

Diffusion Coefficients of Rb^+ and Cs^+ Ions in Molten Nitrate Systems

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The tracer diffusion coefficients of ^{86}Rb and ^{137}Cs ions in the molten $(\text{Li-Na})\text{NO}_3$, $(\text{Li-K})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ systems have been measured by means of a paper strip method. Results from the paper strip method in some pure nitrates are compared with the results from capillary and optical interferometric methods. With increasing concentration of LiNO_3 , the diffusion coefficients at 350°C are found to decrease in the $(\text{Li-Na})\text{NO}_3$ system and to increase in the $(\text{Li-K})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ systems. For ^{86}Rb in $(\text{Li-K})\text{NO}_3$ an increase is followed by a decrease. These findings are discussed by taking into consideration the free space in the solvent system and the ionic interaction between the diffusing and the surrounding ions.

Introduction

A relatively large number of papers dealing with diffusion coefficients in molten nitrate systems has been published in recent years [1–19]. In order to explain the observed diffusion coefficient isotherms, an anion polarization model [20, 21] or an association model [3] has been adopted by several authors with the assumption that the radius, the polarizability, and the mass of an ion determine its rate of diffusion. However, considering the fact that Rb and Tl in pure [19, 22] and mixed [6, 18] nitrates diffuse with almost the same rate in spite of the large differences in their masses (85 and 204) and polarizabilities, it may be supposed that the near equality of the radii of these two ions is more significant than the difference in their mass and polarizability. According to [19] the mobilities of Rb and Tl would differ by only 3%.

High-dilution diffusion of K^+ , Rb^+ , Cs^+ , and Tl^+ in the molten $(\text{Li-K})\text{NO}_3$ system has previously been studied with optical interferometry [23], and the isotherms of the diffusion coefficients have been discussed from the viewpoint of the ionic radii, the free space in the solvent, and the interaction between the diffusing and the surrounding ions. Diffusion in the solvent systems $(\text{Li-Na})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ should also be investigated systematical-

ly, but it would be difficult to apply the interferometric method to some of these systems at some compositions, because the changes of the refractive indices would be too small.

Therefore, in the present work the tracer diffusion coefficients of ^{86}Rb and ^{137}Cs ions in the molten $(\text{Li-Na})\text{NO}_3$, $(\text{Li-K})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ systems have been measured by means of a paper strip method. The results are discussed in a similar way as was done for D_K , D_{Rb} , D_{Cs} , and D_{Tl} in the molten $(\text{Li-K})\text{NO}_3$ system [23].

The paper strip method used in the present work originates from the paper electrophoresis method developed by Arnikaar [24] and improved by Honig [25] for the measurement of ionic mobilities of molten salts. For the measurement of diffusion coefficients in molten salts the paper strip method is rather simpler than other methods [26–31]. Several series of experiments can be performed at the same time with the same experimental conditions, making this method particularly useful for the investigation of the diffusion coefficient isotherms.

Experimental

The principle of a paper strip method and its application to the measurement of diffusion coefficients in molten salts have been already described in detail elsewhere [25, 32].

A strip of glass fibre paper ($120 \times 5 \times 0.2 \text{ mm}$), uniformly impregnated with the solvent salt ($\sim 3 \text{ mg/mm}$) on a supporting Pyrex glass plate, is horizontally placed on an aluminum tray in a electric furnace flushed with dried nitrogen gas. The experiment is initiated by dropping a small crystal

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of tracer salt (<1 mg) on the center of the strip through a stainless steel tube. The tracers used in the present work were ⁸⁶Rb ($t_{1/2}$ = 19 days) and ¹³⁷Cs ($t_{1/2}$ = 33 years) purchased from The Radiochemical Center Ltd. in England, which were applied as nitrates of known specific activity ($\sim 50 \mu\text{Ci/g}$). After 18–20 hours diffusion, the paper strip was quickly removed from the furnace and allowed to cool for solidification of the salts. The distribution of the radioactivity in the paper strip was measured at 2 mm or 4 mm intervals by means of a GM counter fitted with a 1 mm lead diaphragm. With the data from the tracer distribution curve, D is calculated from the equation

$$C(x, t) = S \exp(-x^2/4Dt) / 2 \sqrt{\pi Dt},$$

where C is the amount of solute per unit length at the distance x from the origin, S the total amount of the solute, and t the diffusion time. The value of D is determined from the gradient of $\ln(C)$ against x^2 .

All the chemicals were of analytical reagent grade and fully dried before use without further purification. The mixtures were prepared by directly weighing each component.

Results and Discussion

In the present paper strip method, paper made of boro-silicate glass fibre and Pyrex glass were used as the strips and the supporting plates, respectively. In some series, the radioactivity in the paper and in the Pyrex glass plate, which were washed out after the measurement, was determined and found to be nearly the same as the background. Therefore, the results obtained are not significantly influenced by exchange of the tracer ions.

The logarithm of D_{Cs} in pure LiNO_3 , NaNO_3 , and KNO_3 is plotted against the reciprocal of the absolute temperature in Figs. 1, 2, and 3, respectively. The data previously measured with a paper strip method [25, 32], with a “diffusion out of a capillary” method [33], and with optical interferometry [23, 34] are also shown in the figures. As can be seen from the figures, the reproducibility of the present method is reasonably good as long as the experimental conditions are properly controlled; the amount of solvent salt impregnated into the glass fibre paper and the radioactivity of the solute should be carefully chosen in order to prevent an unwanted

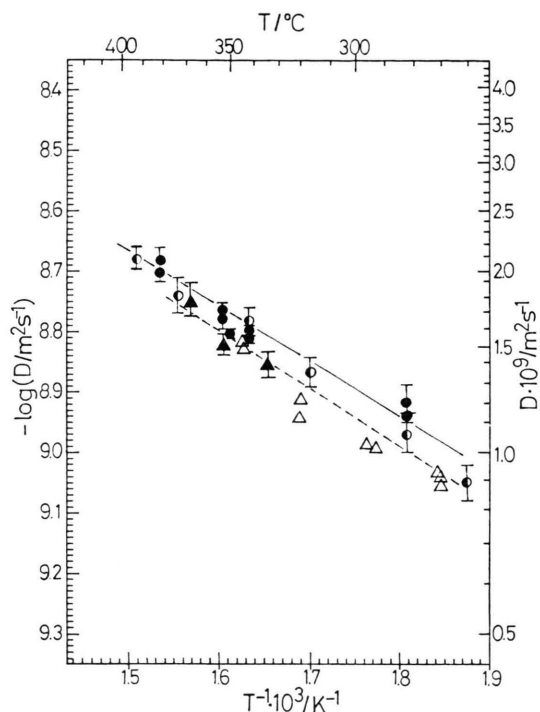


Fig. 1. Diffusion coefficients of Cs⁺ in molten

LiNO_3 . ●, present work; ○, Ref. 32; ▲, Ref. 23; △, Ref. 34.

influence from eddy flow and surface convection, to minimize the statistical counting error, etc. Since the concentrations of solute required in the present method ($\sim 0.3 \text{ mol}\%$) and in optical interferometry ($\sim 1 \text{ mol}\%$) are low enough to neglect their influence on the diffusion coefficient, D obtained from the present method and also from the capillary method (i.e. tracer diffusion coefficient) may be identical with that from optical interferometry (i.e. high-dilution diffusion coefficient). The present results are in good agreement with those from the capillary method. The present values for D_{Cs} in NaNO_3 and KNO_3 are about 15% higher than those from optical interferometry, while the agreement is better for D_{Cs} in LiNO_3 . Although the difference of the results could not be clearly judged in the present work, it is not surprising considering the large difference in the experimental conditions; the duration of an experiment is 18–20 hours in the former and about half an hour in the latter, and the measured quantity used for determining D is the tracer

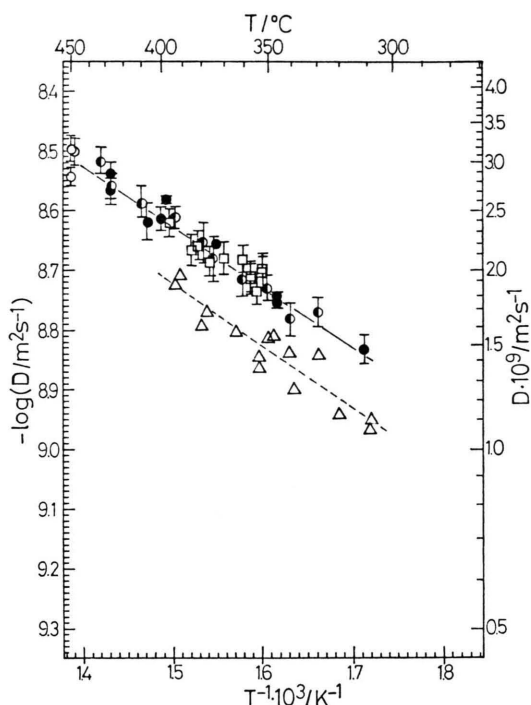


Fig. 2. Diffusion coefficients of Cs^+ in molten NaNO_3 . \bullet , present work; \circ , Ref. 25; \square , Ref. 32; \square , Ref. 33; \triangle , Ref. 34.

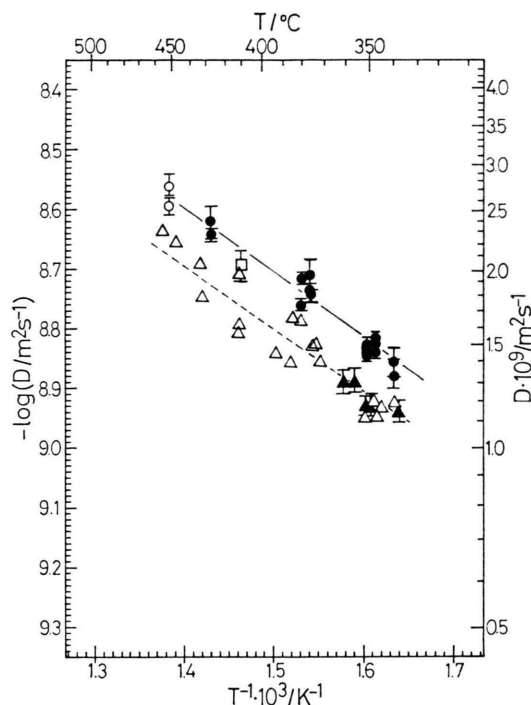


Fig. 3. Diffusion coefficients of Cs^+ in molten KNO_3 . \bullet , present work; \circ , Ref. 25; \square , Ref. 33; \blacktriangle , Ref. 23; \triangle , Ref. 34.

distribution curve in the former and the refractive index difference in the latter.

The isotherms of D_{Rb} and D_{Cs} in the molten $(\text{Li-Na})\text{NO}_3$, $(\text{Li-K})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ systems at 350°C are shown in Figs. 4 and 5, respectively. The results for D_{Rb} and D_{Cs} in the $(\text{Li-K})\text{NO}_3$ system obtained by optical interferometry [23] are also shown in the figures for comparison. As can be seen from the figures, D_{Rb} and D_{Cs} slightly decrease in the $(\text{Li-Na})\text{NO}_3$ system and almost monotonously increase in the $(\text{Li-K})\text{NO}_3$, $(\text{Li-Rb})\text{NO}_3$, and $(\text{Li-Cs})\text{NO}_3$ systems with increasing LiNO_3 concentration except for Rb in the $(\text{Li-K})\text{NO}_3$ system, where D_{Rb} shows a pronounced positive deviation from a linear dependence on the concentration. There is some difference between the present results and those from optical interferometry, especially for D_{Cs} in the region rich in KNO_3 . However, the tendency of the concentration dependence is considered to be nearly the same in both cases. Using the same assumption as adopted for the interpretation of D_{K} , D_{Rb} , and D_{Ti} in the system $(\text{Li-K})\text{NO}_3$ [23], these diffusion coefficient isotherms are then explained by taking into account

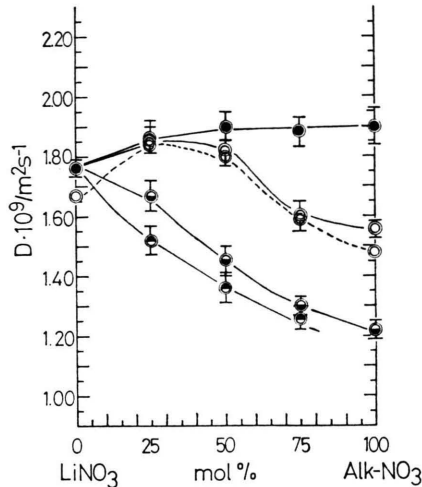


Fig. 4. Isotherms of the diffusion coefficients of Rb^+ in the molten $(\text{Li-Alk})\text{NO}_3$ systems at 350°C . \bullet : in $(\text{Li-Na})\text{NO}_3$, \circ : in $(\text{Li-K})\text{NO}_3$, \square : in $(\text{Li-Rb})\text{NO}_3$, \square : in $(\text{Li-Cs})\text{NO}_3$, — present work, - - - high-dilution diffusion [23].

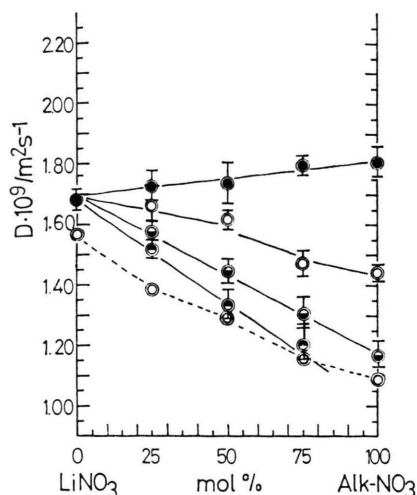


Fig. 5. Isotherms of the diffusion coefficients of Cs⁺ in the molten (Li-Alk)NO₃ systems at 350°C. \circ : in (Li-Na)NO₃, \square : in (Li-K)NO₃, \triangle : in (Li-Rb)NO₃, \diamond : in (Li-Cs)NO₃, ——— present work, - - - - high-dilution diffusion[23].

two effects, i. e. the interaction of the diffusing ion with the surrounding solvent ions and the free space in the solvent system.

According to a molecular dynamics simulation of equimolar (Li-Rb)Cl [35], the relative velocity and the selfdiffusion coefficients of the Rb⁺ and Cl⁻ ions in this mixture are larger than those in pure RbCl, i. e. the motion of the solvent becomes more active with increasing Li⁺-concentration. Considering the thermal velocities and the data on the sound velocity in the corresponding salts [36–39], it is expected that the diffusive motions in RbNO₃ and CsNO₃ are rather slow compared with those in LiNO₃. Therefore, the effect of the interaction on adding LiNO₃ to RbNO₃ or CsNO₃ would be quite large and increase steeply in the region rich in LiNO₃. Even though the free space in the solvent systems may become smaller for the motion of Rb⁺ and Cs⁺ ions in the region rich in LiNO₃, the effect of the interaction causes the monotonous increase of D_{Rb} and D_{Cs} in the systems (Li-Rb)NO₃ and (Li-Cs)NO₃ with increasing LiNO₃ concentration.

In the (Li-K)NO₃ system, the thermal motion does not change so much as in (Li-Rb)NO₃ and (Li-Cs)NO₃ with increasing LiNO₃ concentration,

and therefore the influence of the free space becomes more pronounced in this system. The Rb⁺ ion is somewhat larger than the free space in mixtures of LiNO₃ and KNO₃, and Cs⁺ is even larger than the free space in pure KNO₃. Thus the effect of the free space would be larger for Rb⁺ than for Cs⁺ in the (Li-K)NO₃ system. Therefore, D_{Rb} shows a positive deviation from a linear dependence on the concentration, while D_{Cs} increases monotonously with increasing LiNO₃ concentration within experimental error.

In the (Li-Na)NO₃ system, the size of the free space must be rather small for the movement of Rb⁺ and Cs⁺ ions. However, since the effect of the interaction would be almost independent of the concentration because both the Na⁺ and Li⁺ ions are very much smaller than the Rb⁺ and Cs⁺ ions, D_{Rb} and D_{Cs} decrease slightly with increasing LiNO₃ concentration as a result of the contribution of the free space to the diffusion.

Thus, the diffusion coefficient isotherms of relatively large ions such as Rb⁺ and Cs⁺ in the molten systems (Li-Na)NO₃, (Li-K)NO₃, (Li-Rb)NO₃, and (Li-Cs)NO₃ can be interpreted by introducing the simple assumption that the interaction between the diffusing and the surrounding ions and the size difference between the diffusing ion and the free space in the solvent system mainly rule the diffusion process.

As the size of the diffusing ion and the motion of the solvent system seem to be the predominant factors in the diffusion process, we have examined the validity of the Stokes-Einstein equation, relating the diffusion coefficients (D) with the radius of the diffusing ion (r) and the viscosity of the solvent (η):

$$D = k_B T / n \pi r \eta. \quad (1)$$

Here, n is the “shape” parameter, and the values of n tabulated in Table 1 are calculated from (1) with the present D -results, the ionic radii from Ref. [40], and interpolated values of the viscosity at 350 °C according to Ref. [41]. As is seen from Table 1, the values of n become larger with increasing size and concentration of the heavier component of the solvent system. However, the variation is rather small. Also n_{Cs} is always slightly smaller than n_{Rb} .

A smaller value of the “shape” factor n for a given ion in solvent A than in solvent B means that the

Table 1. "Shape" parameter n of the Stokes-Einstein equation for Rb⁺ and Cs⁺ tracer ions in the molten (Li-Alk)NO₃ systems at 350°C.

LiNO ₃ mol%	(Li-Na)NO ₃		(Li-K)NO ₃		(Li-Rb)NO ₃		(Li-Cs)NO ₃	
	n_{Rb}	n_{Cs}	n_{Rb}	n_{Cs}	n_{Rb}	n_{Cs}	n_{Rb}	n_{Cs}
100	3.38	3.10	3.38	3.10	3.38	3.10	3.38	3.10
75	3.60	3.40	3.75	3.66	4.10	3.80	4.68	4.10
50	3.85	3.68	4.19	4.10	4.94	4.33	5.55	4.93
25	4.08	3.73	4.68	4.46	5.17	4.49	5.52	5.07
0	4.04	3.71	4.36	4.11	4.75	4.49	—	—

diffusion coefficient is relatively higher in solvent A than in B for same viscosity value. Now the viscosity is mainly dependent on the free space volume and on thermal motion, but independent naturally of the size of the tracer ion. Thus we may conclude that a smaller value of n means a smaller influence on the diffusion of free space of the solvent and a greater influence of the ionic radius and of the interaction of the diffusing ion with its surroundings. The decrease of n with increasing concentration of LiNO₃, leading to a decrease in solvent free space, can thus be explained, and also the decrease on going from Rb⁺ to the larger Cs⁺ ion.

Although it is difficult to give an explicit interpretation of the diffusion in the molten nitrate systems from the Stokes-Einstein equation with the present results, it is considered that the Stokes-Einstein equation has a reasonable degree of validity for relating the diffusion coefficient with the viscosity, leading us to the conclusion that diffusion can be explained by simple assumptions taking into account the size difference between the diffusing ion and the free space formed by the solvent system and the interaction between the diffusing and the surrounding ions.

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