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A Method for the Determination of Mutual Diffusion Coefficients of Electrolytes in Water by Means of Conductivity Measurements

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A method for determining diffusion coefficients of electrolytes was studied by the use of a conductance cell made of a Pyrex glass tube (4—7 cm in diameter and 6.5 cm in length). A pair of platinized platinum electrodes are sealed into the tube at a position 10 mm below the top of the glass tube. The diffusion was carried out from solution in the cell to an outer solvent, and the rate was measured from the decrease in conductance at a fixed position in the cell. In the graphical relation between the measured diffusion coefficient and the time, the differential diffusion coefficient at the initial concentration of the diffusing solution was estimated by extrapolation of the linear portion of the plot to time→0. The differential diffusion coefficients obtained in 0.1 mol dm^{-3} solutions at 25 °C were as follows: HCl, $(3.12\pm0.08)\times10^{-5}$; KI, $(1.909\pm0.020)\times10^{-5}$; NaCl, $(1.520\pm0.016)\times10^{-5}$; $\frac{1}{2}Na_2SO_4$, $(1.059\pm0.028)\times10^{-5}$; $CuSO_4$, $(0.610\pm0.033)\times10^{-5}$ cm^2 s^{-1}.

The diffusion coefficients of electrolytes have been measured by a number of different methods. For example, the rate of diffusion from solution to solvent through a porous plate is measured.[1] The widely used methods such as the schlieren or the capillary method[2] were carried out on a system with a sharp boundary between the solution and solvent at the start of diffusion. A method for the determination of the diffusion coefficient of electrolytes by means of conductance measurements was already reported by H. S. Harned *et al.*[3] The apparatus is complicated because it has two electrode couples and also a shearing mechanism for the formation of the boundary between solution and solvent. Further, the measurement must be extended over several days. The capillary method is applied to the measurement of self-diffusion coefficients of various ions or molecules in water by means of isotopic tracers; the inner diameter of the cell should be very small in order to avoid random flow in systems with very small density-gradients. It was shown in a previous paper[4] that the system of sharp density-gradient is resistant to convection or to random flow. If the capillary method is applied to the measurement of mutual-diffusion coefficients, the inner diameter may be larger than that of the capillary used for measuring the self-diffusion coefficient.

The diffusion coefficient of an electrolyte in agar or gelatin gel had been measured by means of a glass tube cell, which is a type of conductance cell, developed in this laboratory.[5,6] The diffusion cell will be applied to the measurement of the mutual-diffusion coefficient of an electrolyte in water. This apparatus has a couple of electrodes, and the boundary between solution and solvent is formed by pouring solvent into a test tube outside the cell filled with solution. Consequently, the apparatus or the mechanism is simple, and the measurement is carried out within ten hours. In the present paper, we deal with cells of different inner diameters and apply them to the measurement of diffusion coefficients in water. In addition, the differential diffusion coefficient will be obtained by extrapolating the measured diffusion coefficients to time $t\to0$.

Principle of the Method

The diffusion cell is a conductance cell which is made of a glass tube equipped with platinized platinum wires. If the cell is filled with a solution and placed vertically in water, the solute diffuses into the outer water with the elapse of time. The diffusing solution in the cell gradually acquires a concentration gradient with time. The decrease in conductance at a fixed position in the cell can then be measured with the electrodes. The measured conductance is converted to concentration by a calibration curve. Under these conditions, the equation for diffusion in one dimension is

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2}, \tag{1}$$

where c is the concentration of the electrolyte at time t, D the diffusion coefficient, x the coordinate along which diffusion takes place. For this diffusion experiment, it may be assumed that (1) the concentration outside the cell is infinitely low during the diffusion experiment, and (2) the cell is infinite in length. Then the following equation is obtained by solving Eq. 1.

$$\frac{c_e}{2c_0}=\frac{1}{\sqrt{2\pi}}\int_0^{x/\sqrt{2Dt}}\exp(\xi^2/2)\mathrm{d}\xi, \tag{2}$$

where c_e is the concentration of the diffusing solution at the electrodes, c_0 the initial concentration at the electrodes, and x the distance between the electrodes and the open end of the cell.

Next we will discuss the stability of the concentration gradient in the cell. The stability is related to the following factors: (1) the inner diameter of cell, (2) the density gradient in the cell, (3) the temperature variation, and (4) the vibration of the apparatus. As the inner diameter is reduced, the concentration gradient becomes stable independently of other factors. The density gradient is related to the concentration of diffusing solution or the kind of solute. In a previous paper it was shown that the intermediate layer between the upper and the lower convection keeps sharp stable density-gradient, when a two-layer system which consists of water (upper layer) and an aqueous solution (lower layer) is heated from one side and cooled from the opposite side.[4] The small temperature-variation during the diffusion experiment may not deform the concentration gradient, because this method is especially applied to the system of a sharp density-gradient in the cell of small inner-diameter. The effect of vibration of the apparatus will also become small for a cell of small inner-diameter and for a system of sharp density-gradient. In spite of the above discussion, there will be turbulence of the concentration gradient in the vicinity of the top of the cell, especially during the pouring of the solvent. Therefore, the distance x_m measured by use of vernier calipers may not be appropriate for calculating the diffusion coefficient; then the effective distance x_e should be applied to Eq. 2. When $c_e\ (2c_o)^{-1}$ at time t is measured, the value of $x/(2Dt)^{0.5}$ is calculated from Eq. 1, and then the distance x is proportional to the square root of diffusion coefficient D. Then the effective x_e can be evaluated from

$$X_e = x_m(D/D_m)^{0.5}. \tag{3}$$

Here, D_m is the diffusion coefficient calculated from Eq. 2 by the use of x_m, and D is the true value of the diffusion coefficient.

Experimental

Materials. All the chemicals were of reagent grade, and were used without further purification. Anhydrides were dried at the following temperatures: KCl, 150 °C; NaCl, 250 °C; KI and Na_2SO_4, 110 °C. The salts were weighed out to give the solutions of indicated concentrations. The HCl solution was prepared by dilution after the determination of concentration by alkalimetry. Water used was distilled after passage through an ion-exchange column. Just prior to use, the water was boiled to remove dissolved gas. The solution was heated near to the boiling point in an Erlenmeyer flask with a glass tube (2 mm × 140 cm) through a rubber stopper, and then the solvent loss was within 0.1%.

Apparatus and Procedure. The diffusion cell is similar to that described previously.[6] The apparatus is shown in Fig. 1. The diffusion cell is made of a Pyrex glass tube (6.5 cm in length) equipped with platinized platinum electrodes at a position 10 mm below the top of the glass tube. The electrodes are wires 0.3 mm in diameter, 1 mm in length and 1.5 mm in distance between the wires.

A solution was poured into the cell, and the cell was set in the test tube (100 mm × 27 mm) in which water was previously placed so as to reach slightly below the top of the cell. The test tube was immersed vertically in a thermostat (Yamato BKR-41) at 25±0.05 °C. After about 20 min, water thermostated at 25 °C was poured into the test tube up to about 15 mm above the top of cell at a flow rate of 1.5 cm^3 min^{-1}, and the diffusion started.

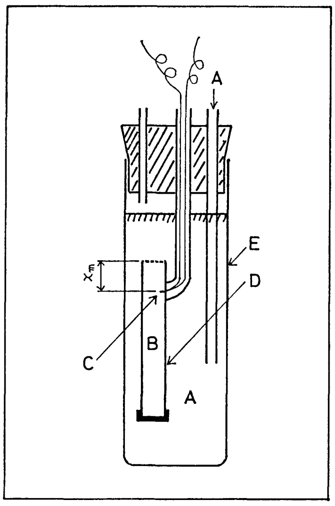

Fig. 1. Apparatus for measuring diffusion.
A: Water, B: diffusing solution, C: electrodes, D: conductance cell, E: test tube.

Measurement of Conductance. The conductance was measured with a universal bridge (Yokogawa-Hewlett Packard 4255A) equipped with a variable condenser (0—1 μF).

Results and Discussion

Determination of Effective Distance. The diffusion experiment was carried out for 0.1 mol dm^{-3} KCl, and the apparent diffusion coefficient was calculated from Eq. 2 by the use of the measured distance, x_m, between the electrodes and the top of the cell. The apparent differential diffusion coefficient, D_m, at 0.1 mol dm^{-3} KCl was obtained by means of an extrapolation method which is described later. The effective distance, x_e, was determined by substituting x_m, D_m, and D (the value in the literature[7,8]) instead of the true value) into Eq. 3, as is shown in Table 1. The ratios x_e/x_m were almost constant for cells of 4 mm in inner diameter, and the mean value was 104.5%. This fact may be taken to indicate that a small limited-amount of the solution is present on top of the cell, and that the concentration gradient is stable.

Differential Diffusion Coefficient. The diffusion coefficient was measured for different electrolytes. The typical relation between the diffusion coefficient D and the time t is shown in Fig. 2. The D values change slightly with time. The increase in D for Na_2SO_4 or $CuSO_4$ may be due to the dependence of diffusion coefficient on the concentration or due to the error caused by the vibration of apparatus or by the temperature variation. The decrease for KCl or NaCl seems to be caused by the increase of the concentration in the test tube in spite of assumption (1) for Eq. 2 or by the obstruction of electrodes (platinum wires) to the diffusion. The D with no such effects may be obtained by extrapolation of the linear portion of the plot to $t \to 0$. The diffusion coefficient D_e esti-

TABLE 1. APPARENT DIFFUSION COEFFICIENTS (D_m) AND EFFECTIVE DISTANCES (x_e) FOR DIFFERENT CELLS[a)]

Cell No.	x_m	Inner diameter	$D_m \times 10^5$ [b)]	x_e/x_m [c)]
	cm	mm	cm^2 s^{-1}	%
1	1.073	4	1.712±0.010	103.8
2	1.105	4	1.683±0.025	104.7
3	1.028	4	1.663±0.021	105.3
4	1.085	4	1.689±0.014	104.5
5	1.069	4	1.695±0.019	104.3
6	1.005	6	1.688±0.022	104.5
7	1.094	7	1.754±0.031	102.5
8	1.099	7	1.802±0.030	101.2

a) Measurements were carried out for KCl in 1.000×10^{-1} mol dm^{-3} soln at 25 °C. b) Average and standard deviation σ_{n-1} of three measurements. c) Calculated from Eq. 3 by substituting $D = 1.844 \times 10^{-5}$ cm^2 s^{-1}.

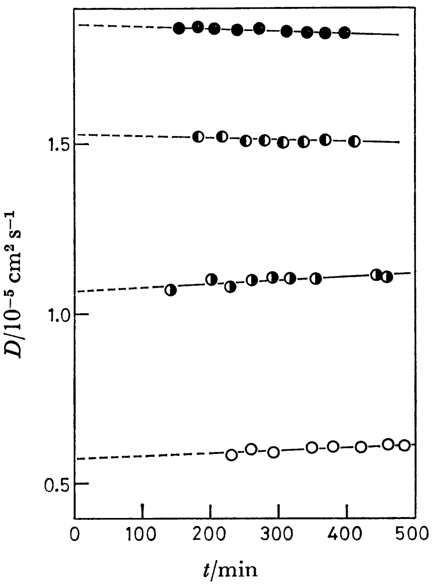

Fig. 2. Plots of D *vs.* t.
The measurements were carried out for the electrolytes in 1.000×10^{-1} mol dm^{-3} solns at 25 °C. ●: KCl, ◐: NaCl, ◑: ½Na_2SO_4, ○: $CuSO_4$.

mated by extrapolation is regarded as the differential diffusion coefficient at the initial concentration of the diffusing solution.

Inner Diameter of Cell. Diffusion experiments were carried out for cells of different inner diameters, and the results are listed in Table 1. The standard deviations of D_e estimated for the cells of large inner diameter (7 mm) are large, compared with the values obtained for the cells of small inner diameters (6 and 4 mm). Therefore, other experiments were carried out for the cells of 4 mm in inner diameter.

Accuracy of the Method. The diffusion coefficient, D_e, estimated by the extrapolation and the diffusion coefficient, D_r, taken from other literature are given in Table 2. If the diffusion coefficient is small, the decrease in concentration at the electrodes during the diffusion experiment is also small, and the error in D_e may become large. For example, the c_e/c_0 was 0.95 after 300 min for the diffusion of $CuSO_4$. The deviations of the D_e values from each D_r were within 2.5% except for $CuSO_4$.

TABLE 2. DIFFUSION COEFFICIENTS (D_e) OF DIFFERENT ELECTROLYTES IN 1.000×10^{-1} mol dm^{-3} SOLNS AT 25 °C

Electrolyte	$D_e \times 10^5$ [a)] cm^2 s^{-1}	$D_r \times 10^5$ cm^2 s^{-1}	D_e/D_r %
HCl	3.12 ±0.08	3.05[b)]	102.2
KI	1.909±0.020	1.865[b)]	102.4
NaCl	1.520±0.016	1.483[b)]	102.5
½Na_2SO_4	1.059±0.028		
$CuSO_4$	0.610±0.033	0.580[c)]	105.2

a) Average and standard deviation σ_{n-1} of four measurements. b) Ref. 7. c) Interpolated from the data in Ref. 9.

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