High-Dilution Diffusion of Tl^+ in Molten $NaNO_3$, KNO_3 and $RbNO_3$ Studied by Wave-Front-Shearing Interferometry

Isao Okada * and Silas E. Gustafsson

Department of Physics, Chalmers University of Technology, Göteborg, Sweden

Z. Naturforsch. **33 a**, 447 – 454 (1978) ; received January 6, 1978

The high-dilution diffusion of Tl^+ in molten $NaNO_3$, KNO_3 and $RbNO_3$ has been measured with wave-front-shearing interferometry. For very low concentrations of $TlNO_3$ the results are

$$D=6.21\times10^{-8}\exp[-(18400\pm\ 800)/R\,T]\quad \text{in } NaNO_3\ (316-387\ {}^\circ C),$$
$$D=5.39\times10^{-8}\exp[-(18800\pm1400)/R\,T]\quad \text{in } KNO_3\ (341-408\ {}^\circ C),$$
$$D=1.87\times10^{-7}\exp[-(25800\pm2200)/R\,T]\quad \text{in } RbNO_3\ (327-419\ {}^\circ C),$$

where D is the diffusion coefficient in $m^2\,s^{-1}$, R the gas constant in $J\,K^{-1}\,mol^{-1}$ and T the temperature in K.

Comparisons are made with high-dilution diffusion of Na^+, K^+, Rb^+, Cs^+ and Ag^+ ions in alkali nitrates, and it is found that both Ag^+ and Tl^+ diffuse faster than expected if the mass and the ionic radius were the sole parameters of importance, i. e. other parameters such as the polarizability also have an influence on the diffusion rate of an ion. For the system $NaNO_3-TlNO_3$, the interdiffusion coefficient has also been measured at 88.8, 73.8, 51.5 and 31.6 mol % $NaNO_3$.

Introduction

The mass, the ionic radius and the polarizability of diffusing ions are parameters that can be expected to have an influence on the rate of diffusion in an ionic melt. Experimental isotope effects in electromigration prove that the mass plays a role in electromigration processes in ionic melts and a molecular dynamics study demonstrates the existence of isotope effects in classical diffusion processes in ionic melts [1], whereas little is experimentally studied. Geometrical considerations of models stress the importance of the radius. An estimation of the relative contribution of the three parameters is complicated by the fact that there exists no pair of ions for which two of the parameters are nearly equal except in the case of isotopic ions. A fundamental problem is of course that the ionic radius is not as well defined as most other parameters, and thus, there is considerable disagreement in the literature concerning preferable radii of ions [2]. (It must also be remembered that all estimates of ionic radii are made for solid compounds with monoatomic ions, while our discussion concerns melts, where the anion is polyatomic.) Besides the three parameters, other factors such as the parameters of more sophisticated pair potentials between diffusing ions should also be taken into consideration.

In the present study a small amount of $TlNO_3$ has been added to $NaNO_3$, KNO_3 and $RbNO_3$, and interdiffusion has been measured by wave-front-shearing interferometry [3 – 5]. The results are compared with our previous work by the same method, where $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$ and $AgNO_3$ were added to alkali nitrates [3, 4] and where $TlNO_3$ was added to $LiNO_3$, loc. cit. [6]. For the system $NaNO_3-TlNO_3$ interdiffusion was studied at several concentrations.

The refractive index of molten $TlNO_3$ is considerably larger than that of molten alkali nitrates, and therefore, it is possible to work with very low concentrations of $TlNO_3$.

Experimental

The arrangement of the wave-front-shearing interferometer used was similar to that employed for the measurement of the thermal conductivity of some ionic melts [7].

A slot in a stainless steel block constituted the diffusion cell (Figure 1). The slot was closed at both ends with quartz windows which were connected to the light ports [7, 8]. The quartz windows were of interferometric quality; the flatness of the surface was better than $\lambda/5$, and the parallelism of both surfaces was within 2″. The light ports were pressed against the diffusion cell with aluminium

---

* Present address: Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan.

Reprint requests to Dr. S. E. Gustafsson, Department of Physics, Chalmers University of Technology, S-402 20 Göteborg, Sweden.

holders and stainless steel screws to keep in position both the quartz plates and the light ports. The detailed arrangement of the light ports was described previously [8]. A He-Ne laser ($\lambda = 632.8$ nm) of 1.5 mW made by Spectra Physics was used as the light source.

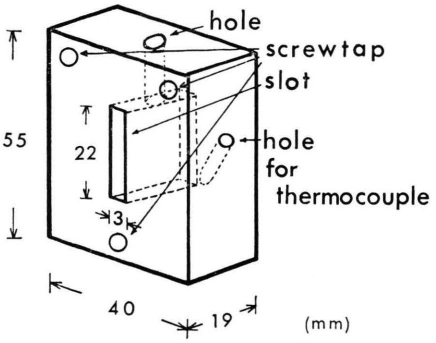

Fig. 1. Diffusion cell.

The chemicals used were of analytical reagent grade. Sodium, potassium and rubidium nitrates were dried in an air bath at 120 °C before use, melted in a glass tube and then poured into the cell through the upper hole to a height of about 20 mm. The crystals of $TlNO_3$ were prepared by melting the salt and then letting it solidify. With this process the air, otherwise likely to be trapped in the substance, was eliminated. The diffusion experiment was initiated by dropping a small crystal of $TlNO_3$ to the bottom of the cell through a glass tube about 1 m long and the upper hole of the cell [3].

In the case of $NaNO_3 - TlNO_3$, the concentration of $NaNO_3$ was chosen at 100, 88.8, 73.8, 51.5 and 31.6 mol% and again a crystal of several mg $TlNO_3$ was dropped. A detailed mathematical consideration of the non-ideal conditions in bottom layer diffusion experiments has been given previously [9].

From the onset of the diffusion, the interferograms were observed with a Nikon F camera and photographed every two minutes. The method of calculating the interdiffusion coefficients from the obtained interferograms has been described previously [3].

The temperature of the diffusion cell was measured with a calibrated chromel-alumel thermocouple, the end of which was placed inside the hole of the diffusion cell (see Fig. 1). The heat capacity of the furnace used was so large that the temperature could be kept constant within ±0.1 °C during an experiment over a period of, say, 1 h.

Results and Discussion

The high-dilution diffusion coefficients of Tl^+ in $NaNO_3$ are given in Table 1. The logarithm of the diffusion coefficients is plotted against the reciprocal of the absolute temperature in Figure 2. These diffusion coefficients have previously been measured at 316 °C with a zone diffusion technique by Forcheri and Wagner [10] (1.85×10^{-9} m²/s and 1.81×10^{-9} m²/s). Their values are about 20% higher than ours. Their values of the self-diffusion coefficients of Na in $NaNO_3$ in the same experiment are also about 20% higher than those measured with a capillary method by Dworkin et al. [11]. There are also other data available on the interdiffusion coefficients of $TlNO_3$ in $NaNO_3$ [12]; these very old data, however, are likely to be too high by a factor of 2 to 3. For comparison, Fig. 2 also shows some results obtained for low concentrations of other ions in $NaNO_3$. Thus, optical interferometry has been used previously to study the diffusion of Rb^+, Cs^+ ang Ag^+ ions [3, 4].

Mostly the radius of Tl^+ is considered to be somewhat smaller than that of Rb^+ (Tl^+ 0.150 nm and Rb^+ 0.166 nm [2]; Tl^+ 0.140 nm and Rb^+ 0.148 nm [13] or both 0.147 nm [14]) and it might be of interest to include for both these ions results ob-

Table 1. High-dilution diffusion coefficients of Tl^+ in molten $NaNO_3$.

T (°C)	$\langle \bar{c} \rangle$ [a] [mol %)	D [b] (10^{-9} m²/s)
316.1	0.21	1.410 ± 0.012
321.9	0.23	1.536 ± 0.012
322.0	0.19	1.502 ± 0.012
322.1	0.42	1.543 ± 0.036
336.4	0.30	1.620 ± 0.031
350.6	0.16	1.793 ± 0.075
362.0	0.18	1.990 ± 0.060
362.7	0.18	1.991 ± 0.056
363.1	0.20	1.900 ± 0.018
363.1	0.24	1.933 ± 0.047
368.7	0.38	1.929 ± 0.072
386.1	0.37	2.092 ± 0.033
386.8	0.23	2.212 ± 0.039

[a] This is the concentration at $\sqrt{2Dt}$, 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.

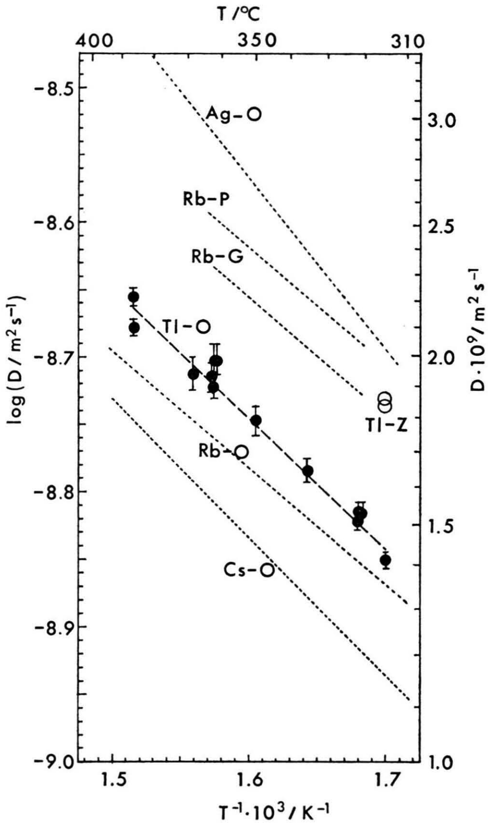

Fig. 2. Comparison of high-dilution diffusion coefficients in $NaNO_3$. ●: present Tl-data; the dashed line corresponds to $D = 6.21 \times 10^{-8} \exp(-18400/RT)$, Tl—Z: zone diffusion [10], Rb—O: optical interferometry [4], Rb—P: porous frit [15], Rb—G: gravimetric and porous frit [15], Ag—O: optical interferometry [3], Cs—O: optical interferometry [4].

tained also by other methods. Thus for Rb^+, measurements have also been made with two porous frit methods, one gravimetric and one with a tracer, as well as with glass-fibre-paper chromatography [16, 17]. The latter is not shown in Fig. 2, since it was made at a temperature considerably higher than that of the other experiments: 3.82×10^{-9} m²/s at 450 °C. However, it can of course be compared with extrapolated values, and it turns out that for highly diluted Rb^+ in $NaNO_3$, the results of the present method are of the order of 25% lower than those obtained by the three other methods.

The interdiffusion coefficients in the $NaNO_3-TlNO_3$ system are listed in Table 2. As the concentration of $TlNO_3$ increases, the relative difference in refractive indices becomes smaller, which means that the interferograms become increasingly difficult to evaluate. In the case of 68.4 mol% $TlNO_3$, the measured diffusion coefficients sometimes also varied due to the fact that the small difference in the densities implied that the initial condition of the diffusion process was not satisfactorily fulfiled. The scattered values are omitted from Table 2. If the diffusion coefficients are expressed in terms of Arrhenius' equations in spite of the small number of data, these become

$$D = 0.621 \times 10^{-7} \exp\left[-(18400 \pm 800)/RT\right] \quad 0.25\ \mathrm{mol\%}\ TlNO_3,$$

$$D = 1.63 \times 10^{-7} \exp\left[-(23500 \pm 2400)/RT\right] \quad 11.2\ \mathrm{mol\%}\ TlNO_3,$$

$$D = 1.65 \times 10^{-7} \exp\left[-(23400 \pm 1000)/RT\right] \quad 26.2\ \mathrm{mol\%}\ TlNO_3,$$

$$D = 0.625 \times 10^{-7} \exp\left[-(18600 \pm 800)/RT\right] \quad 48.5\ \mathrm{mol\%}\ TlNO_3,$$

$$D = 5.36 \times 10^{-7} \exp\left[-(28300 \pm 1200)/RT\right] \quad 68.4\ \mathrm{mol\%}\ TlNO_3,$$

where D is the diffusion coefficient in $m^2\,s^{-1}$, R the gas constant in $J\,K^{-1}\,mol^{-1}$ and T the temperature in K.

Table 2. Interdiffusion coefficients in the $NaNO_3-TlNO_3$ system.

$NaNO_3$: 88.8 mol %		73.8 mol %		51.5 mol %		31.6 mol %	
T (°C)	D (10^{-9} m²/s)	T (°C)	D (10^{-9} m²/s)	T (°C)	D (10^{-9} m²/s)	T (°C)	D (10^{-9} m²/s)
300.3	1.033 ± 0.029	281.8	1.058 ± 0.023	281.6	1.070 ± 0.049	250.1	0.839 ± 0.039
300.8	1.172 ± 0.041	282.5	1.058 ± 0.015	282.3	1.111 ± 0.026	250.5	0.794 ± 0.008
301.4	1.182 ± 0.013	293.2	1.199 ± 0.028	282.5	1.060 ± 0.031	289.8	1.260 ± 0.040
320.3	1.400 ± 0.005	294.3	1.142 ± 0.010	310.6	1.341 ± 0.038	295.5	1.402 ± 0.027
321.5	1.441 ± 0.015	319.0	1.431 ± 0.015	310.8	1.396 ± 0.034	307.3	1.465 ± 0.043
321.8	1.352 ± 0.010	319.4	1.426 ± 0.010	310.9	1.414 ± 0.017	318.8	1.640 ± 0.041
322.6	1.356 ± 0.011	320.4	1.431 ± 0.030	344.3	1.667 ± 0.030		
348.2	1.672 ± 0.011			368.5	1.925 ± 0.015		
359.5	1.980 ± 0.027						

In the system $NaNO_3 - TlNO_3$, the isotherm of the interdiffusion coefficients at 316 °C has been obtained over the whole concentration range by Forcheri and Wagner [10]. According to them the interdiffusion coefficient increases with the concentration of $NaNO_3$. The present data, not covering the range of very concentrated $TlNO_3$, do not show much change with concentration.

Concerning the high-dilution diffusion coefficients of Tl^+ in molten KNO_3, there are no data available except the very old ones (3.2, 3.3 and 3.4×10^{-9} m²/s at 345, 365 and 380 °C, respectively [12]); these values are about twice as high as the present high-dilution values, which are listed in Table 3. In Fig. 3 the present results are compared with previous studies by the same method on the diffusion of Na^+, Rb^+, Cs^+ and Ag^+ ions [3, 4].

Table 3. High-dilution diffusion coefficients of Tl^+ in molten KNO_3.

T (°C)	$\langle \bar{c} \rangle$ (mol %)	D (10^{-9} m²/s)
340.5	0.18	1.305 ± 0.023
345.9	0.22	1.450 ± 0.039
357.1	0.26	1.490 ± 0.022
357.3	0.19	1.507 ± 0.014
357.3	0.18	1.553 ± 0.035
387.1	0.30	1.720 ± 0.019
387.9	0.15	1.953 ± 0.065
388.2	0.29	1.773 ± 0.024
388.6	0.34	1.965 ± 0.053
390.0	0.38	1.778 ± 0.036
401.2	0.33	1.917 ± 0.030
403.3	0.22	1.950 ± 0.090
404.0	0.22	1.810 ± 0.051
408.0	0.33	1.939 ± 0.033

The high-dilution diffusion coefficients of Tl^+ in $RbNO_3$ are given in Table 4 and in Fig. 4, where the corresponding results for Ag^+ also are shown [3]. For comparison, data on the self-diffusion of Rb^+ are also shown, according to zone diffusion [16–19], porous frit [20] and "diffusion-into-a-capillary" [21] measurements.

The diffusion of highly diluted Na^+, K^+, Rb^+, Cs^+ and Tl^+ ions in $LiNO_3$ has been studied previously by optical interferometry [4, 6]. Just above the melting point D_{Tl} was lower than D_{Cs}, while at 350 °C, D_{Tl} was about equal to D_{Rb}. This latter result for $LiNO_3$ together with the observation that D_{Tl} and D_{Rb} nearly coincide in $NaNO_3$ and KNO_3

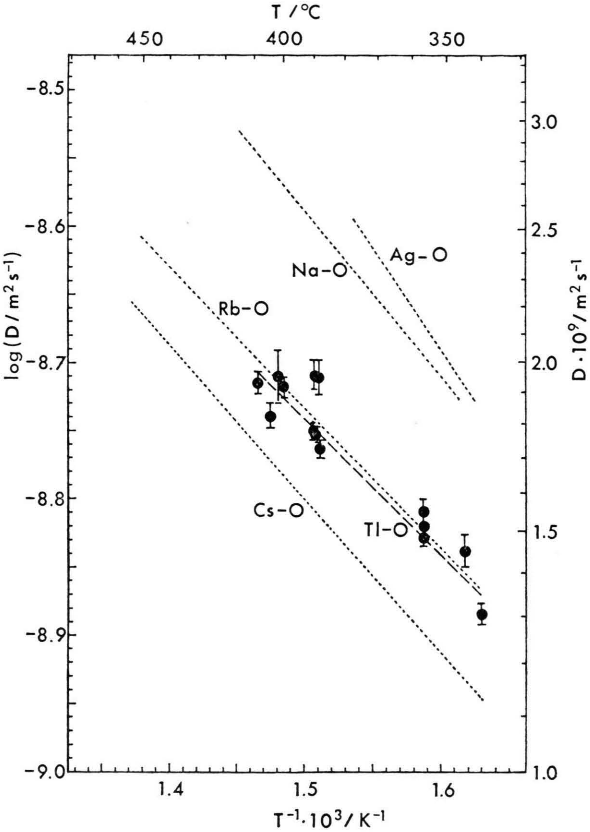

Fig. 3. Comparison of high-dilution diffusion coefficients in KNO_3 studied by optical interferometry. ●: present Tl-data; the dashed line corresponds to $D = 5.35 \times 10^{-8} \times \exp(-18800/R\,T)$, Na–O, Rb–O, Cs–O and Ag–O: previous studies [3, 4].

Table 4. High-dilution diffusion coefficients of Tl^+ in molten $RbNO_3$.

T (°C)	$\langle \bar{c} \rangle$ (mol %)	D (10^{-9} m²/s)
327.4	0.18	1.199 ± 0.018
327.5	0.16	1.101 ± 0.039
330.5	0.13	1.034 ± 0.037
331.0	0.15	1.081 ± 0.059
331.8	0.19	1.077 ± 0.042
344.7	0.21	1.230 ± 0.033
345.3	0.14	1.195 ± 0.036
345.9	0.16	1.197 ± 0.023
346.0	0.15	1.149 ± 0.050
364.2	0.24	1.345 ± 0.014
366.2	0.28	1.506 ± 0.015
366.3	0.26	1.447 ± 0.018
366.8	0.18	1.551 ± 0.021
382.2	0.29	1.454 ± 0.069
418.9	0.23	2.187 ± 0.045
419.2	0.14	2.203 ± 0.036

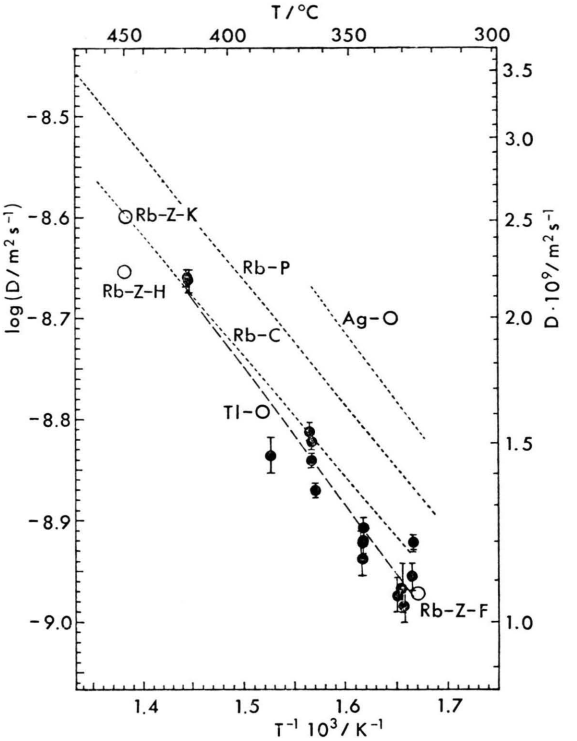

Fig. 4. Comparison of high-dilution diffusion coefficients in $RbNO_3$. ●: present Tl-data; the dashed line corresponds to $D = 1.87 \times 10^{-7} \times \exp(-25800/RT)$, Ag—O: optical interferometry [3]. Self-diffusion coefficient of Rb^+ studied by various methods: Rb—Z—H: zone diffusion [16, 17], Rb—Z—K: zone diffusion [18], Rb—Z—F: zone diffusion [19], Rb—P: porous frit [20], Rb—C: capillary [21].

(Fig. 2 and 3) could be taken as evidence that the radius of the ion is the predominant parameter, were it not for the following fact: In $NaNO_3$ the obtained D_{Ag} is larger than the self-diffusion coefficient [11] (measured by another method of course), while it is a common observation for molten salts that the diffusion coefficient for a certain ion tends to be smaller when its concentration is low than when that ion is abundant. As for KNO_3, taking into account the experimental error, one could consider D_{Ag} and D_{Na} in it to be nearly equal, while there is some uncertainty whether in a melt the radius is larger for Ag^+ than for Na^+ or if they are about equal [22].

Hence, for diffusion at high-dilution of monovalent cations in alkali nitrates the studies so far made by optical interferometry indicate that Ag^+ and Tl^+ ions do not necessarily follow the same systematics as the alkali ions. The two former ions have a higher polarizability than alkali ions with nearly the same radius. (The polarizability and also the mass increase in the order Li^+, Na^+, K^+, Rb^+, Ag^+, Cs^+, Tl^+ [23], while as stated above, the likely order for the radii is Li^+, Na^+, Ag^+, K^+, Tl^+, Rb^+, Cs^+.) The finding that the difference between D_{Na} and D_{Ag} is somewhat clearer than that between D_{Rb} and D_{Tl} would suggest that the difference in polarizability between Na^+ and Ag^+ might have a greater influence on diffusion than that between Rb^+ and Tl^+.

Since both the abundant and impurity ions are involved in the process of interdiffusion, some information on the interaction can be obtained. If the motion of the abundant ions were dominating the transport, one would expect nearly the same interdiffusion coefficients for all impurities in a certain melt, which is claimed by Zuca and Constantinescu [24] to be the case for the alkali nitrates, except $LiNO_3$, and for $AgNO_3$. However, our results show that the parameters of the highly diluted ions are of importance for interdiffusion.

Diffusion coefficients and the radius of the diffusing particles have often been correlated by means of the Stokes-Einstein equation:

$$D = kT/n\pi r\eta \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature and η the viscosity of the solvent. If r is chosen as the radius of the ion of low concentration, and D is the interdiffusion coefficient, a value of n can be calculated for an interdiffusion system. For the studies made so far by optical interferometry, this is done in Table 5, using the radii suggested by Pauling [13], where data of D and η are interpolated or extrapolated to $1.1\,T_m$, T_m being the melting point. It has been stated by Forcheri and Wagner [10] that if a value of 4.6 is chosen for n, the low-concentration diffusion coefficients of many univalent cations in univalent nitrates can be expressed fairly well by Equation (1). As can be seen from Table 5, n tends to fall between 2.5 and 3.5 for diffusion in $LiNO_3$ and to be larger than 5 for the diffusion of alkali ions in KNO_3. For highly diluted Ag^+ ions n is either low or "normal" depending on which alternative is preferred for the ionic radius. If the small radius is chosen for Ag^+ the values of n tend to be nearly the same for Ag^+ and Tl^+ ions.

Since the upper accessible temperature range is limited in these experiments because of the thermal

Table 5. The Stokes-Einstein coefficients n [cf. Eq. (1)] for the diffusion in molten alkali nitrates at 1.1 T_m (T_m: $LiNO_3$: 527 K, $NaNO_3$: 583 K, KNO_3: 610 K, $RbNO_3$: 589 K [25]). High-dilution diffusion coefficients measured with the present method are used for the calculation. The values of η are taken from Ref. [25, 35] and the used radii are according to Pauling.

Solvent	Diffusing ion						
	Na^+	K^+	Rb^+	Cs^+	Ag^+		Tl^+
						(a)	
$LiNO_3$	3.5	2.6	2.9	2.7	—		3.4
$NaNO_3$	—	—	4.9	4.7	3.4	4.5	4.7
KNO_3	5.5	—	5.0	5.1	3.7	4.9	5.4
$RbNO_3$	—	—	—	—	3.5	4.6	4.7

[a] The size of Ag^+ is assumed here to be the same as that of Na^+, that is, $r = 0.095$ nm.

decomposition of the nitrates, it cannot be judged from the present data whether Arrhenius plots of the diffusion coefficients deviate from a straight line. In Table 6 the Arrhenius coefficients for Tl^+ are listed together with those for other cations obtained by optical interferometry and for Rb^+ also by other methods. The Arrhenius coefficients for Tl^+, although the standard deviation of errors is large, seem to agree well with the corresponding ones for Rb^+ in the solvents $NaNO_3$, KNO_3 and $RbNO_3$. Furthermore, concerning Rb^+ Table 6 shows that irrespective of the methods or the investigators the Arrhenius coefficients agree well with one another within experimental errors in the same solvents even in the case the diffusion coefficients themselves do not agree. It might not be fortuitous that the Arrhenius coefficients for the solvent $NaNO_3$ are somewhat smaller than those for KNO_3 and distinctly smaller than those for $RbNO_3$. This order can be found also for the temperature coefficients of the molar volume of these solvents; on the basis of the density data [25], the molar volume is expressed adequately as $V_M = 4.465 \times 10^{-5} + 1.74 \times 10^{-3} (T' - 310)$ for $NaNO_3$, $V_M = 5.405 \times 10^{-5} + 2.18 \times 10^{-8} \quad (T' - 337)$ for

Table 6. Comparison of Arrhenius coefficients H for the high-dilution diffusion in molten alkali nitrates. For the purpose of comparing the values for Tl^+ with those for Rb^+, the results for Rb^+ obtained with other methods are also included.

Diffusing ion	Solvent	D_0 [a] (10^{-8} m²/s)	H [a] (J/mol)	Temp. range (°C)	Method [c]	Ref.
Na^+	$LiNO_3$	6.39	17800 ± 1800	272 – 384		[4]
K^+		31.9	25800 ± 5000	267 – 343		[4]
Rb^+		9.06	20700 ± 700	272 – 393		[4]
Cs^+		7.02	19800 ± 2100	268 – 341		[4]
Tl^+		39.5	28400 ± 1400	262 – 354		[6]
Rb^+	$NaNO_3$	3.82	16300 ± 3200	309 – 395		[4]
		6.00	16700 ± 5900	320 – 364	Porous frit (tracer)	[15]
		5.49	16700 ± 4300	322 – 362	Gravimetric and porous frit	[15]
Cs^+		6.49	19700 ± 2000	308 – 393		[4]
Ag^+		29.1	24300 ± 1400	313 – 383		[3]
Tl^+		6.21	18400 ± 800	316 – 387		This work
Na^+	KNO_3	17.3	23300 ± 2300	348 – 414		[4]
Rb^+		6.16	19400 ± 1600	340 – 452		[4]
Cs^+		7.97	21700 ± 2000	340 – 455		[4]
Ag^+		52.1	28800 ± 3400	342 – 378		[3]
Tl^+		5.39	18800 ± 1400	340 – 408		This work
Rb^+	$RbNO_3$	15.7 [b]	23700 ± 1300 [b]	318 – 499	Porous frit (tracer)	[20]
		11.6	23000 ± 400	327 – 466	Diffusion into capillary	[21]
Ag^+		33.0	26700 ± 1400	323 – 365		[3]
Tl^+		18.7	25800 ± 2200	327 – 419		This work

[a] D_0 and H are calculated from the formula: $D = D_0 \exp\{-H/RT\}$. These values are recalculated from the original data of D given in the literature with a least squares fit of non-linear forms [36].

[b] Since in this case the original data of D are not given numerically, the values given here are the ones given in the literature in which only the units are changed into the SI units.

[c] Unless otherwise noted, high-dilution diffusion coefficients measured with the present method are taken. Except in the case of self-diffusion coefficients of Rb^+, the other diffusion coefficients quoted here are taken from experimental work at such low concentrations that a meaningful comparison is possible.

KNO_3, and $V_M = 5.954 \times 10^{-5} + 2.42 \times 10^{-8}$ $(T' - 316)$ for $RbNO_3$ (V_m in $m^3 mol^{-1}$) in the temperature range from the melting point to about 100 °C above it, where T' is the temperature in °C. This fact would support the assumption that in these solvents the free space plays a significant role in diffusion. In $LiNO_3$, where the volume of the free space is supposed to be very small relative to the size of Rb^+ or Tl^+, other factors would be more predominant; in $LiNO_3$ the Arrhenius coefficients have been measured by the present method to be 20700 J/mol for Rb^+ [4] and 28400 J/mol for Tl^+ [6], while the molar volume is expressed by $3.872 \times 10^{-5} + 1.22 \times 10^{-8}$ $(T' - 254)$.

In the present experiments, the concentration of the diffusing ion is so low that it would be safe to regard the obtained diffusion coefficients approximately as the thermodynamical diffusion coefficients [26]. In a very dilute concentration of a diffusing cation the equivalent electrical conductivity of a pure solvent, Λ, the thermodynamical interdiffusion coefficient, D_{12}', and the ratio of internal mobilities of the two cations (b_1/b_2) are expressed in terms of the friction coefficients r_{ij} [27, 28]:

$$\Lambda/F^2 = 2/r_{23}, \tag{2}$$

$$D_{12}'/RT = 2/(r_{12} + r_{13}), \tag{3}$$

$$b_1/b_2 = (r_{12} + r_{23})/(r_{12} + r_{13}), \tag{4}$$

where the subscripts 1, 2 and 3 denote the diffusing cation, i. e., Tl^+ in this case, the cation of the solvent and the solvent anion, respectively. Here, the internal mobility of the cations is the mobility with reference to the anion.

From Eqs. (2), (3) and (4), it follows

$$r_{12} = 2\,\{(b_1/b_2)\,(RT/D_{12}') - F^2/\Lambda\}, \tag{5}$$

$$r_{13} = 2\,\{(1 - (b_1/b_2)\,(RT/D_{12}') + F^2/\Lambda\}, \tag{6}$$

$$r_{23} = 2\,F^2/\Lambda. \tag{7}$$

For the systems $TlNO_3 - LiNO_3$ [29], $TlNO_3 - NaNO_3$ [10] and $TlNO_3 - RbNO_3$ [29] the values of (b_1/b_2) are available. For these systems, r_{12}, r_{13} and r_{23} are calculated and tabulated in Table 7. In a previous article [6] the friction coefficient r_{12} in $LiNO_3$ was calculated on the assumption $b_1 = b_2$. Since this assumption experimentally proved not to be proper [29] the friction coefficient is recalculated here. The negative values of r_{12} in $LiNO_3$ would reflect the situation that in $LiNO_3$ the mobility of Tl^+ ions is restricted very much due to the small volume of the free space as compared with the volume of a Tl^+ ion. Thus, it should be emphasized that the negative value of r_{12} calculated from Eq. (5) would not necessarily mean that the formation of complexes or associated species. The extraordinary change of b_1/b_2 with temperature and concentration in the $TlNO_3 - LiNO_3$ system can be interpreted without assuming the presence of any associated species [29]. Recently, the ratio of the internal cationic mobilities in the $RbNO_3 - LiNO_3$ system has also been measured in a wide range of temperatures and concentrations [30]. The results show that the situation is very similar to that of the $TlNO_3 - LiNO_3$ system.

As seen from Table 7, the friction coefficients in $RbNO_3$ obey the general rule for three-component systems that the friction coefficients are positive

Table 7. Friction coefficients between ions in a very dilute solution of Tl^+ in molten alkali nitrates.

Solvent	Temperature (°C)	b_1/b_2 Ref.	Λ [25] (10^{-3} S m^2 mol^{-1})	r_{12} (10^{12} J s m^{-2} mol^{-1})	r_{13}	r_{23}
$LiNO_3$	288 [a]	0.179 [29]	3.87	−3.0	13.3	4.8
	310	0.300 [29]	4.37	−1.7	10.2	4.3
$NaNO_3$	316 [b]	0.843 [10]	4.53	1.6	5.2	4.1
KNO_3	390	—	4.35	(1.9) [c]	(4.3) [c]	4.3
$RbNO_3$	316	1.066 [29]	2.60	3.7	6.5	7.2
	380	1.046 [29]	3.49	1.7	5.0	5.3

[a] Since the value of b_1/b_2 cannot be extrapolated below 288 °C, the friction coefficients are calculated at the lowest temperature.

[b] Since the value of b_1/b_2 is available only at 316 °C in the literature, the friction coefficients are calculated at this temperature.

[c] No data of b_1/b_2 are available; the friction coefficients are calculated on the assumption $b_1/b_2 = 1$.

and decrease with increasing temperature. In $NaNO_3$ and KNO_3, in which the value and the temperature dependence of b_1/b_2 have not been determined yet, there is reason to believe that the situation would be similar to that in $RbNO_3$.

In conclusion, in molten $NaNO_3$, KNO_3 and $RbNO_3$, the high-dilution diffusion coefficients of Tl^+ measured with optical interferometry seem to be similar in magnitude to those of Rb^+, and in KNO_3 that of Ag^+ is nearly equal to that of Na^+, while in $NaNO_3$ that of Ag^+ is distinctly higher than the self-diffusion coefficient of Na^+. In $LiNO_3$ the high-dilution diffusion coefficients of Na^+ and Rb^+ seem to be higher than those of Ag^+ and Tl^+, respectively, particularly at low temperatures. (The interdiffusion coefficients of Ag^+ in $LiNO_3$ have been determined with other method [31 – 34]. Since the values of diffusion coefficients determined with different methods or by different investigators do not necessarily agree well with each other, we cannot decisively conclude what factors determine a diffusion process.

Acknowledgement

The authors wish to express their gratitude to Professor A. Lundén for his continued support and many helpful discussions and suggestions during the work. This investigation has been financially supported by the Swedish Board of Technical Development and by Carl-Bertel Nathhorst vetenskapliga och allmännyttiga stiftelse.

[1] F. Lantelme, P. Turq, and P. Schofield, J. Chem. Phys. **67,** 3869 (1977).
[2] R. Shannon and C. Prewitt, Acta Cryst. **25 B,** 925 (1969) and **26 B,** 1046 (1970).
[3] S. E. Gustafsson, L.-E. Wallin, and T. E. G. Arvidsson, Z. Naturforsch. **23 a,** 1261 (1968).
[4] T. E. G. Arvidsson, S.-Å. Afsenius, and S. E. Gustafsson, J. Chem. Phys. **53,** 2621 (1970).
[5] T. E. G. Arvidsson, S.-Å. Afsenius, and S. E. Gustafsson, Z. Naturforsch. **26 a,** 752 (1971).
[6] I. Okada and S. E. Gustafsson, Electrochim. Acta **18,** 275 (1973).
[7] S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **23 a,** 44 (1968).
[8] S. E. Gustafsson, Optical Instruments and Techniques, Ed. by J. H. Dickson, Oriel Press, Newcastle-upon-Tyne 1970, pp. 167.
[9] L.-E. Wallin and S. E. Gustafsson, Z. Naturforsch. **24 a,** 436 (1969).
[10] S. Forcheri and V. Wagner, Z. Naturforsch. **22 a,** 1171 (1967).
[11] S. Dworkin, R. B. Escue, and E. R. Van Artsdalen, J. Phys. Chem. **64,** 872 (1960).
[12] From Ref. in A. Klemm, Molten Salt Chemistry, Ed. by M. Blander, Wiley Interscience, New York 1964, pp. 592.
[13] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York 1960, pp. 581.
[14] L. H. Ahrens, Geochim. Cosmochim. Acta **2,** 155 (1952).
[15] A. Behn and C.-A. Sjöblom, Z. Naturforsch. **25 a,** 700 (1970).
[16] E. P. Honig, Thesis, Amsterdam 1964.
[17] J. A. A. Ketelaar and E. P. Honig, J. Phys. Chem. **68,** 1596 (1964).
[18] I. C. Th. Kwak, Thesis, Amsterdam 1967.
[19] S. Forcheri, V. Wagner, and E. Berra, Electrochimica Metallorum **III,** 123 (1968).
[20] A. Behn and C.-A. Sjöblom, Z. Naturforsch. **24 a,** 464 (1969).
[21] S. Zuca and M. Constantinescu, Rev. Roum. Chim. **17,** 385 (1972).
[22] M. Blander, J. Phys. Chem. **36,** 1092 (1962).
[23] M. Blander, Molten Salt Chemistry, Ed. by M. Blander, Interscience, New York 1964, pp. 161.
[24] S. Zuca and M. Constantinescu, Z. Naturforsch. **29 a,** 497 (1974).
[25] G. J. Janz, Molten Salts Handbook, Academic Press, New York 1967.
[26] R. W. Laity, J. Phys. Chem. **63,** 80 (1959).
[27] R. W. Laity, J. Chem. Phys. **30,** 682 (1959).
[28] A. Klemm, Z. Naturforsch. **15 a,** 173 (1960).
[29] K. Kawamura, I. Okada, and O. Odawara, Z. Naturforsch. **30 a,** 69 (1975).
[30] I. Okada, T. Takagi, and K. Kawanura, to be published.
[31] C.-A. Sjöblom and A. Behn, Z. Naturforsch. **23 a,** 1774 (1968).
[32] S. Sternberg and C. Herdlicka, Rev. Roum. Chim. **14,** 991 (1969).
[33] K. Kawamura, Denki Kagaku **38,** 12 (1970).
[34] G. A. Mazzochin and G. Shiavon, J. Electroanal. Chem. **38,** 229 (1972).
[35] I. G. Murgulescu and S. Zuca, Electrochim. Acta **11,** 1383 (1966).
[36] W. E. Deming, Statistical Adjustment of Data, Wiley, New York 1946.