High-Dilution Diffusion of K^+, Rb^+, Cs^+, and Tl^+ in the Molten System (Li-K)NO_3 Studied by Wave-Front-Shearing Interferometry

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The high-dilution diffusion coefficients of K^+, Rb^+, Cs^+, and Tl^+ in molten $LiNO_3-KNO_3$ mixtures are measured over a wide range of temperatures and concentrations by means of wave-front-shearing interferometry. A slightly positive deviation from linearity is found for the concentration dependence of the diffusion coefficient of K^+, Rb^+, and Tl^+, while no deviation is found for Cs^+ within the experimental error. This is qualitatively discussed from the viewpoint of the ionic radii, the free space in the solvent, and the interaction between the diffusing and the surrounding ions.

Introduction

Wave-front-shearing interferometry has first been applied Gustafsson et al. [1] to the measurement of high-dilution diffusion coefficients of molten salts. This method was remarkably successful [2 – 4] by the use of "light ports" through the wall of the electric furnace, the inside of the light ports being evacuated (~100 Pa). The light could thus travel without being disturbed by the temperature gradient along the wall of the furnace, and this made it possible to obtain reliable data even at high temperatures. The main advantages of this method in comparison with the capillary method are: (a) the duration of one run of diffusion experiments is relatively short (~1 hr), (b) the interferograms can be observed continuously through a camera and horizontality of the fringes assures absence of convection, and (c) the values of D can be calculated in principle from each pair of fringes for interferograms taken at any time, and therefore D can be determined from many data by statistical treatment.

In the present study this method is applied to the measurement of high-dilution diffusion coefficients of K^+, Rb^+, Cs^+, and Tl^+ in (Li-K)NO_3 mixtures. Since Lantelme and Chemla have already measured tracer diffusion coefficients of Li^+, Na^+, and K^+ in the same solvent with a "diffusion out of a capillary" method [5], our results can be compared with theirs.

(Li-K)NO_3 was chosen as the solvent system because its properties can be varied continuously by changing its composition.

Experimental

The principle of wave-front-shearing interferometry and its application to the measurement of diffusion coefficients of molten salts have already been described in detail [1, 6].

The optical system of the interferometer constructed in our laboratory was similar to that employed for the measurement of diffusion coefficients of some molten nitrates by Gustafsson et al. [2]. A diffusion cell with a 22×3 mm slot was closed tightly from both sides with quartz window plates (flatness better than $\lambda/5$, parallelism within 2″ of arc). The cell was placed in an electric furnace of large heat capacity. In order to keep the temperature of the diffusion cell as constant as possible, it was placed inside a small stainless steel cover in the furnace, dried argon flowing outside the cover. The variation of the temperature of the diffusion cell was no more than 0.5 °C during a run. Light ports as used in [2 – 4] were in the wall of the furnace.

The chemicals used were of analytical reagent grade. The mixtures of $LiNO_3$ and KNO_3 were dried at 120 °C for several hours, once melted at 300 °C and stored in a desiccator. The concentration of the solvent was checked by flame spectrophotometry. A small amount of the solvent salt (~3 g) was melted in a glass tube with a filter at the bottom and introduced into the diffusion cell through the filter. After the image of the slot became clear (~3 hr), a small crystal of solute was dropped into the cell from a height of about 1 m. The crystals were prepared by melting the solute material in a nitrogen

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atmosphere and allowing it to cool. The initial condition of the bottom layer in this method has already been discussed [7]. After the image of the shear became clearly detectable, the interferograms were recorded with appropriate intervals.

Results and Discussion

In the present optical interferometry, high-dilution diffusion coefficients D are calculated from the refractive index variation caused by the distribution of the concentration of the solute material. For this reason, some difference in the refractive indices between solute and solvent is indispensable. The refractive indices of molten alkali nitrates have been measured accurately with a modified thermooptic technique by Karawacki [8]. The values of the refractive indices μ and the molar refractivities A calculated from the Lorentz-Lorenz formula (Eq. (1)) at 350 °C ($\lambda = 632.8$ nm) are tabulated in Table 1 together with their molar weight M and the density ϱ [9]:

$$A = (M/\varrho)(\mu^2 - 1)/(\mu^2 + 2). \quad (1)$$

Application of (1) to the mixture gives [10]

$$(\mu^2 - 1)/(\mu^2 + 2) = p_1 \varrho_1 A_1/M_1 + (1 - p_1)\varrho_m A_m/M_m, \quad (2)$$

where

$$\varrho_m = (p_2 \varrho_2 + p_3 \varrho_3)/(1 - p_1), \quad (3)$$

$$M_m = (p_2 M_2 + p_3 M_3)/(1 - p_1). \quad (4)$$

Here, the subscript 1 denotes the solute and 2 and 3 stand for the components of the solvent. The subscript m means the solvent mixture and the mole fractions obey the relation $p_1 + p_2 + p_3 = 1$. Differentiation of the refractive index in (2) with respect to the concentration of the solute C ($= p_1 \varrho_1$) gives

$$(\partial\mu/\partial C) = (3/2)(A_1/M_1 - \varrho_m A_m/(\varrho_1 M_m)) \cdot (1 - p_1 \varrho_1 A_1/M_1 - (1 - p_1)\varrho_m A_m/M_m)^{-3/2} \cdot (1 + 2 p_1 \varrho_1 A_1/M_1 + 2(1 - p_1)\varrho_m A_m/M_m)^{-1/2}, \quad (5)$$

and on neglection of p_1

$$(\partial\mu/\partial C) = (3/2)(A_1/M_1 - \varrho_m A_m/(\varrho_1 M_m)) \cdot (1 - \varrho_m A_m/M_m)^{-3/2}(1 + 2\varrho_m A_m/M_m)^{-1/2}. \quad (6)$$

Alternatively, $(\partial\mu/\partial C)$ can be obtained from [1]

$$(\partial\mu/\partial C) = k\lambda(\pi D t)^{1/2}(S l)^{-1} \cdot \{\exp(-(x_j + b/2)^2/4Dt) - \exp(-(x_j - b/2)^2/4Dt) - \exp(-(x_{j+k} + b/2)^2/4Dt) + \exp(-(x_{j+k} - b/2)^2/4Dt)\}^{-1}, \quad (7)$$

where S is the total amount of the solute divided by the bottom area, k the number of the fringes counted from the fringe of level x_j, l the geometric length of the melt along the light path, and b the shear produced by the polariscope of the interferometer. In Table 2 the calculated values for $(\partial\mu/\partial C)$ of KNO_3, $RbNO_3$, and $CsNO_3$ from Eq. (6) at 350 °C are given, and those for $TlNO_3$ calculated from Eq. (7) are also tabulated.

The number of fringes n_f is related to the concentration by [11]

$$n_f \approx -l(\partial\mu/\partial C)(C/\lambda). \quad (8)$$

From Eq. (8), the lowest $\partial\mu/\partial C$ for obtaining a suitable number of fringes is estimated to be $\approx 10^{-2}$ cm³/mol, as long as the length l is not extended. As is seen from Table 2, $\partial\mu/\partial C$ is very small for the measurement of K^+ in

Table 1. Molar refractivities of molten alkali nitrates at 350 °C (λ = 632.8 nm).

Salt	Molar weight [9] M/g·mol⁻¹	Density [9] ϱ/g·cm⁻³	Refractive index [8]	Molar refractivity A/cm³·mol⁻¹
$LiNO_3$	68.95	1.728	1.4547	10.82
$NaNO_3$	85.01	1.875	1.4187	11.44
KNO_3	101.10	1.861	1.4093	13.44
$RbNO_3$	147.49	2.443	1.4165	15.97
$CsNO_3$	194.92	2.894 *	1.4409 *	17.78

* extrapolated value.

Table 2. Concentration dependence of the refractive index $(\partial\mu/\partial C)$ in the system (Li-K)NO_3 at 350 °C. The values of $(\partial\mu/\partial C)$ are given in cm³/mol, and those in parentheses are given in cm³/g.

Diffusing Ion	Concentration of $LiNO_3$ (mol%) 100	75	51	25	0
K^+	−2.507 (−0.0248)	−1.233 (−0.0122)	−0.475 (−0.0047)	−0.051 (−0.0005)	–
Rb^+	−2.330 (−0.0158)	−0.929 (−0.0063)	−0.088 (−0.0006)	0.383 (0.0026)	0.442 (0.0030)
Cs^+	−0.936 (−0.0048)	0.604 (0.0031)	1.540 (0.0079)	2.047 (0.0105)	2.105 (0.0108)
Tl^+	11.455 (0.043)	12.521 (0.047)	13.054 (0.049)	13.586 (0.051)	13.586 (0.051)

$LiNO_3$(25 mol%) − KNO_3(75 mol%) and of Rb^+ in $LiNO_3$(51 mol%) − KNO_3(49% mol%). Since $\partial\mu/\partial C$ for $TlNO_3$ is large as compared with that for alkali nitrates, more reliable data could be obtained. The refractive index of $TlNO_3$ at 350 °C is estimated to be about 1.67 from the data in Table 2 by use of Eqs. (6) and (1), which is in good agreement with that directly measured [12].

The high-dilution diffusion coefficients of K^+ in pure $LiNO_3$ and of Rb^+ and Cs^+ in pure $LiNO_3$ and KNO_3 were also remeasured at some temperatures in order to assure that there is virtually no systematic difference between the data obtained by the interferometer used by Gustafsson et al. [2] and by ours. The present data are given in Table 3.

The logarithms of D_K, D_{Rb}, D_{Cs}, and D_{Tl} in

$LiNO_3$(75 mol%) − KNO_3(25 mol%),
$LiNO_3$(51 mol%) − KNO_3(49 mol%),
and $LiNO_3$(25 mol%) − KNO_3(75 mol%)

mixtures are plotted against the reciprocal of the absolute temperature in Figs. 1, 2, and 3, respectively. The results for the tracer diffusion of Li^+, Na^+, and

Table 3. High-dilution diffusion coefficients of K^+ in molten $LiNO_3$ and those of Rb^+ and Cs^+ in molten $LiNO_3$ and KNO_3.

Diffusing Ion	in $LiNO_3$			in KNO_3		
	T (°C)	$\langle C\rangle$ [a] (mol%)	$D\times10^9$ [b] ($m^2\,s^{-1}$)	T (°C)	$\langle C\rangle$ [a] (mol%)	$D\times10^9$ [b] ($m^2\,s^{-1}$)
K^+	332	0.48	1.85±0.03			
	346	0.52	2.01±0.05			
	349	0.60	1.95±0.06			
	353	0.55	2.00±0.03			
	364	0.63	2.15±0.08			
	370	0.64	2.49±0.08			
Rb^+	332	0.55	1.36±0.06	338	1.77	1.22±0.11
	349	0.78	1.52±0.08	340	1.50	1.22±0.08
	364	0.64	1.68±0.08	348	1.66	1.25±0.08
				348	1.74	1.38±0.04
				349	1.95	1.29±0.07
Cs^+	332	1.81	1.40±0.11	338	0.77	1.15±0.02
	349	1.34	1.50±0.14	348	0.85	1.17±0.03
	364	2.01	1.79±0.11	350	0.73	1.16±0.04
				356	0.89	1.30±0.06
				360	0.93	1.29±0.09

[a] This is the concentration at $\sqrt{2\,D\,t}$, i.e. the inflexion point of the concentration curve, t being set as the earliest time when the interferograms are read for the calculation of the diffusion coefficients.

[b] The sign ± represents the standard deviation of errors.

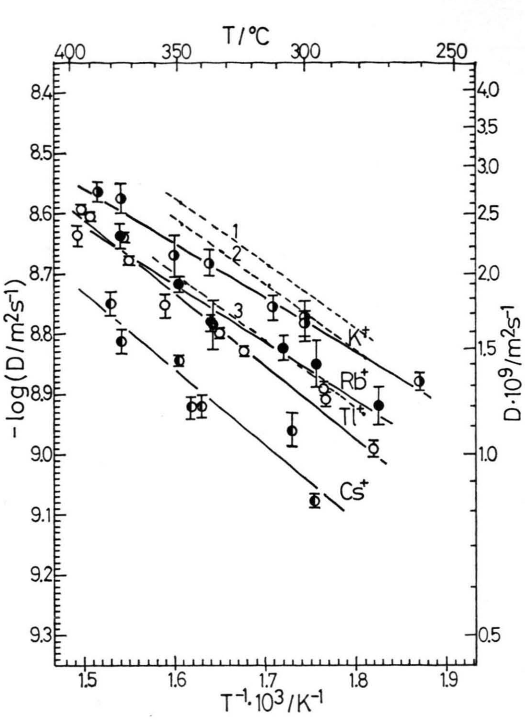

Fig. 1. High-dilution diffusion coefficients of alkali ions and Tl^+ in molten $LiNO_3$ (75 mol%) − KNO_3 (25 mol%) mixture. ◑: K^+, ●: Rb^+, ◐: Cs^+, ○: Tl^+; the dashed lines: tracer diffusion coefficients [5]. 1-Li^+, 2-Na^+, 3-K^+.

K^+ by Lantelme and Chemla [5] are also shown in the figures for comparison.

Arrhenius type equations are assumed for D, and D_∞ and E for $D = D_\infty \times \exp(-E/R\,T)$ are calculated with a least squares fit of non-linear form. The results are tabulated in Table 4, in which D_∞ and E for D_{Tl} in pure $LiNO_3$ and KNO_3 are taken from Refs. [3] and [4], respectively, and those for D_K in pure KNO_3 from Ref. [13]. Those for D_K in pure $LiNO_3$ and D_{Rb} and D_{Cs} in pure $LiNO_3$ and KNO_3 are recalculated, based on the data of Gustafsson et al. [2] and ours.

Our values for D_K are about 10% higher than those for the corresponding tracer diffusion coefficients of Lantelme and Chemla. It could not be clearly judged whether this difference arises only from the combined experimental errors of both experiments or if it is caused by the concentration gradient of the solute in the present method. However, there seems to be no systematic difference between the values of D measured with Lantelme and Chemla's method and the present one. (For example, $D_{Na} \times 10^9/(m^2\,s^{-1})$ in nearly pure $LiNO_3$ at 350 °C:

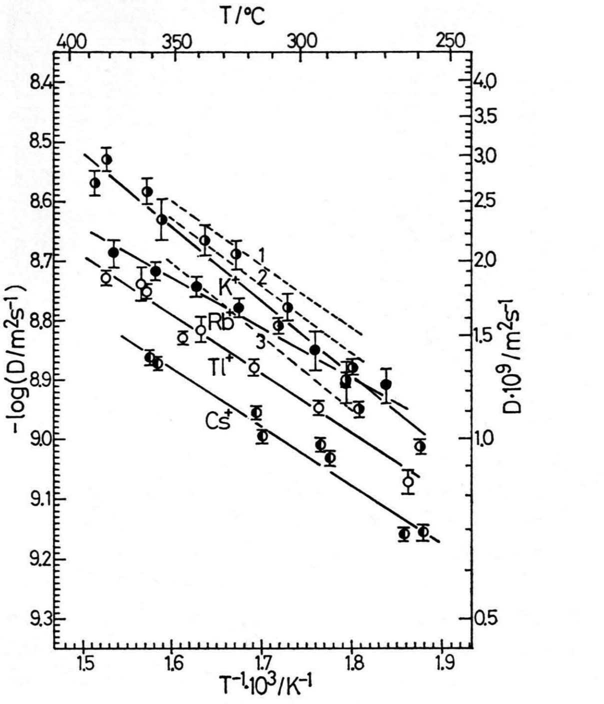

Fig. 2. High-dilution diffusion coefficients of alkali ions and Tl^+ in molten $LiNO_3$ (51 mol%) — KNO_3 (49 mol%) mixture. ◐ : K^+, ● : Rb^+, ◐ : Cs^+, ○ : Tl^+; the dashed lines: tracer diffusion coefficients [5]. 1-Li^+, 2-Na^+, 3-K^+.

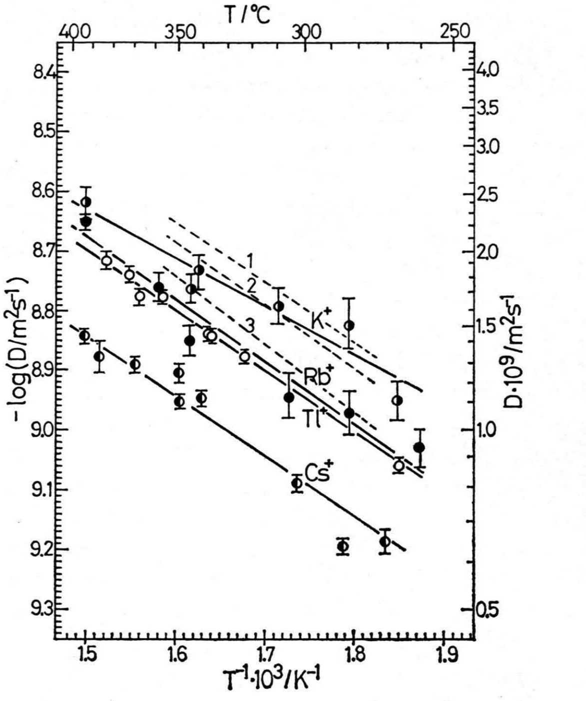

Fig. 3. High-dilution diffusion coefficients of alkali ions and Tl^+ in molten $LiNO_3$ (25 mol%) — KNO_3 (75 mol%) mixture. ◐ : K^+, ● : Rb^+, ◐ : Cs^+, ○ : Tl^+; the dashed lines: tracer diffusion coefficients [5]. 1-Li^+, 2-Na^+, 3-K^+.

2.48 in the former [5] and 2.08 in the latter [2], while in nearly pure KNO_3: 1.82 in the former [5] and 1.90 in the latter [2].) The high values of D_{Rb} in $LiNO_3$(51 mol%) – KNO_3(49 mol%) in comparison with D_{Tl} might be caused by the high concentration of the solute (5 – 8 mol%), which is inevitable for obtaining a suitable number of fringes, since $(\partial\mu/\partial C)$ of $RbNO_3$ is small in a solvent of this concentration.

The values of D_{Tl} seem to be lower than those of D_{Rb} at relatively low temperature. This trend has clearly been found in $LiNO_3$ [3], in which the average distance between Rb^+ or Tl^+ and the nearest neighbouring NO_3^- would be rather short, since the free space is small. In the solid state the well of the pair potential between Tl^+ and Cl^- [14] is somewhat deeper at the minimum than that between Rb^+ and Cl^- [15], the difference at the minimum being 4×10^{-20} J, although it is quite the same at larger distance (>0.46 nm). In view of this fact, Tl^+ is expected to be more attracted by NO_3^- than Rb^+. This may be the reason why D_{Tl} is lower than D_{Rb}

Diffusing Ion	Concentration of $LiNO_3$ (mol%) 100	75	51	25	0
K^+	2.26±0.25 (1.67)	1.80±0.10 (0.70)	2.36±0.18 (2.11)	1.52±0.20 (0.38)	2.30 (1.32)
Rb^+	2.05±0.11 (0.85)	1.87±0.19 (0.69)	1.46±0.08 (0.31)	2.01±0.25 (0.78)	1.97±0.13 (0.65)
Cs^+	2.07±0.15 (0.86)	2.29±0.40 (1.12)	1.77±0.13 (0.40)	2.00±0.18 (0.54)	2.18±0.15 (0.73)
Tl^+	2.84±0.14 (3.95)	2.34±0.17 (1.66)	1.97±0.13 (0.72)	2.00±0.08 (0.70)	1.88±0.14 (0.54)

Table 4. Parameters of Arrhenius type equation $D_\infty \times \exp(-E/RT)$. Arrhenius coefficients $E \cdot 10^{-4}$ are given in J/K·mol and pre-exponential constants $D_\infty \cdot 10^7$ in parentheses are given in m^2/s.

at lower temperatures. At higher temperatures, D_{Tl} and D_{Rb} are nearly equal.

It has been found that D_{Tl} and D_{Rb} are nearly equal in pure $NaNO_3$, KNO_3, and $RbNO_3$ over a wide range of temperatures [4], and in the system $(Rb\text{-}Tl)NO_3$ at 320 °C [16]. This can be explained on the assumption that under these conditions the pair potentials for $Rb^+\text{-}NO_3^-$ and $Tl^+\text{-}NO_3^-$ would be quite the same.

The isotherms of D_K, D_{Rb}, D_{Cs}, and D_{Tl} at 350 °C are shown in Figure 4. The results for D_{Li}, D_{Na}, and D_K with a "diffusion out of a capillary" method [5] and for D_{Ag} with polarography and chronopotentiometry [17] are also shown in the figure. Although the present data of D_K are about 10% higher than those with the capillary method, the tendency of the concentration dependence is nearly the same in both cases. As can be seen from Fig. 5, the diffusion coefficients of these cations in the system $(Li\text{-}K)NO_3$ at 350 °C become smaller in the following order:

$D_{Li} > D_{Na} > D_K$ (tracer diffusion),
$D_K > D_{Rb} \geqq D_{Tl} > D_{Cs}$ (high-dilution diffusion).

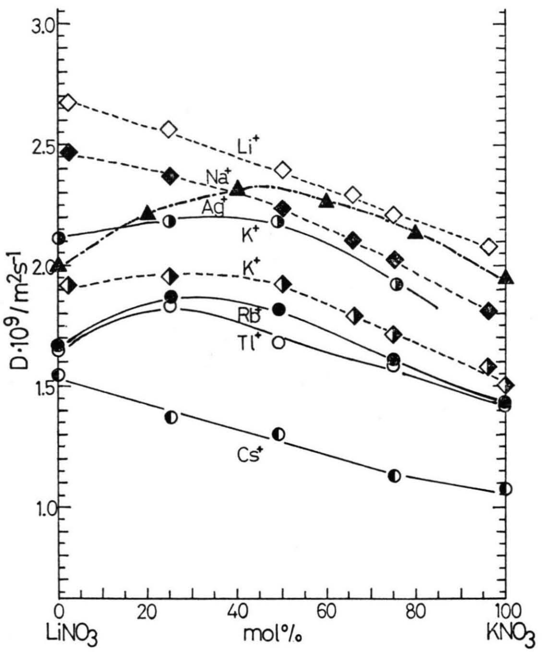

Fig. 4. Isotherms of the diffusion coefficients of alkali ions, Tl^+, and Ag^+ in the molten $(Li\text{-}K)NO_3$ system at 350 °C. ◑: K^+, ●: Rb^+, ◐: Cs^+, ○: Tl^+, ——— present work. ◇: Li^+, ◆: Na^+, ⬗: K^+, – – – tracer diffusion [5]. ▲: Ag^+, –·–·– polarographic and chronopotentiometric diffusion [17].

The finding that $D_{Tl} > D_{Cs}$ seems to show that the ionic radius of the solutes is a more significant factor than the mass for a diffusion process.

The values of D_{Li}, D_{Na}, and D_{Cs} are almost linearly dependent on the concentration of the solvent. D_K, D_{Rb}, D_{Ag}, and D_{Tl}, however, seem to deviate positively from linearity. For interpreting this difference, two effects are taken into consideration. One is the interaction of the diffusing ion with the solvent ions and the other is the free space in the solvent. The diffusive motion of the solvent ions will become more active with increasing concentration of $LiNO_3$, since the size and the mass of Li^+ are small. On the other hand, the volume of the solvent will decrease with increasing concentration of $LiNO_3$, because the free space is supposed to be proportional to the molar volume which is linearly dependent on the concentration.

It is expected that the effect of the free space would not substantially influence the diffusive motion of such small solute ions as Li^+ and Na^+. Thus, D_{Li} and D_{Na} would become larger with concentration of $LiNO_3$ due to the effect of the motion of the solvent ions. Meanwhile, for the motion of somewhat larger ions such as K^+, Rb^+, and Tl^+, the influence of the free space would become effective in the region rich in $LiNO_3$. Also in the data on the internal electrical mobilities of Rb^+ and Tl^+ in the respective systems $(Li\text{-}Rb)NO_3$ [18] and $(Li\text{-}Tl)NO_3$ [19], the effect of the free space is evident at high concentration of $LiNO_3$. Thus, it is expected that D_K, D_{Rb}, and D_{Tl} would increase first on adding $LiNO_3$ to KNO_3 and then decrease in the region rich in $LiNO_3$.

As for Cs^+, the free space formed even by pure KNO_3 at this temperature may be so small in comparison with its size that an increase of concentration of $LiNO_3$ would not contribute to an effective decrease of the free space for Cs^+; therefore, D_{Cs} would increase almost linearly with increasing concentration of $LiNO_3$ apparently only by the effect of increasing motion of the solvent ions.

With respect to Ag^+, the value of D_{Ag} in $LiNO_3$ measured with polarography [17] is appreciably lower than that of D_{Na} measured with the tracer diffusion method [5], while the former seems to be in agreement with that of D_{Na} measured with the present method [2]; however, the data of D_{Na} with the present method are few in number. Further careful measurements D_{Ag} and D_{Na} in the system $(Li\text{-}K)NO_3$ with the same method would be required to judge whether D_{Ag} and D_{Na} are really different in this solvent and to discuss the reason for the difference.

Thus, the diffusion coefficients of the alkali ions and Tl^+ in the system (Li-K)NO_3 measured in the present study could qualitatively be explained on the assumption that the size of the diffusing ions as compared with that of the free space and the pair potential between cation and anion would be the main factors which govern a diffusion process as well as an electromigration process [18, 19]. Tracer diffusion coefficients of Rb^+ and Cs^+ have been measured in the systems (Li-Na)NO_3, (Li-K)NO_3, (Li-Rb)NO_3, and (Li-Cs)NO_3 with a paper strip method [20]; the results can also be explained qualitatively on the same assumption.

[1] S. E. Gustafsson, L.-E. Wallin, and T. E. G. Arvidsson, Z. Naturforsch. **23 a**, 1261 (1968).
[2] T. E. G. Arvidsson, S.-Å. Afsenius, and S. E. Gustafsson, J. Chem. Phys. **53**, 2621 (1970).
[3] I. Okada and S. E. Gustafsson, Electrochim. Acta **18**, 275 (1973).
[4] I. Okada and S. E. Gustafsson, Z. Naturforsch. **33 a**, 447 (1978).
[5] F. Lantelme and M. Chemla, C. R. Acad. Sci. Paris **258**, 1484 (1964).
[6] O. Bryngdahl, Ark. Fys. **21**, 289 (1962).
[7] L.-E. Wallin and S. E. Gustafsson, Z. Naturforsch. **24 a**, 436 (1969).
[8] E. Karawacki, Thesis, Göteborg 1977.
[9] G. J. Janz, Molten Salts Handbook, Academic Press, New York 1967, p. 42.
[10] M. Born and E. Wolf, Principles of Optics, Pergamon Press, Oxford 1964, p. 89.
[11] O. Odawara, I. Okada, and K. Kawamura, J. Chem. Eng. Data **22**, 222 (1977).
[12] S. S. Batsanov and Yu. I. Vesnin, Zh. Strukt. Khim. **4**, 98 (1962).
[13] A. S. Dworkin, R. B. Escue, and E. R. Van Artsdalen, J. Phys. Chem. **64**, 872 (1960).
[14] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).
[15] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).
[16] S. Zuca and M. Constantinescu, Z. Naturforsch. **32 a**, 1435 (1977).
[17] K. Kawamura, Denki Kagaku **38**, 12 (1970).
[18] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34 a**, 498 (1979).
[19] K. Kawamura, I. Okada, and O. Odawara, Z. Naturforsch. **30 a**, 69 (1975).
[20] O. Odawara, J. C. T. Kwak, and J. A. A. Ketelaar, to be published.