Self-diffusion of Iodide Ion and Strontium Ion in Strontium Iodide Solutions

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Self-diffusion coefficients of iodide ion in hydrogen iodide, sodium iodide, potassium iodide and rubidium iodide solutions were measured by Mills and Kennedy[1]. They showed that in every iodide solution studied the product of self-diffusion coefficient of iodide ion and relative viscosity of the solution, i.e., $D\eta/\eta_0$, was linear against the square root of the concentration, $\sqrt{c}$, up to considerably high concentrations. In the case of self-diffusion of sodium, potassium, chloride and sulfate ions, however, no such linear relations were found. Matuura and Shimozawa[2] showed that the self-diffusion of calcium and strontium ions in chloride solutions was very complicated with respect to the concentration of the solution and found that the $D\eta/\eta_0$ vs. $\sqrt{c}$ curves had two minima and one maximum. The important difference of iodide ion from the other ions cited above in connection with the kinetic behaviors in aqueous solutions may be in its large size and poor hydration. A simple picture of the self-diffusion process for such "unhydrated" ions was suggested by Mills and Kennedy, which, in the case of monovalent counter ions, seems to explain the iodide ion self-diffusion satisfactorily. It is very interesting to investigate whether or not the same picture could be extended to the iodide of the divalent counter ions. The present work has been performed with the solution of strontium iodide in order to check this point and to obtain further knowledge

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[1] R. Mills and J. W. Kennedy, *J. Am. Chem. Soc.*, 75, 5696 (1953).

[2] R. Matuura and R. Shimozawa, *Mem. Faculty of Science, Kyushu University, Ser. C*, 2, 53 (1955).

of the behavior of ions in electrolyte solutions.

Experimental

Apparatus. — The diffusion apparatus was essentially the same as that proposed by Anderson and Saddington[3] and modified by Wang[4]. The schematic diagram of the apparatus is shown in Fig. 1. A three-necked flask of one liter capacity (A) was fitted with capillary holders (B) and a mercury seal stirrer (D). A plastic paddle (E) was turned slowly by an electric motor. The flask and contents were immersed in a thermostat (F) of 25±0.01°C. The capillary diffusion cells (C) were prepared as follows. The different diameter capillaries of Pyrex glass were used and the inside diameter was calibrated by filling with pure mercury. They were 0.0612 and 0.0780 cm. The capillaries were cut to different lengths and the top end of each capillary was ground flat with fine carborundum. The other end was sealed with glass to make a flat bottom. The length of each capillary was measured precisely with a micrometer caliper. These lengths varied from 2.97 to 5.19 cm.

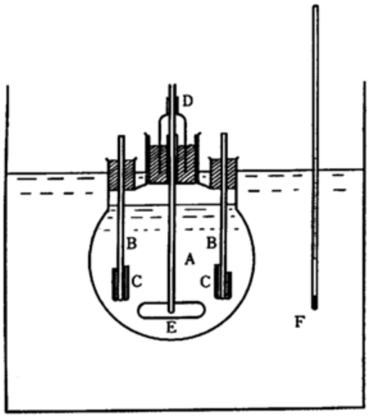

Fig. 1. Diffusion apparatus.

Procedure.—Capillaries were filled with a radiotracer solution of known concentration by using a fine pipette drawn from a glass tubing. They were then held vertically in a flask containing one liter of inactive strontium iodide solution of the same concentration as the capillary solution. The air above the solution in the flask had been replaced by nitrogen gas so that the strontium iodide solution might not be decomposed by oxygen in air. Also, in order to avoid the effect of light, the outer surface of the flask had been coated with black paint. Each capillary was immersed in the flask solution up to just below the upper end of the capillary and left standing for about 30 min. in order to secure thermal equilibrium between the solution inside and outside of the capillary. Then the capillaries were dipped completely into the flask solution and the diffusion was allowed to start. The nitrogen gas in the flask was renewed after setting the capillary cells in it. During the diffusion period the flask solution was stirred by turning a paddle (see Fig. 1) at a constant rate 90 r. p. m. This turning rate was chosen in order to minimize the Δl correction according to Mills and Kennedy[1]. After each diffusion period (3 to 7 days) the capilliaries were taken out of the flask and the radioactivity of the solution in each capillary was measured by a counter. The radioactivity of the original solution was also measured at the same time and two values of radioactivity, that is, before and after diffusion corrected for natural decay, was compared on the same volume unit.

The viscosity of the solution was measured with an Ostwald viscometer at 25°C.

Materials. — The tracers used in the present experiment were ^{131}I and ^{89}Sr. ^{131}I (half-life 8.0 days) was obtained in the form of chloride in weak basic sodium bisulfite solution. The bisulfite was removed by titration with hydrogen iodide to a pH of about 5. A drop of this solution was added to a quantity of strontium iodide solution. The concentration of iodide in this solution was measured volumetrically. Since the concentration of cations other than strontium in this solution was negligibly small, this was used as a tracer solution for iodide ion diffusion in strontium iodide solutions. The radioactivity of ^{131}I in the solution was measured by a proportional gas counter.

^{89}Sr (half-life 54 days) was obtained as a carrier-free chloride. This contained less than 10% ^{90}Sr (half-life 25 years) which decays into ^{90}Y (half-life 65 hr.). A drop of the original solution was dried up and dissolved in the strontium iodide solution of known concentration to make a capillary solution. After diffusion the solution was drawn out of a capillary by means of a fine pipette. The capillary was washed several times with a large excess of distilled water. The sample solution, together with all washings, was evaporated to dryness and its radioactivity (c_{av}) was measured by a G. M. counter. The radioactivity (c_0) of the original solution was also measured at the same time. It was found that the ratio c_{av}/c_0 depended upon the duration after the diffusion had been stopped, because of the destruction of equilibrium between ^{90}Sr and ^{90}Y caused by the difference in the diffusion rate of the two species. So the measurement of c_{av} and c_0 was made week by week until the constant value of c_{av}/c_0 was obtained. It took two to four weeks to attain the complete equilibrium between ^{90}Sr and ^{90}Y. From this constant value of c_{av}/c_0 the diffusion coefficient of strontium ion in strontium iodide solutions was calculated.

It was found that strontium iodide decomposes gradually in air and by light, resulting in the liberation of iodine which makes the solution colored. So it was necessary to use a fresh sample for each experiment. The strontium

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[3] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, **1949**, S 381.

[4] J. H. Wang, *J. Am. Chem. Soc.*, **73**, 4181 (1951).

iodide solution was prepared from strontium carbonate and hydrogen iodide just before each run of diffusion and viscosity measurement. Rigorous precautions were made for the solution not to change by air and light during the experiment, as already mentioned. The solution was slightly acidic. Its concentration was determined gravimetrically as strontium sulfate and also volumetrically as silver iodide. Both methods agreed well.

Calculations

Under the present experimental conditions the Fick's diffusion equation is solved as follows[5].

$$\frac{c_{av}}{c_0}=\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2Dt/4l^2\right] \tag{1}$$

where, c_{av} is the average concentration of the tracer ion in the capillary solution after diffusion, c_0 is its initial concentration, l is the length of the capillary, t is the diffusion time and D is the self-diffusion coefficient. For the value of Dt/l^2 greater than 0.2 the series in the Eq. 1 converges so rapidly that all terms following the first can be neglected with an error smaller than 0.2%. This condition was always kept in the present experiment. Thus the equation

$$2.303\log\frac{\pi^2}{8}\cdot\frac{c_{av}}{c_0}=-\frac{\pi^2Dt}{4l^2} \tag{2}$$

was always used for the calculation of the self-diffusion coefficient of iodide ion and strontium ion in the strontium iodide solutions.

TABLE I. SELF-DIFFUSION COEFFICIENT OF IODIDE ION IN STRONTIUM IODIDE SOLUTIONS AT 25°C

c (mol. SrI_2/l.)	$D_{I^-}\times10^5$ (cm^2/sec.)
0.00042	1.995±0.03
0.0024	1.991±0.02
0.0042	1.928±0.02
0.0111	1.869±0.03
0.0128	1.881±0.02
0.0138	1.880±0.03
0.056	1.841±0.03
0.187	1.791±0.02
0.223	1.76 ±0.03
0.375	1.694±0.02
0.438	1.663±0.01
0.713	1.613±0.04

Results

Self-diffusion coefficients of iodide ion and strontium ion in strontium iodide solution of various concentrations are shown in Tables I and II, respectively.

TABLE II. SELF-DIFFUSION COEFFICIENT OF STRONTIUM ION IN STRONTIUM IODIDE SOLUTIONS AT 25°C

c (mol. SrI_2/l.)	$D_{Sr^{2+}}\times10^5$ (cm^2/sec.)
0.0038	0.788±0.002
0.0116	0.744±0.003
0.0125	0.762±0.012
0.0242	0.748±0.013
0.096	0.743±0.010
0.0985	0.734±0.003
0.2197	0.719±0.02
0.500	0.704±0.018
0.7245	0.681±0.008
0.985	0.630±0.017

Values of relative viscosity of strontium iodide solutions at 25°C are shown in Table III.

TABLE III. RELATIVE VISCOSITY OF STRONTIUM IODIDE SOLUTIONS AT 25°C

c (mol. SrI_2/l.)	η/η_0
0.001	0.995
0.01	0.993
0.1	1.012
0.2	1.033
0.4	1.059
0.6	1.096
0.8	1.139
1.0	1.186
1.2	1.248
1.4	1.322
1.6	1.391
1.8	1.469
2.0	1.588
2.2	1.741
2.4	1.884

Discussion

In the dilute solution the self-diffusion of an ion is mainly controlled by the relaxation of ionic atmosphere around the ion. On the basis of Onsager's limiting law for the diffusion coefficient[6], Gosting and Harned[7] derived an equation for the variation of self-diffusion coefficient of the ion with its concentration, which in the case of self-diffusion of the ion (chemical

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[5] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry", John Wiley & Sons, Inc., New York (1951), p. 77.

[6] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[7] L. J. Gosting and H. S. Harned, *J. Am. Chem. Soc.*, **73**, 159 (1951).

species 1) in its binary electrolyte (chemical species 1 and 2) solutions, may be put into the following form.

$$D_1=\frac{\boldsymbol{R}T\lambda^0_1}{|Z_1|\boldsymbol{F}^2}-2.694\times10^{16}\frac{\lambda^0_1|Z_1|\boldsymbol{F}}{3\boldsymbol{N}\varepsilon}\sqrt{\frac{4\pi}{\varepsilon\boldsymbol{R}T}}\times\left(1-\sqrt{d(\omega_1)}\right)\sqrt{\sum_i c_iZ_i^2} \qquad (3)$$

where, D_1 is the self-diffusion coefficient of the ion (in cm²/sec.), Z_1 and λ^0_1 are its number of the charge and limiting equivalent conductance (in coulomb/sec. × cm²/V.), respectively, c_i is the concentration of the i-th ion (in mol./l.), ε is dielectric constant of the solvent, and $\boldsymbol{R}$, $\boldsymbol{F}$, $\boldsymbol{N}$ and T are gas constant (in joule/deg. mol.), Faraday constant (in coulomb), Avogadro number and absolute temperature, respectively. $d(\omega_1)$ in Eq. 3 is given by

$$d(\omega_1)=\left(\frac{|Z_1|}{|Z_1|+|Z_2|}\right)\left(\frac{1}{2}+\frac{|Z_2|\lambda^0_2}{|Z_2|\lambda^0_1+|Z_1|\lambda^0_2}\right) \qquad (4)$$

For the self-diffusion of iodide ion and strontium ion in strontium iodide solutions we use[8)]

$$\lambda_{\mathrm{I}^-}=76.8$$
$$\lambda_{\mathrm{Sr}^{2+}}=59.46$$

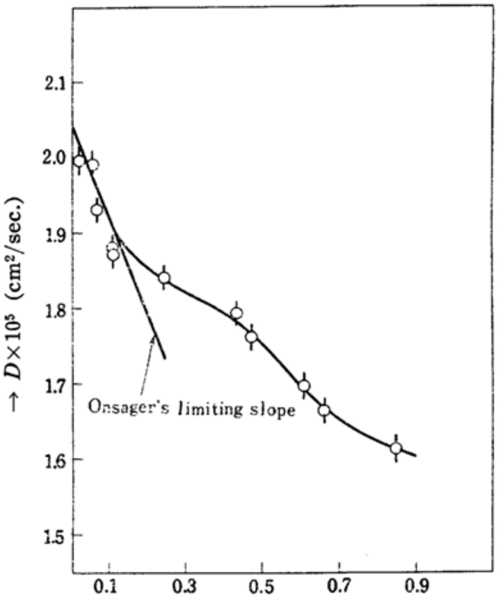

Fig. 2. Self-diffusion coefficient of I^- in SrI_2 solutions against square root of the concentration at 25°C.

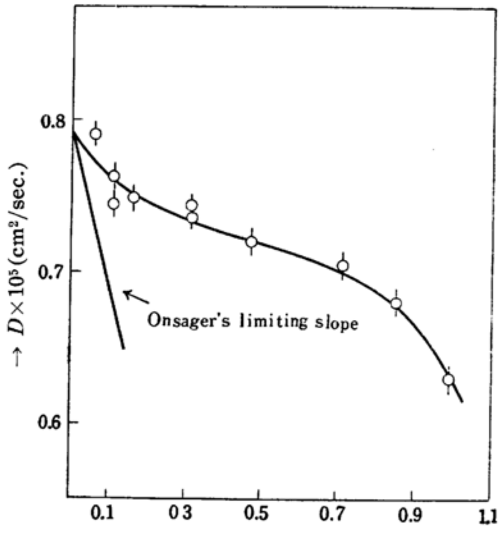

Fig. 3. Self-diffusion coefficient of Sr^{2+} in SrI_2 solutions against square root of the concentration at 25°C.

and we obtain the following equations by inserting the numerical values in Eq. 3:

$$D_{\mathrm{I}^-}\times10^5=2.045-1.12\sqrt{c} \qquad (5)$$

$$D_{\mathrm{Sr}^{2+}}\times10^5=0.792-1.04\sqrt{c} \qquad (6)$$

where, c is expressed in mol. SrI_2/l. These are limiting laws for the self-diffusion in the present case. In Figs. 2 and 3 are shown measured D_{I^-} and $D_{\mathrm{Sr}^{2+}}$ against $\sqrt{c}$, respectively. It is seen that the experimental data fit the limiting law fairly well.

At higher concentrations the situation is much more complicated. Of various factors which control the ionic self-diffusion three may be considered most important, i.e., the viscosity of the solution, the hydration of the diffusing ion (i.e., the interaction between ion and solvent) and the state of ionic atmosphere (i.e., the interaction between ions). The correction for viscosity of the solution is usually made simply by multiplying D with η/η_0. In Fig. 4 $D\eta/\eta_0$ for iodide ion is plotted against $\sqrt{c}$. The curve for iodide ion is approximated by two straight lines. The straight line of lower concentrations can be extrapolated exactly to the Nernst limiting value, D_0, while that of higher concentrations gives a lower value by extrapolation to the zero concentration. Mills and Kennedy[1)] showed that the $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for iodide ion in the solution of iodide of monovalent

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[8)] D. A. McInnes, "The Principles of Electrochemistry", Reinhold Publishers Corp., New York (1950), p. 342.

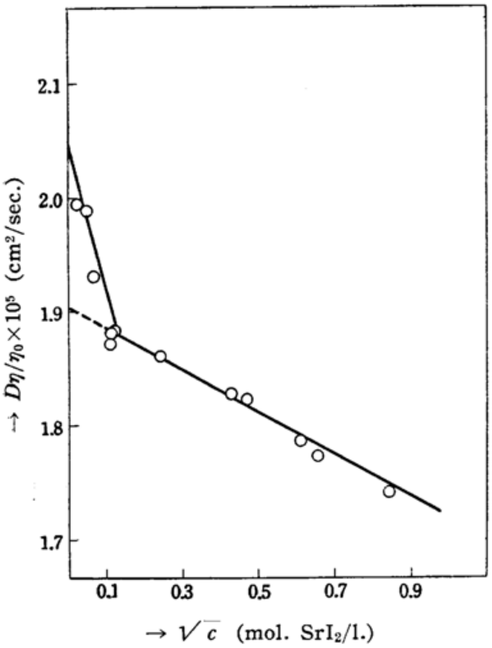

Fig. 4. $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for I^- in SrI_2 solutions at 25°C.

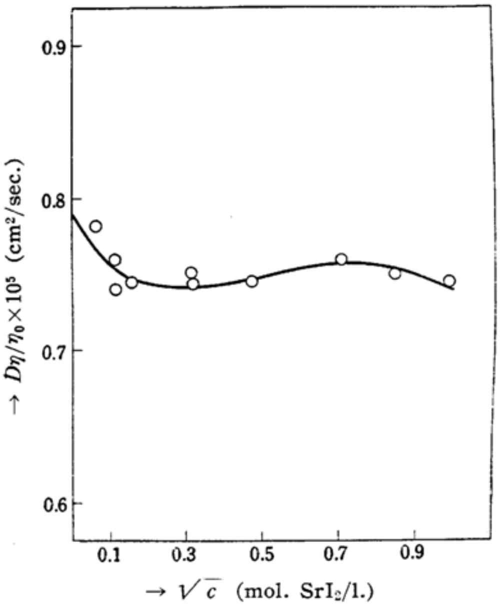

Fig. 5. $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for Sr^{2+} in SrI_2 solutions at 25°C.

metal or hydrogen is linear all through from low to considerably high concentrations and extrapolated to the Nernst limiting value. It is not perfectly evident why the self-diffusion of iodide ion in strontium iodide is markedly different from that in the iodides which Mills and Kennedy studied, but one might ascribe it to the difference in the state of ionic atmosphere around the diffusing iodide ion.

The $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for strontium ion in the solution of strontium iodide is shown in Fig. 5. This curve is much more complicated than and quite different in nature from the curve for iodide ion. It is well known that strontium ion is strongly hydrated, while iodide ion is "unhydrated". Matuura and Shimozawa[2)] applied an empirical equation to the self-diffusion of strongly hydrated ions, which is

$$D\eta/\eta_0 = D_0 - k_1\sqrt{c} + k_2 c \log c + k_3 c \qquad (7)$$

where, k_1, k_2 and k_3 are constants. Of these k_1 is a limiting slope $D\eta/\eta_0$ vs. $\sqrt{c}$ relation and can be calculated from Fig. 5. Eq. 7 may be checked by plotting

$$F(D) \equiv \frac{D\eta/\eta_0 - D_0 + k_1\sqrt{c}}{c} \qquad (8)$$

against $\log c$. In Fig. 6 this plot is shown. It is seen that Eq. 7 is a fair expression for the self-diffusion of strontium ion in strontium iodide solutions.

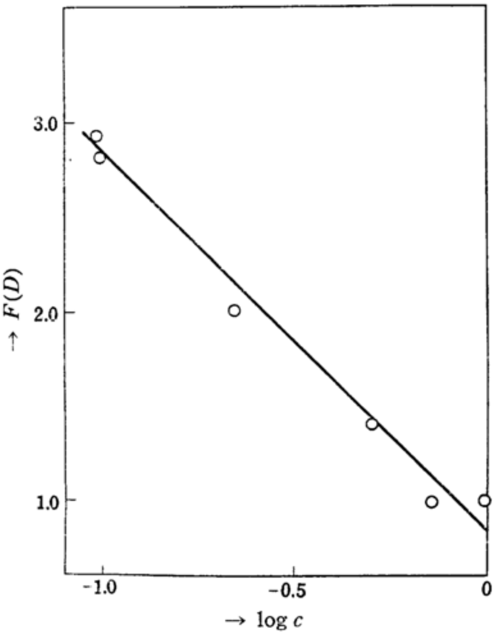

Fig. 6. $F(D)$ vs. $\log c$ relation for Sr^{2+} in SrI_2 solutions.

From the straight line in Fig. 6 the values of k_2 and k_3 are calculated as shown in Table IV. In the same table the data are given for the self-diffusion of strontium ion in strontium chloride solutions and of sodium ion in sodium iodide and sodium chloride solutions[2].

TABLE IV. VALUES OF k_2 AND k_3 FOR STRONTIUM AND SODIUM ION

System	k_2	k_3
Sr^{2+} in SrI_2	−1.98	0.84
Sr^{2+} in $SrCl_2$	−1.54	0.93
Na^+ in NaI	−0.67	0.24
Na^+ in NaCl	−0.51	0.35

It is clear from Table IV that the absolute values of both k_2 and k_3 are larger for strontium ion than for sodium ion. Since Eq. 7 is an empirical one, the physical meaning of k_2 and k_3 is not definitely given, but one may conclude that k_2 and k_3 are mainly concerned with the charge (and of course also with the hydration) and size of the diffusing ion.

Summary

The self-diffusion coefficient of iodide ion and strontium ion in aqueous strontium iodide solutions has been measured by a capillary method. It has been found that the Onsager's limiting equation can be applied to the self-diffusion of both ions. The $D\eta/\eta_0$ vs. $\sqrt{c}$ relation for iodide ion has been represented by two straight lines, while that for strontium ion has been shown by a much more complicated curve. The latter has been represented successfully by an empirical equation for strongly hydrated ions presented by Matuura and Shimozawa.

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