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Diffusion Coefficients of Bolaform Electrolytes in Aqueous Solution

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The diffusion coefficients of sodium salts of *m*-benzene disulfonate, 1,5-naphthalenedisulfonate, 1,2-ethanedisulfonate, and 1,4-butanedisulfonate in aqueous solutions were measured at 25°. The concentration dependence of the diffusion coefficients for sulfonates decreased with increasing charge distance and was smaller than that of the corresponding ordinary 2 : 1 electrolytes. The concentration dependence of diffusion coefficient for sodium *m*-benzenedisulfonate was the largest. It is shown that bolaform electrolytes behave like normal 1 : 1 electrolytes in the concentration range where the ion atmosphere around each charged group is independent.

Bolaform electrolytes are a peculiar type of 2 : 1 electrolyte and the physico-chemical properties of their aqueous solutions are unusual. However, the cause of this peculiarity is not yet clarified. It was shown by Atkinson, Yokoi and Hallada[1] that the electrolytic conductances of bolaform electrolytes (*m*-benzenedisulfonate, 4,4′-biphenyl-disulfonate *etc.*) in aqueous solutions were interpreted by means of the Fuoss-Onsager equation. According to them, these behave as a spherical 2 : 1 strong electrolyte, irrespective of the position of sulfonic groups and the distance between them. Thomson, Rice and Nagasawa[2] found that the diffusion coefficients of potassium salts of *p*-benzene and 4,4′-biphenyldisulfonates in aqueous solutions show no concentration dependence. In contrast to their behavior in conductance, the diffusion coefficients of bolaform electrolytes are not explained by the theory of the ordinary strong electrolyte.

Bonner and Rogers,[3] and Bonner, Rushing and Torres[4] obtained the osmotic and activity coefficients for several bolaform electrolytes in which two sulfonic groups were separated by varying distance. They found that the thermodynamic properties of bolaform electrolytes markedly differed from those of normal electrolytes, especially in dilute solutions.

Thus, it is expected that the diffusion coefficients of bolaform electrolytes depend on the distance between the ionized groups and their positions. For the sake of confirmation, the diffusion coefficients were measured for sodium salts of *m*-benzenedisulfonate (*m*-Na_2BDS), 1,5-naphthalenedisulfonate (Na_3NDS). 1,2-ethanedisulfonate (Na_2EDS) and 1,4-buthanedisulfonate (Na_2BuDS) in aqueous solutions at 25°.

Experimental

The purification of sulfonates has been described elsewhere.[5]

The diffusion experiments were performed at 25±0.01° using a Spino Model-diffusion apparatus a Rayleigh interferometer. The standard 11 ml cell was used. For a typical run, nine photographic exposures were made at intervals ranging from 15 min. to 3 hr. Kodak type M glass photographic plates (4 in. by 5 in.) were used. The concentration difference in the solution on both sides of the diffusion boundary was so adjusted that the total number of Rayleigh fringe was 50 or 60. The procedure was the same as already reported.[6]

Deionized water was employed as the solvent for these systems. All the solutions were prepared by weight. Weighing was corrected to vacuum. The molar concentrations of solutions were calculated by means of the solution densities, which were mesurred with a 30 ml sprengel pycnometer at 25±0.01°.

To obtain the limiting diffusion coefficients, the conductances of the solutions were measured. The procedure was the same as that described.[5]

Results and Discussion

The mean concentration of each diffusion experiment and the corresponding value of diffusion coefficient are given in the Table. The diffusion coefficient for each salt at infinite dilution was calculated from the limiting mobility by the Nernst equation.

The values of the limiting equivalent conductances, $\lambda°$, of aqueous Na_2EDS and Na_2BuDS solutions determined from the plots of equivalent conductance against $(\text{normality})^{1/2}$, are 114.0 and 103.2 $\text{cm}^2\ \text{ohm}^{-1}\ \text{equiv}^{-1}$, respectively. It is not necessary to take into account the formation of ion-pair for the sulfonates. The values of $\lambda°$ for *m*-Na_2BDS and Na_2NDS were taken from the works of Atkinson, Yokoi and Hallada,[1] and Eloworthy,[7] respectively.

The diffusion coefficient of 2 : 1 type electrolyte in an aqueous solution can be written in the form[8]

$$D = (D_0+\Delta_1)\left(1+c\frac{\mathrm{d}\ln y}{\mathrm{d}c}\right) \tag{1}$$

where D_0 is the Nernst limiting value of the diffusion coefficient, c the molarity, and y the activity coefficient in the molarity scale. Δ_1 is the first-order electrophoretic term and is expressed by the following equation for aqueous solutions at 25°

$$\Delta_1 = -8.07\times10^{-6}\frac{(z_1\lambda_2{}^0+z_2\lambda_1{}^0)^2}{\lambda_0{}^2z_1z_2}\cdot\frac{\sqrt{I}}{1+0.3291\,a\sqrt{I}} \tag{2}$$

where I is the ionic strength, λ_1 and λ_2 are the limiting

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[1] G. Atkinson, M. Yokoi, and C. J. Hallada, *J. Amer. Chem. Soc.*, **83**, 1570 (1961).

[2] G. Thomson, S. A. Rice, and M. Nagasawa, *ibid.*, **85**, 2537 (1963).

[3] O. D. Bonner and O. C. Rogers, *J. Phys. Chem.*, **65**, 981 (1961).

[4] O. D. Bonner, C. Rushing, and A. L. Torres, *ibid.*, **72**, 4290 (1968).

[5] H. Uedaira and H. Uedaira, This Bulletin, **37**, 1885 (1964).

[6] H. Uedaira and H. Uedaira, *ibid.*, **42**, 2140 (1969).

[7] P. H. Eloworthy, *J. Chem. Soc.*, **1962**, 3718.

[8] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London (1959).

TABLE. DIFFUSION COEFFICIENTS OF BOLAFORM ELECTROLYTES IN WATER AT 25°

Electrolytes	$c\times 10^2$ (mol/l)	$D\times 10^5$ (cm²/sec)
m-Na_2BDS	0	1.089
	0.7859	1.000_5
	2.3033	0.967_4
	3.8024	0.956_5
	5.4785	0.945_8
	9.4533	0.932_3
	14.8556	0.930_0
	19.3046	0.927_2
	21.9850	0.927_2
Na_2NDS	0	1.015
	0.8284	0.938_1
	2.3180	0.915_0
	3.5434	0.904_8
	4.9252	0.898_1
	6.0324	0.892_5
	9.8049	0.887_8
	11.4480	0.886_2
Na_2EDS	0	1.121
	1.0305	1.039_5
	2.4100	1.011_9
	5.7150	0.997_5
	12.0290	0.991_0
	15.1731	0.989_1
Na_2BuDS	0	1.029
	0.8123	0.967_9
	2.4649	0.941_3
	4.1902	0.931_2
	8.8209	0.917_2
	16.3539	0.911_1

mobilities of cation and anion, respectively, and z_1 and z_2 are the valencies of cation and anion, respectively. a is the parameter and its value is determined from the activity coefficient data.[8]

The values of the molal activity coefficients were obtained experimentally only for m-Na_2BDS and Na_2EDS.[3,4] In general, the activity coefficient of an electrolyte with a large ionic radius is not given by the Debye-Hückel formula. We used the following expression of the rational activity coefficient for 2 : 1 electrolyte solutions at 25°.[8]

$$\ln f = -\frac{4.08\sqrt{c}}{1+0.57\,a\sqrt{c}} + bc \tag{3}$$

where a and b are the constants adjustable to fit the experimental curve.

Using the molal activity coefficient data,[3,4] and the densities, we obtain the following equation of the rational activity coefficients:

$$\ln f = -\frac{4.08\sqrt{c}}{1+3.899\sqrt{c}} + 0.0089\,c \quad (c<0.5\,\mathrm{mol/l}) \tag{4}$$

for m-Na_2BDS solution, and

$$\ln f = -\frac{4.08\sqrt{c}}{1+2.256\sqrt{c}} + 0.335\,c \quad (c<0.5\,\mathrm{mol/l}) \tag{5}$$

for Na_2EDS solution. An HITAC 8400 computer was used to apply the least square method to the data. The values of a in Eq. (3) for m-Na_2BDS and Na_2EDS are 6.84 and 3.96 A, respectively. Thus the theoretical equation for the diffusion coefficient of m-Na_2BDS in aqueous solution is

$$D\times 10^5 = \left(1.089-\frac{1.480\sqrt{c}}{1+3.899\sqrt{c}}\right) \times\left[1+0.0089\,c-\frac{2.04\sqrt{c}}{(1+3.899\sqrt{c})^2}\right] \tag{6}$$

Similarly, the equation for the diffusion coefficient of Na_2EDS in aqueous solution is

$$D\times 10^5 = \left(1.121-\frac{1.448\sqrt{c}}{1+2.256\sqrt{c}}\right) \times\left[1+0.335\,c-\frac{2.04\sqrt{c}}{(1+2.256\sqrt{c})^2}\right] \tag{7}$$

The theoretical curves of diffusion coefficients for m-Na_2BDS and Na_2EDS are given in Figs. 1 and 2. For the sake of comparison, the experimental curves of diffusion coefficients for m-Na_2BDS and Na_2EDS are included in the Figures. In both cases, the

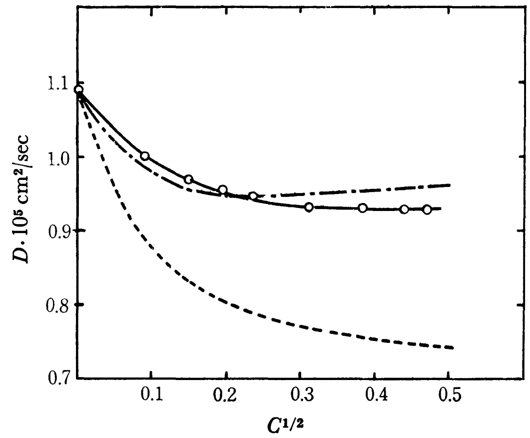

Fig. 1. Diffusion coefficients of m-Na_2BDS in aqueous solution.
—○—: in water, ——: Nernst-Hartley equation, ------: Eq. (6).

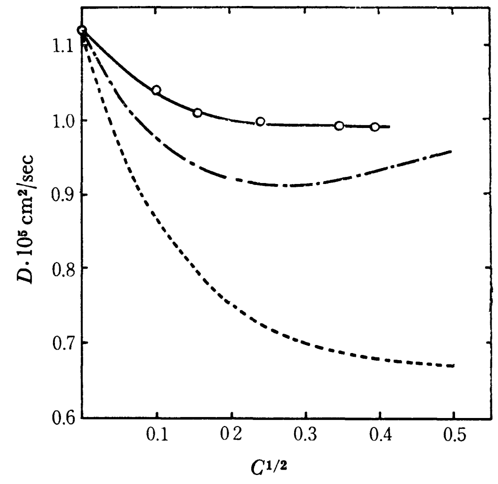

Fig. 2. Diffusion coefficients of Na_2EDS in aqueous solution.
—○—: in water, ——: Nernst-Hartley equation, ------: Eq. (7).

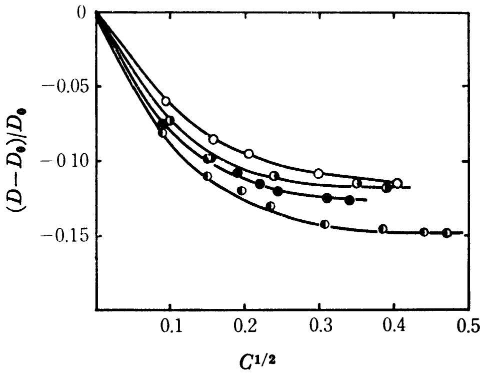

Fig. 3. Relative diffusion coefficients of sodium sulfonates in aqueous solution.
—○—: Na_2BuDS, —◑—: Na_2EDS, —●—: Na_2NDS, —◐—: m-Na_2BDS.

experimental values of diffusion coefficients are larger than the calculated values. That is, the concentration dependencies of the experimental values are remarkably smaller than those expected from Eqs. (6) and (7). A similar situation is expected also for Na_2NDS and Na_2BuDS.

From Eqs. (1), and (2), and (3), the concentration depedence of the diffusion coefficient decreases with increasing ionic radius, since parameter a is proportional to the ionic radius. Fig. 3 shows the relation $(D\text{-}D_0)/D_0$ against $c^{1/2}$ for various sulfonates in aqueous solutions. The ionic radius dependence of the diffusion coefficient holds for the aromatic and the aliphatic homologues, but the concentration dependence of the diffusion coefficient of Na_2EDS is smaller than that of Na_2NDS.

The experimental diffusion coefficients for these sulfonates show a tendency to approach constant values (Fig. 3), in contrast to normal electrolytes. The concentrations (c_t) at which the diffusion coefficints become constant are in the region 0.09∼0.16 mol/l. The value of c_t for m-Na_2BDS is the largest.

As Eqs. (4) and (5) well reproduce the experimental values of activity coefficients, the chief discrepancy between the experimental and calculated values of the diffusion coefficients is caused by the overestimation of electrophoretic effect in Eq. (1).

On the assumption that the center of negative charge of a sulfonic group is located at the sulphur atom, the distance between two sulfonic groups are found to be 4.6 for Na_2EDS and m-Na_2BDS, and 7 A for Na_2BuDS and Na_2NDS. Only at an extreme dilution where $1/\kappa > R$, it is appropriate to assume that the bolaform ion is divalent and that the ion atmosphere is spherically symmetric. R is the charge distance of sulfonate ion and κ has the usual meaning. Atkinson, Yokoi and Hallada[1] explained the electrolytic conductances of m-Na_2BDS in aqueous solution by means of the Fuoss-Onsager equation for the spherical 2 : 1 strong electrolyte. The concentration range of their experiments was $0\sim45\times10^{-4}$ mol/l. At the concentration 45×10^{-4} mol/l, $1/\kappa$ is 26 A, thus $1/\kappa > R$. However, under experimental conditions of most diffusion measurements, we have $1/\kappa < R$, as the concentration range is 0,01∼0,2 mol/l (the concentrations corresponding to 4.6 and 7 A are 0.145 and 0.0629 mol/l, respectively). Under these conditions, Eq. (1) does not hold. Thus, it is a reasonable to assume that the ion atmosphere about each charge is almost independent. Rice[9] showed that the electrophoretic effect for a bolaform ion was just twice that for an oridnary ion. The absolute value of this additional retarding effect increases with increasing concentration. However, Figs. 1 and 2 show that the effect of Δ_1 in Eq. (1) is overestimated. Thus Rice's theory not hold either, in which the retarding effect based on the asymmetry of the ion atmosphere is added to Δ_1 of Eq. (1).

In the diffusion of a single electrolyte, cation and anion should diffuse with the same final velocity. When the ion atmosphere about each ionized group is almost independent at the concentration $1/\kappa < R$, the motion of bolaform electrolyte approximates that of 1 : 1 electrolyte. Therefore, it is postulated that the electrophoretic effect on the bolaform electrolyte is the same as that on 1 : 1 electrolyte. For 1 : 1 electrolyte, this effect is expressed by the following relation.

$$\Delta_1 = -8.07\times10^{-6}\frac{(\lambda_1{}^0-\lambda_2{}^0)^2}{\lambda_0{}^2}\cdot\frac{\sqrt{c}}{1+\kappa a} \tag{8}$$

Thus, Δ_1 of the right hand side in Eq. (1) should be expressed by Eq. (8) under the condition $1/\kappa < R$.

Generally, the absolute value of Δ_1 for 1 : 1 electrolyte is small.[8] As an example, the value of $\lambda_2{}^0$ is 49.0 cm^2 ohm^{-1} $equiv^{-1}$ for methanesulfonate ion,[10] of which EDS ion consists, and the value of Δ_1 for sodium methanesulfonate (NaMS) is in the order of 10^{-10} from Eq. (8). Under the condition $1/\kappa < R$, the values of Δ_1 for the other sulfonates will be in the same order as that of NaMS, and can be neglected in comparison with D_0 in Eq. (1) (the value of D_0 is in the order of 10^{-5}). Thus Eq. (1) becomes the following Nernst-Hartley equilation.

$$D = D_0\left(1+c\frac{\mathrm{d}\ln y}{\mathrm{d}c}\right) \tag{9}$$

We see from Figs 1 and 2 that the values calculated from Eq. (9) lie nearer the experimental values than that of Eq. (1). The calculated value for m-Na_2BDS agrees with the experimental value. Thus it is clear that the concentration dependence of diffusion coefficient of bolaform electrolyte with long R is smaller than that of bolaform electrolyte with short R, as κ^2 is proportional to the concentration of electrolyte.

The frictional coefficient of non-spherical molecule depends on the size and shape. In the case of bolaform ion, the frictional coefficient is also affected by the ionic atmosphere. A rod like bolaform ion such as aliphatic sulfonate ion behaves like a monovalent ion, under the conditions where the ion atmosphere about each charge is almost independent. Therefore, the frictional coefficient of bolaform ion decreases, and the value of D_0 in Eq. (9) increases. Hence, the calculated value from Eq. (9) approaches

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9) S. A. Rice, *J. Amer. Chem. Soc.*, **80**, 3207 (1958).

10) L. R. Dawson, M. Golben, G. R. Leader, and H. K. Zimmerman Jr., *J. Phys. Colloids Chem.*, **55**, 1499 (1951).

more closely the experimental value. Due to the bulkiness of molecule the frictional coefficient of aromatic sulfonate ion is little affected by the asymmetry of the ion atmosphere. The difference between Fig. 1 and 2 is thus accounted for.

The diffusion coefficient of a bolaform electrolyte will always be larger than the diffusion coefficient of a corresponding ordinary 2 : 1 electrolyte not in line with Rice's theory.

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