

## Tracer-diffusion in Liquids. II. The Self-diffusion as Sodium Ion in Aqueous Sodium Chloride Solutions<sup>1</sup>

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The self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions have been determined both by the diffusion tube method<sup>2</sup> and by the diaphragm cell method.<sup>3</sup> In the first method, in order to get enough intensity of  $\gamma$ -radiation to be measured, Jehle had to use a diffusion tube of 11 cm. inside diameter. With such a large diffusion tube it becomes extremely difficult to eliminate convection during the measurement. Later in a modification of Jehle's method,<sup>4</sup> Wang and Kennedy used a plastic cell which has tubes of 1.7 mm. inside diameter. They used a shearing mechanism to sample out the solution and measured the  $\beta$ -radiation after evaporating the sample solution to dryness. It is doubtful whether their method warrants complete elimination of convection. Furthermore, in their method a slight amount of grease used to lubricate the interfaces between plastic parts might be carried into the diffusion tube during the shearing process, causing the actual cross-sectional area of the tubes to be a little smaller than that estimated from geometric measurements. The diaphragm cell has the disadvantage that appreciable error in the measured value of diffusion coefficient may be introduced by the adsorption of ions on the large surface of the sintered glass disk.<sup>3</sup> Furthermore, Stokes showed<sup>5</sup> that the cell constant seemed to vary appreciably with the density gradient of liquid across the sintered glass disk unless internal stirring was used. Since no internal stirring has been used in diaphragm cell measurements of self-diffusion,<sup>6</sup> the reliability of the self-diffusion coefficients obtained by the diaphragm cell method becomes doubtful inasmuch as it is uncertain whether the cell-constant obtained by calibrating the cell with salt-diffusion measurement (where the density gradient is finite) can be regarded as equal to that for self-diffusion (where the density gradient is zero). However, the capillary method, which was first used by Anderson and Saddington<sup>7</sup> and later improved by Wang,<sup>1,3</sup> has no calibration difficulties because the dimensions of the uniform capillaries used are known. Moreover since the inside diameter of capillaries used (*ca.* 0.5 mm.) are still large as compared to that of the hydrated ions, it can easily be shown that the possible adsorption error in 0.005 formalar-weight per liter solution is less than 0.2% even if we assume that the entire surfaces of the capillaries are covered by a mono-

molecular layer of ions. The diffusion potential should be negligible if solutions inside and outside of each capillary have been carefully prepared to be of equal chemical concentration. The convection error in these capillaries has been shown to be negligible in Paper I of this series. Thus it seems desirable to redetermine the self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions by the capillary method.

### Results

In the present work the self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions of concentration between 0.005 to 5.000 formalar-weight per liter at 25° have been determined by the capillary method. The principle and technique of the experimental method used have already been described in Paper I<sup>1</sup> of this series. The results are listed in Table I.

TABLE I  
TRACER-DIFFUSION COEFFICIENTS OF Na<sup>+</sup> IN NaCl(AQ.) AT 25°

Concentration of NaCl solution (formalar-weight per liter)	$D \times 10^8$ (cm. <sup>2</sup> /sec.)
0.005	1.32 ± 0.02
.010	1.31 ± .03
.050	1.30 ± .02
.100	1.31 ± .02
.1750	1.313 ± .021
.200	1.32 ± .03
.300	1.35 ± .038
.350	1.34 ± .035
.500	1.32 ± .02
.625	1.31 ± .03
1.000	1.25 ± .03
2.000	1.13 ± .02
3.000	1.02 ± .025
4.000	0.904 ± .016
5.000	0.796 ± .018

### Discussion

The Onsager equation<sup>9</sup> for tracer diffusion is

$$D_i = \omega_i [kT - (\kappa e_i^2 / 3D) (1 - \sqrt{d(\omega_i)})] \quad (1)$$

with

$$\omega_i = \frac{RT \lambda_i^0}{|Z_i| \bar{c}^2} \quad (2)$$

$$d(\omega_i) = \frac{\bar{\lambda}}{\bar{\Gamma}} \sum_j \frac{t_j}{(\omega_i + \omega_j)} \quad (3)$$

$$\bar{\lambda} = \sum_j n_j e_j^2 \omega_j \quad (4)$$

$$t_i = n_i e_i^2 \omega_i \bar{\lambda} \quad (5)$$

$$\kappa^2 = (4\pi / DkT) \bar{\Gamma} \quad (6)$$

$$\bar{\Gamma} = \sum_j n_j e_j^2 \quad (7)$$

where  $D_j$  is the diffusion coefficient of tracer ions of the  $j$ th kind in a given salt solution,  $e_i$  is the absolute electric charge,  $Z_i$  the charge in electronic units of ion  $i$ ,  $\kappa_i$  is the inverse mean radius of ion-atmospheres,  $n_i$  the concentration in number of ions per cc.,  $\lambda_i^0$  the limiting ionic conductance of ion  $i$ ,  $D$  the dielectric constant of solvent,  $k$  the Boltz-

(9) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(1) Paper I, *THIS JOURNAL*, **74**, 1182 (1952).

(2) L. Jehle, Ph. D. Thesis, University of California, Berkeley, 1938.

(3) A. W. Adamson, J. W. Cobble and J. M. Nielson, *J. Chem. Phys.*, **17**, 740 (1949).

(4) J. H. Wang and J. W. Kennedy, *THIS JOURNAL*, **72**, 2080 (1950).

(5) R. H. Stokes, *ibid.*, **72**, 763, 2243 (1950).

(6) When the present note was in press an article by Nielsen, Adamson and Cobble appeared (*ibid.*, **74**, 446 (1952)). These authors measured self-diffusion by means of diaphragm cells with internal stirring. They also showed that both sintered-glass and stainless steel diaphragms may cause serious errors in diffusion measurements due to surface adsorption.

(7) J. S. Anderson and K. Saddington, *J. Chem. Soc.*, 5381 (1949).

(8) J. H. Wang, *THIS JOURNAL*, **73**, 510 (1951); *ibid.*, **73**, 4181 (1951).

mann constant,  $R$  the gas constant,  $\mathcal{F}$  the Faraday constant, and  $T$  the absolute temperature.

If we express  $\lambda_i^0$  in (coulomb/sec.) (cm.<sup>2</sup>/volt),  $\mathcal{F}$  in coulombs,  $R$  in joules per ° C. per mole, and replacing  $n_i$  by  $c_i$  which denotes concentration in moles per liter, equation (1) can be written as

$$D_i = \frac{RT \lambda_i^0}{|Z_i| \mathcal{F}^2} - \frac{\lambda_i^0 |Z_i| \mathcal{F}}{3N\mathcal{D}} \times 2.694 \times 10^{18} \sqrt{\frac{4\pi}{\mathcal{D}RT}} [1 - \sqrt{d(\omega_i)}] \sqrt{\sum_i c_i Z_i^2} \quad (8)$$

For the diffusion of tracer amounts of radioactive ions of chemical species No. 1 in salt solution containing non-radioactive ions of chemical species No. 1 and No. 2, we have

$$c_1 |Z_1| = c_2 |Z_2| \quad (9)$$

For uni-univalent electrolyte  $|Z_1| = |Z_2| = 1$ , and equation (3) can be written as

$$d(\omega_1) = \frac{1}{2} \left[ \frac{1}{2} + \frac{\lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right] \quad (10)$$

If we take  $\lambda_1^0 = 50.11$  for the sodium ion and  $\lambda_2^0 = 76.36$  for the chloride ion<sup>10</sup> at 25°, equations (8) and (10) can be combined to give

$$D \times 10^6 = 1.334 - 0.268 \sqrt{c} \quad (11)$$

for the diffusion of tracer amount of radioactive sodium ion in aqueous sodium chloride solutions at 25°.

The self-diffusion coefficients of sodium ion in aqueous sodium chloride solutions at 25° listed in Table I are plotted *vs.* the square root of concentration in Fig. 1. The straight line in the dilute concentration region represents equation (11) according to Onsager's theory. Figure 1 indicates that the measured self-diffusion coefficients agree with the values predicted by the Onsager equation within experimental uncertainty at concentrations below 0.04 formalar-weight per liter. Above 0.05 formu-

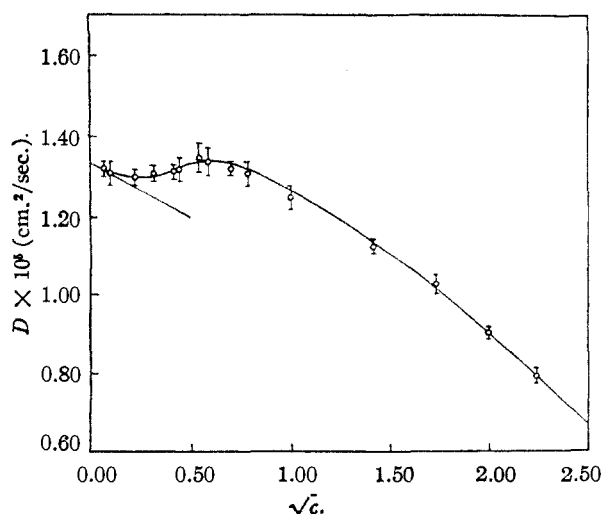


Fig. 1.—Self-diffusion coefficient of Na<sup>+</sup> in aqueous sodium chloride solutions at 25°.

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Appendix A.

lar-weight per liter the self-diffusion coefficient increases with increasing salt concentrations, reaches a maximum value near 0.4 formalar-weight per liter and then starts again to decrease with increasing salt concentration. The general shape of the present  $D$  *vs.*  $\sqrt{c}$  curve resembles that for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution, but the peak of the  $D$  *vs.*  $\sqrt{c}$  curve obtained in the present work appears at  $c = 0.4$  instead of at  $c = 1.3$  for the diffusion of tracer amount of sodium ion in aqueous potassium chloride solution. A possible explanation is given below.

In an aqueous potassium chloride solution containing tracer amount of sodium ion, the potassium ions, because of their smaller radii, tend to have closer association with chloride ions than the tracer amount of sodium ions. Consequently the nearest chloride ions surrounding each sodium ion are pulled away from the sodium ion by the potassium ions. Because of this effect the average center to center distance between each of the tracer amount of sodium ions and its nearest chloride ions in aqueous potassium chloride solution becomes larger than the corresponding distance in a pure sodium chloride solution of the same chemical concentration. Consequently, the forces that produce the maximum in the  $D$  *vs.*  $\sqrt{c}$  curve for the tracer-diffusion of sodium ion in potassium chloride solution should come into play and produce a similar effect on the shape of  $D$  *vs.*  $\sqrt{c}$  curve for the self-diffusion of sodium ion in sodium chloride solution at a more dilute concentration. The large difference between the two concentrations at the maxima of the two  $D$  *vs.*  $\sqrt{c}$  curves is not too startling because for a given directional distribution of ions, the average distance between nearest neighbors varies inversely with  $c^{1/2}$ . However, in view of the complexity of the present problem, it appears unlikely that a quantitative correlation of these two concentrations can successfully be made before a satisfactory theory of liquid water has been formulated.

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### Tracer-diffusion in Liquids. III. The Self-diffusion of Chloride Ion in Aqueous Sodium Chloride Solutions

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The self-diffusion coefficients of chloride ion in aqueous sodium chloride solutions at 35° have been determined by Jehle.<sup>1</sup> However, extrapolation of Jehle's values yields a limiting tracer-diffusion coefficient at infinite dilution for chloride ion which is almost 20% higher than Nernst's limiting value as calculated from conductance and transference data. In view of the extensive work done by Harned and

(1) L. Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.