given cation would be enhanced or hindered according to the polarization direction. The stand of a cation near the anion will cause a sort of "co-operative act"<sup>30</sup> during the diffusion, which may explain the approximate constance of the diffusion activation energy for all the ions in the same melt, irrespective of the different  $\alpha$  values.

Interactions of this type are of major importance for electrical mobilities, the effect of the polarization being in this case magnified because the cations and anions travel in opposite directions.

Finally one can observe that the transport behaviour of  $(Na-Tl)NO_3$  is rather similar to that of alkali-nitrate binary systems<sup>7</sup>. It seems therefore that the variation of the LONDON dispersion forces between the cations in mixtures which have some influence on the equilibrium properties of this system<sup>40</sup> are not so markedly significant in irreversible processes.

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<sup>35</sup> Metal Reference Book, Butterworths, London 1962, p. 136.

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