Diffusion Coefficients for Aqueous Solutions of Benzene and α-Naphthalene Sulfonates at 25°C*

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Aromatic sulfonate ions consist of two distinct parts, a hydrophilic part (sulfonic group) and a hydrophobic part (aromatic ring). These two parts interact differently with water. The effect of these interactions on the limiting conductance of four kinds of sulfonates has been reported on previously.1)

It now seems to be important to investigate the effect of these interactions on the other physicochemical properties of aromatic sulfonates. In this paper, the diffusion coefficients of sodium benzenesulfonate (BSNa) and sodium α-naphtalenesulfonate (NSNa) in water at 25°C were measured by the magnetically-stirred porous diaphragm method, and their apparent molar volumes were obtained by a density method. From the measured cell integral diffusion coefficients, the integral and differential diffusion coefficients were calculated by Stokes method.2)

Experimental

Materials.—The BSNa and NSNa were purified as before.1) The potassium chloride was of an analytical grade (Merck) and was used without further purification. The conductance water was boiled before use in order to make it air-free. Its specific conductance was less than $1\times10^{-6}\,\mathrm{cm}^{-1}\,\Omega^{-1}$.

Diffusion Cell.—The diaphragm-cell was the same type as has been described by Stokes.3) Modifications were, however, made in the lower stopper and in the magnet. In order to avoid disturbing the liquid in the diaphragm upon withdrawing or inserting the lower stopper, grooves were cut in both the stopper and the neck of the lower compartment, as is shown in the figure. The lower compartment was completely closed by rotating the stopper. When the cell was dipped in the thermostat water, the lower stopper was sealed by air.

A ring ferrite magnet was used instead of a horseshoe magnet. This magnet is so strong and light that it can be rotated smoothly by a small induction motor (Yokogawa SM-Q; output 2W) at a rate of 30 or 50 r.p.m.

The Calibration of Cell and Measurements of the Diffusion Coefficient and Density.—The cell integral diffusion coefficient, $\overline{D}$, is given by:

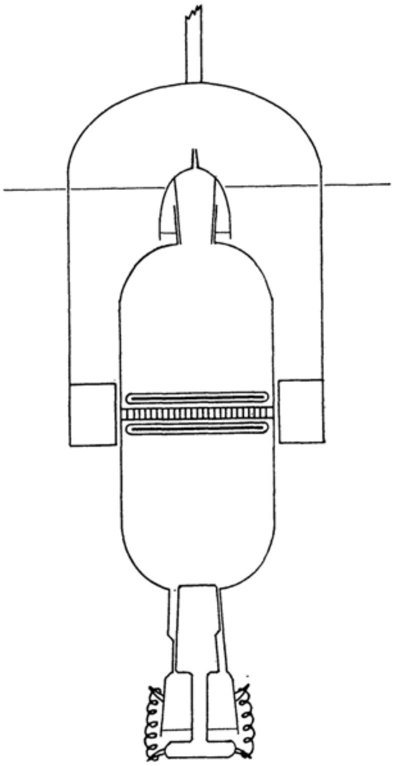

Fig. 1. The diaphragm cell.

$$\overline{D}=\frac{1}{\beta t}\ln\frac{c_1-c_2}{c_3-c_4} \tag{1}$$

where β is the cell constant and t is the duration of the experiment (sec.). c_2 (invariably zero, as recommended by Stokes2)) and c_4 are the initial and the final molar concentrations in the upper compartment respectively, while c_3 is the final concentration in the lower compartment. The initial lower concentration, c_1 (mol./l.), is obtained by the Stokes method.4)

The cell constant, β, was determined by the measurement of the diffusion of 0.08—0.1 N potassium chloride in water and by comparing the results with the data of Stokes.2,4) The concentrations of potassium chloride were determined by measuring the conductances of the solutions, using the conductance data

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1) H. Uedaira and H. Uedaira, This Bulletin, **37**, 1885 (1964).

2) R. H. Stokes, *J. Am. Chem. Soc.*, **72**, 2243 (1950); **73**, 3527 (1951).

3) B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, **51**, 1641 (1955).

4) R. A. Robinson and R. H. Stokes, "Electrolye Solutions," 2nd. ed. Butterworths Scientific Publns., London (1959), Chap. 10.

obtained by Shedlovsky[5] and Stokes[6].

The time necessary for the concentration gradient in the diaphram to attain a steady state was estimated by Gordon's equation.[7]

The molar concentrations of BSNa and NSNa were determined by measuring the conductance of the solution. The conductance-concentration relation had been measured peviously.

The apparent molar volume, ϕ_v, was calculated from the density, which was determined with a springel pycnometer 30 ml. in capacity. ϕ_v is expressed in the dilute solution by the following Masson relation:[8]

$$\phi_v=\phi_v{}^\circ+S_v c^{1/2} \tag{2}$$

where $\phi_v{}^\circ$ is the ϕ_v at an infinite dilution and S_v is the limiting slope.

Results and Discussion

The experimental equation of the density for a BSNa solution calculated by the method of least squares at 25°C is ($c<1.0$ mol./l.):

$$d=0.99707+(0.0837\pm0.0013)c-(0.0106\pm0.0015)c^{3/2} \tag{3}$$

while the equation for NSNa is: ($c<0.25$ mol./l.)**

$$d=0.99707+(0.09443\pm0.00056)c-(0.0076\pm0.0013)c^{3/2} \tag{4}$$

Thus, from Eqs. 2, 3 and 4, the apparent molar volumes for BSNa and NSNa solutions can be given by the following equations:

$$\phi_v=96.70+10.61c^{1/2} \tag{5}$$

$$\phi_v=136.2+7.620c^{1/2} \tag{6}$$

The cell integral diffusion coefficients, $\overline{D}$, for BSNa and NSNa solutions are shown in Tables I and II. The limiting diffusion coefficients at the infinite dilution, D°, as calculated by Nernst's limiting law are 10.97×10^{-6} and 9.840×10^{-6} (cm^{2}sec^{-1}) for BSNa and NSNa respectively, where the limiting equivalent conductances of sodium, BS$^-$ and NS$^-$ ions were 50.10,[4] 34.99[9] and 29.3[1] (cm$^2\Omega^{-1}$ equiv^{-1}) respectively. The integral diffusion coefficients, $\overline{D}^\circ$, at the concentration c_m, where $c_m=(c_1+c_3)/2$, could then be calculated from Stokes' equation[4]; they are shown in Tables I and II.

The differential diffusion coefficient, D, is calculated from $\overline{D}^\circ$ by Stokes' equation. The equations obtained for the D of BSNa and NSNa solutions are as follows:

TABLE I. DIFFUSION COEFFICIENTS FOR BSNa

c_1, mol./l.	0.16223	0.23577	0.33732	0.49813
$c_1{}^{1/2}$	0.4027	0.4856	0.5808	0.7058
$c_m{}^{1/2}$	0.3917	0.4704	0.5627	0.6845
$\overline{D}\times10^6$ cm^2 sec^{-1}	10.5_4	10.5_1	10.3_9	10.2_9
$\overline{D}^\circ(c_m)\times10^6$ cm^2 sec^{-1}	10.5_6	10.5_4	10.4_2	10.3_2

TABLE II. DIFFUSION COEFFICIENTS FOR NSNa

c_1, mol./l.	0.086599	0.15603	0.20588
$c_1{}^{1/2}$	0.2943	0.3950	0.4537
$c_m{}^{1/2}$	0.2859	0.3850	0.4406
$\overline{D}\times10^6$ cm^2 sec^{-1}	9.70_5	9.60_4	9.57_5
$\overline{D}^\circ(c_m)\times10^6$ cm^2 sec^{-1}	9.71_1	9.61_4	9.58_2

$$D\times10^6=10.96-0.476c^{1/2} \tag{7}$$

$$D\times10^6=9.840-0.280c^{1/2} \tag{8}$$

The integral and differential diffusion coefficients for BSNa and NSNa solutions decrease linearly with the square root of the concentration, whereas for most aqueous inorganic electrolyte systems, D initially decreases rapidly with the concentration passes through a broad minimum at $c\approx0.2-0.5$ mol./l., and thereafter increases slowly.

The concentration dependence of the diffusion coefficient and the apparent molar volume for NSNa are smaller than those for BSNa. The limiting slopes of the equivalent conductances for BSNa and NSNa solutions show a similar tendency.[10]

The experimentally-found values of the slopes for D versus $c^{1/2}$ curves do not agree exactly with that predicted by the Harned theory;[11] nevertheless, the agreement is good with regard to the sign and the order of magnitude. The discrepancy for NSNa is larger.[12]

In a previous paper,[1] it was shown that the effect of the hydrophobic part-water interaction on the mobilities of aromatic sulfonate ions was larger for the NS$^-$ ion. Wen and Saito[13] showed that, in the case of the aqueous solutions of tetraalkylammonium salts, the value of S_v for the more hydrophobic ion was smaller. The parallel relation between the conductances and the diffusion coefficients for BSNa and NSNa may be caused by the water interaction.

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[5] T. Shedrovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

[6] J. F. Chamber, J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, **60**, 985 (1956).

[7] A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

[8] D. O. Masson, *Phil. Mag.*, (7) **8**, 219 (1929).

** As the saturate concentration of NSNa is low, measurement at higher concentration was not made.

[9] M. Yokoi and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 4367 (1961).

[10] The limiting slopes for BSNa and NSNa solutions are respectively, 79.56 and 78.32 at 25°C.

[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd. ed., Reinhold, New York (1958), Chap. 6.

[12] The limiting slopes for BSNa and NSNa solutions are respectively, 0.670×10^{-6} and 0.639×10^{-6}.

[13] W.-Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).