The Diffusion of Dye Solutions

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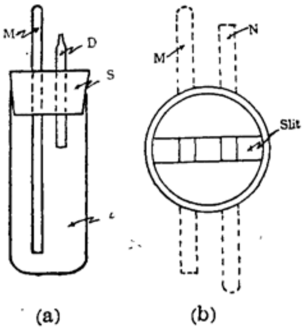
Numbers of method are known by which the particle size of colloid is determined. Among these, the measurement of the diffusion velocity is used especially for the colored solution, since the distribution of the concentration can easily be estimated by the colorimetry. Diffusion methods have already been described by R. Auerbach,(1) Wo. Ostwald and A. Quast,(2) and K. Brass and K. Eisner.(3) These methods, however, contain some ambiguity in the calculation of the diffusion coefficient. In the present report, the results of determination of the particle size of congo red solutions containing sodium chloride will be described by using the calculation method developed by the author.

The apparatus used is shown in Fig. 1 (a). M is the diffusion cell, made of a capillary tube, 10 cm. in length, 0.13 cm. in inner diameter and sealed at one end. S is a rubber stopper and D is another capillary tube which was used to make flow out the excess of the solution in A. The experimental procedure is as follows. The diffusion cell, M, is filled with distilled water or some other solvent and then dipped upside-down into the dye solution, A, as shown in the figure. After about 24 hours, the cell is taken out and the diffused amount of dye is determined by the colorimetry. The standard solutions are prepared by diluting the original dye solution. A number of capillary tubes which have the same thickness with M are filled with the standard solutions. One of the tubes, N, is placed side by side with M as shown in Fig. 1 (b) and the colors are compared. The position of the color of the same intensity in the tube M with the standard solution is found by this way. The distribution of the concentration of dye in the



(a) (b)

Fig. 1.

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(1) R. Auerbach, *Kolloid-Z.*, **35**, 202 (1924); **37**, 379 (1925).

(2) Wo. Ostwald and A. Quast, *Kolloid-Z.*, **48**, 83 (1929); **51**, 273, 361 (1930).

(3) K. Brass and K. Eisner, *Kolloid-Beih.*, **37**, 56 (1933).

tube M is determined by using the standard solutions of various dilutions.

The relation between concentration c and the diffused distance x is expressed by Fick's equation

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

where D_e is the apparent diffusion coefficient, and t the time. D_e is considered as a constant. This equation is solved under the initial and and boundary conditions:

$$\left.\begin{array}{ll} \text{at} \quad t = 0 \text{ and } x > 0, & c = 0, \\ \text{and at} \quad t \geqq 0 \text{ and } x = 0, & c = c_0, \end{array}\right\} \tag{2}$$

and the result,

$$D_e = \frac{x^2}{t} \varphi(v), \tag{3}$$

$$\text{where} \qquad v = c_0/c, \tag{4}$$

and $\varphi(v)$ is defined as follows:

$$\begin{aligned} 1/v &= c/c_0 \\ &= 1 - (2/\sqrt{\pi}) \int_0^{1/(2\sqrt{\varphi})} \exp.\,(-\xi^2) d\xi. \end{aligned} \tag{5}$$

The value of $\varphi(v)$ has been calculated as a function of v by R. Fürth⁽⁴⁾ for $v \geqq 2$. The value of $\varphi(v)$ for $v < 2$ was newly calculated and tabulated in Table 1, together with that of R. Fürth. It should be noticed that the value $\varphi = 3.80$ for $v = 1$ used by Wo. Ostwald and A. Quast⁽²⁾ and A. Nistler⁽⁵⁾ is entirely faulty.

An example of data obtained for congo red solution is given in Table 2. It is seen that the apparent diffusion coefficient D_e varies with the concentration at distance x. Referring to other data, it is seen that the apparent diffusion coefficient varies also with the concentration.

Table 1

The Value of $\varphi(v)$

v	$\varphi(v)$	v	$\varphi(v)$	v	$\varphi(v)$
1	∞	1.9	1.25	10	0.185
1.1	38.2	2	1.099	12	0.166
1.2	11.26	3	0.532	15	0.147
1.3	5.80	4	0.379	16	0.142
1.4	3.73	5	0.303	24	0.120
1.5	2.68	6	0.262	32	0.107
1.6	2.09	7	0.234	48	0.0931
1.7	1.71	8	0.212	64	0.0854
1.8	1.47	9	0.197		

Since the diffusion coefficient D is a function of concentration, Fick's equation should be written over again as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right). \tag{6}$$

Referring to the calculation of R. Fürth⁽⁴⁾ and using the initial and boundary conditions of Eq. (2), this is solved as

$$\frac{1}{v} = \frac{c}{c_0} = \frac{\displaystyle\int_{x/\sqrt{t}}^{\infty} (1/D) \exp.\left\{-\int_0^{\lambda} (\lambda/2D) d\lambda\right\} d\lambda}{\displaystyle\int_0^{\infty} (1/D) \exp.\left\{-\int_0^{\lambda} (\lambda/2D) d\lambda\right\} d\lambda}, \tag{7}$$

Table 2

Diffusion of Congo Red in Distilled Water

Concentration at distance, x		$\varphi(v)$	Distance diffused, x, cm.	Apparent diffusion coefficient, D_e 10^{-6}cm.²/sec.	Differential diffusion coefficient, D 10^{-6}cm.²/sec.
c, g./l.	v				
0.0231	44	0.0965	1.35	2.14	2.25
0.0253	40	0.100	1.32	2.12	2.25
0.0675	15	0.147	1.07	2.05	2.22
0.1012	10	0.185	0.94	1.99	2.22
0.1265	8	0.212	0.88	2.00	2.21
0.1519	6.8	0.240	0.83	2.01	2.20
0.2531	4	0.379	0.65	1.94	2.19
0.3374	3	0.532	0.52	1.76	2.16
0.5062	2	1.099	0.33	1.46	2.12
0.6327	1.6	2.09	0.23	1.34	2.10

Concentration of original solution: $c_0 = 1.012$ g./l.
Temperature: $T = 25$°C.
Time of diffusion: $t = 0.823 \times 10^5$ sec.
$\alpha = 1.537$; $\beta = 0.277$; $D_0 = \alpha^2 = 2.36 (10^{-6}\text{cm.}^2/\text{sec.})$.

where D is considered as a function of a parameter λ. D is often called as "differential" diffusion coefficient. Now, this equation may be rewritten in the form:

$$D = -\frac{1}{2t} \cdot \frac{dx}{dc} \int_0^c x dc. \tag{8}$$

From the experiment described above, c is obtained as a function of x, and D can be calculated. Since the numerical calculation is, however, somewhat troublesome, some other device is desirable. One method may be to recalculate the apparent diffusion coefficient to differential diffusion coefficient. As shown in Fig. 2, where the data of Table 1 was plotted,

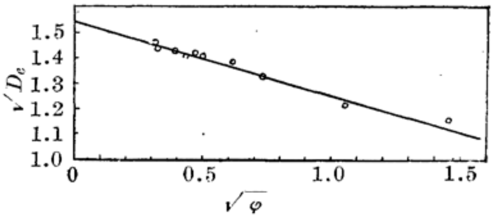

Fig. 2.

the empirical formula

$$\sqrt{D_e} = \alpha - \beta\sqrt{\varphi} \tag{9}$$

is approximately valid. Then, Eq. (8) be-

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(4) R. Fürth, *Phys. Z.*, **26**, 719 (1925); *Kolloid-Z.*, **41**, 300 (1927).

(5) A. Nistler, *Kolloid-Beih.*, **31**, 1 (1930).

comes to

$$D = \alpha^2 \left\{ 1 - \frac{\sqrt{\pi}}{2} \frac{\beta}{\alpha} \frac{1}{v} \exp.(1/4\varphi) \right\}. \tag{10}$$

The differential diffusion coefficient calculated from this equation decreases with the increase of the concentration at distance x, though it is not affected with the concentration of original solution. Such a variation of differential diffusion coefficient is usually thought to be due to the decrease of activity coefficient of solute with the increase of its concentration, and Einstein-Sutherland's equation

$$D = \frac{RT}{N \cdot 6\pi\eta r} \tag{11}$$

is valid only for the infinite dilution. In this equation, R is the gas constant, T is the absolute temperature, N is Avogadro's number, η is the viscosity of solvent, and r is the radius of the diffusing particles. The diffusion coefficient at infinite dilution D_0 is given by

$$D_0 = \alpha^2. \tag{12}$$

For congo red solution at 25°, the values for D_0 were found as: 2.46×10^{-6} cm.^{2}/sec. for original concentration of 5.062 g./l., 2.45×10^{-6} cm.^{2}/sec. for 3.037 g./l., 2.36×10^{-6} cm.^{2}/sec. for 1.012 g./l., and the average 2.42×10^{-6} cm.^{2}/sec. (±3%).

The effect of diffusion potential should be considered on the diffusion of colloidal electrolyte. When a colloidal electrolyte diffuses, counter ions go faster than colloidal ions, and diffusion potential is established. This accelerates the diffusion of colloidal ions. Extremely large diffusion coefficient is, therefore, obtained for entirely pure colloidal electrolyte in pure water. Such a diffusion potential can be eliminated if neutral salt, or "supporting electrolyte", is added in the diffusion column, as stated by G. S. Hartley and C. Robinson,(6) C. Robinson,(7) E. Valkó,(8) and S. Lenher and J. E. Smith.(9) But the addition of electrolyte may cause the aggregation of colloidal particles, so the estimation of particle size by diffusion is a delicate matter.

The diffusion coefficient of congo red solution in presence of sodium chloride was measured and the result is cited in Table 3, where D_0 is the differentical diffusion coefficient at infinite dilution, and particle radius r is calculated from Eq. (11). Molecular weight M is calculated from the equation

$$M = \frac{4}{3} \pi r^3 N d \tag{13}$$

where N is Avogadro's number and d is the density of the particle assumed to be $d = 1.5$. *Dividing the molecular weight by the formula* weight of congo red, 696, the degree of association is obtained. Diffusion data for pure congo red solution without sodium chloride, obtained by many investigators, are cited in Table 4. E. Valkó and C. Robinson used extremely purified congo red and conductivity water, so that very large diffusion coefficient was obtained, and other authors used usual distilled water and obtained somewhat smaller values, which coincide with that in Table 3. Referring to these data, it is supposed that the diffusion potential may be reduced by the existence of only a trace of electrolyte. From this standpoint, it can be supposed that the decrease of diffusion coefficient by the addition of sodium chloride may be due to the association of particles. The increase of association degree is initially gradual, and then a rapid

Table 3

Particle Size of Congo Red (18°C.)

Concentration of NaCl, N	Diffusion coefficient, D_0 10^{-6} cm.^{2}/sec.	Particle radius, Å.	Molecular weight, M	Degree of association
0	2.16	9.3	3100	4.5
0.1002	1.80	11.0	5100	7.3
0.2004	1.67	11.8	6300	9.1
0.3006	1.44	13.5	9300	13
0.4008	1.12	17.3	20000	29
0.5010	0.96	19.8	30000	43

Concentration of congo red in original solution is 3.202 g./l.

Table 4.

Diffusion of Congo Red

Temperature, °C.	Diffusion coeffiient, 10^{-6}cm.^{2}/sec.	Particle radius, Å.	Observers
20	0.81∼1.16	24.1 ∼18.2	Wo. Ostwald and Quast(2)
18	0.94∼1.31	21.0 ∼15.1	A. Nistler(5)
6.9	0.78∼1.26	18.3 ∼11.3	Herzog and Polotzky(10)
18	1.56∼1.85	12.6 ∼10.6	Fürth and Ullmann(11)
25	6.63∼7.75	3.78∼ 3.23	Valkó(8)
20	5.67∼5.68	3.74∼ 3.73	Robinson(7)

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(6) G. S. Hartley and C. Robinson, *Proc. Roy. Soc.* (London), **A 134**, 20 (1932).

(7) C. Robinson, *Proc. Roy. Soc.* (London), **A148**, 681 (1935); *Trans. Faraday Soc.*, **31**, 245 (1935).

(8) E. Valkó, *Trans, Faraday Soc.*, **30**, 231 (1935).

(9) S. Lenher and J. E. Smith, *J. Phys. Chem.*, **40**, 1005 (1936).

(10) R. O. Herzog and A. Polotzky, *Z. physik. Chem.*, **A 87**, 449 (1914).

(11) R. Fürth and E. Ullmann, *Kolloid-Z.*, **41**, 304 (1927).

increase bigins when the concentration of sodium chloride exceeds about 3 N, and at last precipitation by coagulation is observed. No tendency to minimize the particle size by a small addition of electrolyte was recognized. Such a peptization effect has been reported by W. Schramek and E. Götte,(12) and contradicted by many authors.

In order to discuss the particle size from diffusion data, some other factors should also be considered; for example, the shape of particle, the distribution of particle size, and so on. As an approximate treatment, however, the discussion described above will be sufficient.

Summary

The apparent diffusion coefficient of congo red in water, obtained by Auerbach-Ostwald's method, changes with concentration. Solving the Fick's equation with the assumption that the diffusion coefficient is a function of concentration, the apparent diffusion coefficient can be recalculated to differential diffusion coefficient. From the value extrapolated to infinite dilution, the particle radius of congo red was calculated using Einstein-Sutherland's equation. On the assumption that the particle is spherical and not hydrated, the particle weight and association degree were obtained. The diffusion coefficient, obtained by this method for congo red solution containing various concentration of NaCl, agrees well with the data reported by others. With the increase of salt concentration, the particle size increases gradually. No decrease was observed in the particle size with a small addition of electrolyte.

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(12) W. Schramek and E. Götte, *Kolloid-Beih.*, **34**, 218 (1932).