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Interpretation of Data for Concentration-dependent Free Diffusion in Two-component Systems

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A formal series solution of the second Fick equation with a concentration-dependent diffusion coefficient is obtained for one-dimensional free diffusion in two-component systems by making use of the method of successive approximations. The diffusion coefficient, $D(C)$, is represented as a function of solute concentration, C, in the form of a Taylor series expanded about the mean concentration, $\bar{C}$, of the two starting solutions. After combining the solution for the concentration distribution with an expression relating refractive index to concentration, equations for the reduced height–area ratio, $\mathfrak{D}_{\mathrm{A}}$, and reduced second moment, $\mathfrak{D}_{2\mathrm{m}}$, of the refractive index gradient curves are obtained. It is shown that $\mathfrak{D}_{\mathrm{A}}$ and $\mathfrak{D}_{2\mathrm{m}}$ vary linearly with $(\Delta C)^2$ for a given value of $\bar{C}$, where ΔC is the concentration difference across the initial boundary. The intercept of either straight line at $\Delta C = 0$ gives the value of D at concentration $\bar{C}$, while the slopes of both straight lines are connected, in a somewhat complicated fashion, with the concentration dependence of D and of the refractive index. On the basis of these relations two methods are presented for determining the diffusion coefficient *versus* concentration relationship from data for $\mathfrak{D}_{\mathrm{A}}$ and $\mathfrak{D}_{2\mathrm{m}}$. In order to test one of the theoretical relations obtained, measurements were performed with the *n*-butanol–water system using the Gouy diffusiometer. In accordance with theory, $\mathfrak{D}_{\mathrm{A}}$ at a given value of $\bar{C}$ was found to vary linearly with $(\Delta C)^2$ over the range of ΔC studied. It is shown that the slope of this straight line is consistent with the value computed from the theoretical equation using data reported by Lyons and Sandquist for the same system.

Several of the precise methods for studying free diffusion in liquids depend on measurements of the refractive index or the refractive index gradient distribution in the diffusion cell as a function of time. To obtain accurate values of the diffusion coefficient from such measurements, it is necessary to consider the effects of (1) the concentration dependence of the diffusion coefficient,[2–8] and (2) deviations from linearity in the relation of the refractive index to solute concentration. (It is here assumed that there is no volume change on mixing.) The first-order effect of these complicating factors is to skew the refractive index gradient curve from the Gaussian shape, but it will be seen below that second-order symmetrical deviations are also produced. As pointed out by Longsworth,[9] the possibility exists that the two sources of skewness, (1) and (2), may partially compensate each other to produce a nearly Gaussian refractive index gradient curve. With *n*-butanol in water, however, markedly skew boundaries are observed because the two effects act in the same direction. Longsworth[9] and Creeth[10] studied boundary skewness with this system using the Rayleigh fringe method, while Lyons and Sandquist[11] used the Gouy method to obtain data over a wide range of concentrations and reported two experiments which indicate that the reduced height–area ratio at a given mean concentration depends on the concentration difference, ΔC, between the initial solutions.

The main purpose of this paper is to present a general theoretical basis for interpreting free diffusion data from systems of this kind, thereby providing reliable methods for determining diffusion coefficients from data obtained with optical diffusiometers. Equations for the reduced height–area ratio, the reduced second moment and the maximum height (and its position) of the refractive index gradient curve are derived through terms of order $(\Delta C)^2$; one of these relations is tested using Gouy diffusiometer data for the *n*-butanol–water system at 25°. However, because no method is available for obtaining reduced second moments from Gouy diffusiometer data for skewed refractive index gradient curves, no test could be made of the relation between the reduced second moment and $(\Delta C)^2$. It is hoped that other apparatus, such as the Rayleigh fringe diffusiometer, will be employed to test this relation.

Theory

Basic Equations.—We consider a one-dimensional free diffusion experiment in a rectangular cell. At the start of the experiment, a sharp boundary is formed between two solutions of a single and homogeneous solute, which are placed above and below the position $x = 0$. Taking the x-axis downward, and assuming that there is no volume change on mixing, the diffusion equation takes the form

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right) \qquad (1)$$

where C is the concentration of the solute expressed as mass or moles per unit volume of solution, t is the time and D is the diffusion coefficient. The initial condition of the experiment is represented mathematically by

$$\begin{aligned} C &= C_{\mathrm{A}} \quad (t = 0, -\infty < x < 0) \\ C &= C_{\mathrm{B}} \quad (t = 0, 0 < x < \infty) \end{aligned} \qquad (2)$$

In practice, it is necessary to place the less dense solution above the more dense one so that gravitational stability will be maintained during the experiment. Hence, for most solutes C_{B} is larger than C_{A}. In addition to initial condition 2, the following boundary condition must be satisfied.

$$\begin{aligned} C &\rightarrow C_{\mathrm{A}} \quad (t > 0, x \longrightarrow -\infty) \\ C &\rightarrow C_{\mathrm{B}} \quad (t > 0, x \longrightarrow \infty) \end{aligned} \qquad (3)$$

In the present study, it is assumed that D is a function of concentration C only and can be repre-

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[11] P. A. Lyons and C. L. Sandquist, *ibid.*, **75**, 3896 (1953).

sented by a Taylor expansion about the mean concentration $\bar{C} = (C_A + C_B)/2$ in the form[12]

$$D(C) = D(\bar{C})[1 + k_1(C - \bar{C}) + k_2(C - \bar{C})^2 + k_3(C - \bar{C})^3 + ..] \quad (4)$$

Here $D(\bar{C})$ is the value of D at $C = \bar{C}$ and the coefficients, k_1, k_2, etc., stand for

$$k_1 = \left[\frac{1}{D(C)}\frac{dD}{dC}\right]_{C=\bar{C}},\ k_2 = \frac{1}{2!}\left[\frac{1}{D(C)}\frac{d^2D}{dC^2}\right]_{C=\bar{C}},\ \text{etc.} \quad (5)$$

It should be noted that these coefficients in the expansion of $D(C)$ are functions of $\bar{C}$.

Introduction of equation 4 and the reduced concentration, ϕ, defined by

$$\phi = 2(C - \bar{C})/\Delta C \quad (6)$$

wherein $\Delta C = C_B - C_A$, changes equation 1 to

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial x}\left\{D(\bar{C})\left[1 + k_1\left(\frac{\Delta C}{2}\right)\phi + k_2\left(\frac{\Delta C}{2}\right)^2\phi^2 + k_3\left(\frac{\Delta C}{2}\right)^3\phi^3 + \ldots\right]\frac{\partial\phi}{\partial x}\right\} \quad (7)$$

Conditions 2 and 3 become, respectively

$$\begin{aligned}\phi &= -1 \quad (t = 0, -\infty < x < 0) \quad (8)\\ \phi &= 1 \quad (t = 0, 0 < x < \infty)\end{aligned}$$

and

$$\begin{aligned}\phi &\longrightarrow -1 \quad (t > 0, x \longrightarrow -\infty) \quad (9)\\ \phi &\longrightarrow 1 \quad (t > 0, x \longrightarrow \infty)\end{aligned}$$

As is well known,[13] a partial differential equation of the form of 7 can be reduced to an ordinary differential equation by introducing a new variable

$$z = x/(2\sqrt{D(\bar{C})t}) \quad (10)$$

Thus equation 7 becomes

$$\frac{d}{dz}\left\{\left[1 + k_1\left(\frac{\Delta C}{2}\right)\phi + k_2\left(\frac{\Delta C}{2}\right)^2\phi^2 + k_3\left(\frac{\Delta C}{2}\right)^3\phi^3 + \ldots\right]\frac{d\phi}{dz}\right\} + 2z\frac{d\phi}{dz} = 0 \quad (11)$$

and conditions 8 and 9 are reduced to a single set of conditions

$$\begin{aligned}\phi &\longrightarrow -1 \quad (z \longrightarrow -\infty) \quad (12)\\ \phi &\longrightarrow 1 \quad (z \longrightarrow \infty)\end{aligned}$$

Solution for the Concentration Distribution by the Method of Successive Approximations.—Equation 11 subject to condition 12 cannot be integrated analytically in closed form because of its non-linearity. However, a formal series solution may be obtained by making use of the method of successive approximations[6,7,14,15] if the magnitude of ΔC is sufficiently small that the desired solution for ϕ may be written as a series in ΔC

$$\phi = \phi_0 + (\Delta C/2)\phi_1 + (\Delta C/2)^2\phi_2 + (\Delta C/2)^3\phi_3 + \ldots \quad (13)$$

Here each ϕ_i (i = 0, 1, 2, etc.) is a function of z to be determined from equation 11 and condition 12.

Introducing equation 13 into equation 11, equating the coefficients of $(\Delta C/2)^0$, $(\Delta C/2)^1$, $(\Delta C/2)^2$, etc., to zero, writing

$$\phi_0 = \psi_0 \quad (14)$$

$$\phi_1 = k_1\psi_1 \quad (15)$$

$$\phi_2 = k_1^2\psi_2 + k_2\psi_3 \quad (16)$$

$$\phi_3 = k_1^3\psi_4 + k_1k_2\psi_5 + k_3\psi_6 \quad (17)$$

$$\cdots\cdots$$

and remembering that k_1, k_2, etc., are independent so that their coefficients may be equated to zero, we have

$$\frac{d^2\psi_0}{dz^2} + 2z\frac{d\psi_0}{dz} = 0 \quad (18)$$

$$\frac{d^2\psi_1}{dz^2} + 2z\frac{d\psi_1}{dz} = -\frac{1}{2}\frac{d^2}{dz^2}(\psi_0)^2 \quad (19)$$

$$\frac{d^2\psi_2}{dz^2} + 2z\frac{d\psi_2}{dz} = -\frac{d^2}{dz^2}(\psi_0\psi_1) \quad (20)$$

$$\frac{d^2\psi_3}{dz^2} + 2z\frac{d\psi_3}{dz} = -\frac{1}{3}\frac{d^2}{dz^2}(\psi_0)^3 \quad (21)$$

$$\frac{d^2\psi_4}{dz^2} + 2z\frac{d\psi_4}{dz} = -\frac{d^2}{dz^2}\left[\psi_0\psi_2 + \frac{1}{2}(\psi_1)^2\right] \quad (22)$$

$$\frac{d^2\psi_5}{dz^2} + 2z\frac{d\psi_5}{dz} = -\frac{d^2}{dz^2}[\psi_0\psi_3 + (\psi_0)^2\psi_1] \quad (23)$$

$$\frac{d^2\psi_6}{dz^2} + 2z\frac{d\psi_6}{dz} = -\frac{1}{4}\frac{d^2}{dz^2}(\psi_0)^4 \quad (24)$$

$$\cdots\cdots$$

Auxiliary conditions to be imposed on the ψ_i's are obtained from equation 12, giving

$$\begin{aligned}\psi_0 &\longrightarrow -1 \quad (z \longrightarrow -\infty) \quad (25)\\ \psi_0 &\longrightarrow 1 \quad (z \longrightarrow \infty)\end{aligned}$$

$$\begin{aligned}\psi_j &\longrightarrow 0 \quad (z \longrightarrow -\infty) \quad (26)\\ \psi_j &\longrightarrow 0 \quad (z \longrightarrow \infty) \quad (j \geq 1)\end{aligned}$$

The above system of equations for the ψ_i's can be solved successively from above to below. In this work we have extended the calculation up to $i = 3$ for ψ_i and $i = 6$ for $d\psi_i/dz$. The equations for $d\psi_4/dz$, $d\psi_5/dz$ and $d\psi_6/dz$ can be obtained without determining those for ψ_4, ψ_5 and ψ_6 because the constants for the first integrals of equations 22–24 are zero.[16] The results obtained are given below[17]

$$\psi_0 = \Phi \quad (27)$$

$$\psi_1 = -\frac{1}{4}\{2(\Phi)^2 + 2z\Phi'\Phi + (\Phi')^2 - 2\} \quad (28)$$

$$\psi_2 = \frac{1}{16}\left\{8(\Phi)^3 + z(18 - 4z^2)\Phi'(\Phi)^2 + (12 - 4z^2)(\Phi')^2\Phi - z(\Phi')^3 - 4z\Phi' - \left(8 - \frac{12\sqrt{3}}{\pi}\right)\Phi - \frac{12\sqrt{3}}{\pi}\Phi(\sqrt{3}z)\right\} \quad (29)$$

$$\psi_3 = -\frac{1}{12}\left\{4(\Phi)^3 + 6z\Phi'(\Phi)^2 + 6(\Phi')^2\Phi - \left(4 - \frac{12\sqrt{3}}{\pi}\right)\Phi - \frac{12\sqrt{3}}{\pi}\Phi(\sqrt{3}z)\right\} \quad (30)$$

$$\frac{d\psi_0}{dz} = \Phi' \quad (31)$$

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(12) The function $D(C)$ is expanded about $\bar{C}$ instead of either C_A or $C = 0$ to facilitate investigation of the maximum refractive index gradient and its position. It is noted that the subsequent solution for the concentration gradient distribution is more general than those given in refs. 6 and 7 where the D *versus* C relation was limited to the linear case.

(13) L. Boltzmann, *Ann. Physik und Chem.* (*Wied.*), **53**, 959 (1894), or see W. Jost, "Diffusion in Solids, Liquids, Gases," Academic Press Inc., New York, N. Y., 1952, p. 31.

(14) K. Hidaka, "Methods of Numerical Integrations," Vol. 2, Iwanami-shoten, Tokyo, Japan, 1943, pp. 51–55.

(15) J. L. Hwang, *J. Chem. Phys.*, **20**, 1320 (1952).

(16) This is readily shown from boundary conditions 26 and the fact that the right-hand sides of equations 22–24 are even functions of z.

(17) To simplify the notation in these equations, $\Phi(z)$ and $\Phi'(z)$ are denoted simply by Φ and Φ', respectively, while $\Phi(\sqrt{3}z)$ is not abbreviated.

$$\frac{\mathrm{d}\psi_1}{\mathrm{d}z} = -\frac{1}{2}\Phi'\{(3 - 2z^2)\Phi - z\Phi'\} \tag{32}$$

$$\frac{\mathrm{d}\psi_2}{\mathrm{d}z} = \frac{1}{8}\Phi'\left\{(21 - 24z^2 + 4z^4)(\Phi)^2 - z(10 - 4z^2)\Phi'\Phi + (1 + z^2)(\Phi')^2 + 4z^2 - \left(6 - \frac{6\sqrt{3}}{\pi}\right)\right\} \tag{33}$$

$$\frac{\mathrm{d}\psi_3}{\mathrm{d}z} = -\frac{1}{12}\Phi'\left\{(18 - 12z^2)(\Phi)^2 - 12z\Phi'\Phi - 3(\Phi')^2 - \left(4 - \frac{12\sqrt{3}}{\pi}\right)\right\} \tag{34}$$

$$\frac{\mathrm{d}\psi_4}{\mathrm{d}z} = -\frac{1}{96}\Phi'\left\{(462 - 708z^2 + 216z^4 - 16z^6)(\Phi)^3 - z(234 - 144z^2 + 24z^4)\Phi'(\Phi)^2 + (66 - 18z^2 - 12z^4)(\Phi')^2\Phi - z(9 + 2z^2)(\Phi')^3 - \left[\left(252 - \frac{216\sqrt{3}}{\pi}\right) - \left(288 - \frac{144\sqrt{3}}{\pi}\right)z^2 + 48z^4\right]\Phi + z\left[\left(60 - \frac{72\sqrt{3}}{\pi}\right) - 24z^2\right]\Phi' - \frac{\sqrt{3}}{\pi}(12 - 72z^2)\Phi(\sqrt{3}\,z)\right\} \tag{35}$$

$$\frac{\mathrm{d}\psi_5}{\mathrm{d}z} = \frac{1}{24}\Phi'\left\{(138 - 152z^2 + 24z^4)(\Phi)^3 - z(102 - 36z^2)\Phi'(\Phi)^2 - (15 - 18z^2)(\Phi')^2\Phi + 6z(\Phi')^3 - \left(20 - \frac{24\sqrt{3}}{\pi}\right)(3 - 2z^2)\Phi + \left(20 - \frac{24\sqrt{3}}{\pi}\right)z\Phi' + \frac{\sqrt{3}}{\pi}(12 + 24z^2)\Phi(\sqrt{3}z)\right\} \tag{36}$$

$$\frac{\mathrm{d}\psi_6}{\mathrm{d}z} = -\frac{1}{4}\Phi'\left\{(6 - 4z^2)(\Phi)^3 - 6z\Phi'(\Phi)^2 - 3(\Phi')^2\Phi + \frac{4\sqrt{3}}{\pi}\Phi(\sqrt{3}z)\right\} \tag{37}$$

where

$$\Phi(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-z^2}\,\mathrm{d}z \tag{38}$$

$$\Phi'(z) = \frac{2}{\sqrt{\pi}}e^{-z^2} \tag{39}$$

Equations for ψ_4, ψ_5 and ψ_6 have not been determined because it was found that they are not required in deriving subsequent equations. In Fig. 1 are shown graphs[18] of each $\mathrm{d}\psi_i/\mathrm{d}z$ ($i = 0,1,...,6$) as a function of z. Numerical tables of $\mathrm{d}\psi_0/\mathrm{d}z$, ..., $\mathrm{d}\psi_6/\mathrm{d}z$ and $\psi_0, \ldots, \psi_3$ in the range $0 \leqslant z \leqslant 3.5$ have been prepared at intervals of $\Delta z = 0.1$ and are available as a microfilm supplement to this article.[19]

The Refractive Index Gradient Distribution.—The equation for the solution refractive index, n, as a function of concentration, C, may be written in the form of a Taylor series about $C = \bar{C}$

$$n(C) = n(\bar{C}) + R(C - \bar{C})[1 + a_1(C - \bar{C}) + a_2(C - \bar{C})^2 + a_3(C - \bar{C})^3 + \ldots] \tag{40}$$

where

$$R = \left(\frac{\mathrm{d}n}{\mathrm{d}C}\right)_{C=\bar{C}} \tag{41}$$

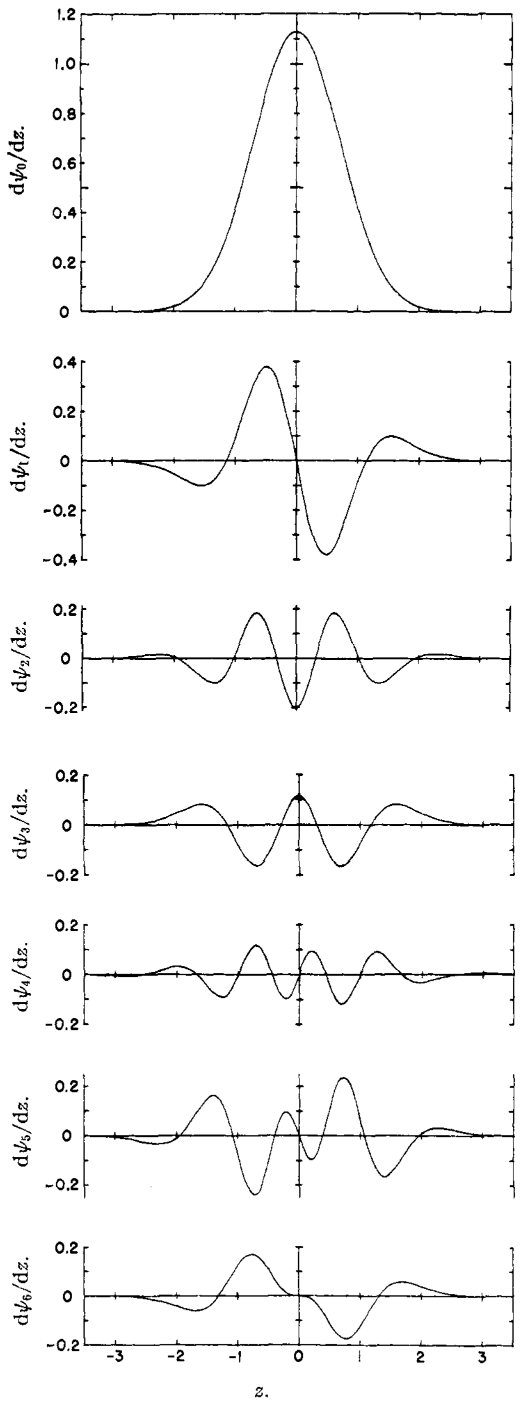

Fig. 1.—Graphs of the functions in equations 31–37. The reduced concentration gradient curve for a free diffusion experiment in which D varies with C is obtained by differentiation of equations 13–17 with respect to z and substitution of these functions.

and

$$a_1 = \frac{1}{2!\,R}\left(\frac{\mathrm{d}^2n}{\mathrm{d}C^2}\right)_{C=\bar{C}},\quad a_2 = \frac{1}{3!\,R}\left(\frac{\mathrm{d}^3n}{\mathrm{d}C^3}\right)_{C=\bar{C}},\ \text{etc.} \tag{42}$$

It should be noted that R, a_1, a_2, etc., are all functions of $\bar{C}$. The values of these quantities may be determined from direct optical measurements or as auxiliary data from optical diffusion measurements.

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(18) Computed with the aid of the "Tables of Probability Functions," Vol. I, Federal Works Agency, Work Projects Administration (Sponsored by the National Bureau of Standards), 1941. Available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

(19) This supplementary table has been deposited as Document number 5060 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Equation 40 may be written in terms of ϕ by utilizing equation 6

$$n(C) = n(\bar{C}) + R\left(\frac{\Delta C}{2}\right)\left[\phi + a_1\left(\frac{\Delta C}{2}\right)\phi^2 + a_2\left(\frac{\Delta C}{2}\right)^2\phi^3 + a_3\left(\frac{\Delta C}{2}\right)^3\phi^4 + \ldots\right] \quad (43)$$

This relation may be then expanded in powers of ΔC using equations 13–17

$$n(C) = n(\bar{C}) + R\left(\frac{\Delta C}{2}\right)\left[\Psi_0 + \left(\frac{\Delta C}{2}\right)\Psi_1 + \left(\frac{\Delta C}{2}\right)^2\Psi_2 + \left(\frac{\Delta C}{2}\right)^3\Psi_3 + \ldots\right] \quad (44)$$

where

$$\Psi_0 = \psi_0 \quad (45)$$

$$\Psi_1 = k_1\psi_1 + a_1(\psi_0)^2 \quad (46)$$

$$\Psi_2 = k_1^2\psi_2 + k_2\psi_3 + 2a_1k_1\psi_1\psi_0 + a_2(\psi_0)^3 \quad (47)$$

$$\Psi_3 = k_1^3\psi_4 + k_1k_2\psi_5 + k_3\psi_6 + a_1k_1^2[(\psi_1)^2 + 2\psi_2\psi_0] + 2a_1k_2\psi_3\psi_0 + 3a_2k_1\psi_1(\psi_0)^2 + a_3(\psi_0)^4 \quad (48)$$

For a given value of $\bar{C}$ the refractive index gradient–distance curve is obtained by differentiating equation 44 with respect to x and utilizing equation 10

$$\frac{\partial n}{\partial x} = \frac{R}{2\sqrt{D(\bar{C})t}}\left(\frac{\Delta C}{2}\right)\left[\frac{\mathrm{d}\Psi_0}{\mathrm{d}z} + \left(\frac{\Delta C}{2}\right)\frac{\mathrm{d}\Psi_1}{\mathrm{d}z} + \left(\frac{\Delta C}{2}\right)^2\frac{\mathrm{d}\Psi_2}{\mathrm{d}z} + \left(\frac{\Delta C}{2}\right)^3\frac{\mathrm{d}\Psi_3}{\mathrm{d}z} + \ldots\right] \quad (49)$$

The Reduced Height–Area Ratio and Reduced Second Moment of the Refractive Index Gradient Curves.—The reduced height–area ratio, $\mathfrak{D}_A$, of the refractive index gradient curve is defined by

$$\mathfrak{D}_A = \frac{(n_B - n_A)^2}{4\pi t(\partial n/\partial x)^2_{\max}} \quad (50)$$

Here $n_B - n_A$ represents the refractive index difference between the starting solutions of concentrations C_B and C_A; using equation 40 it may be written in the form

$$n_B - n_A = R\Delta C\,\{1 + (\Delta C/2)^2a_2 + O[(\Delta C)^4]\} \quad (51)$$

To obtain an expression for the height of the maximum refractive index gradient, $(\partial n/\partial x)_{\max}$, its position on the z coördinate must first be determined by solving the equation

$$\frac{\mathrm{d}^2n}{\mathrm{d}z^2} = 0 \quad (52)$$

for z. It is shown readily that this value of z approaches zero as ΔC becomes vanishingly small. Therefore, we may seek the desired root, z_*, of equation 52 in the form of a power series in ΔC for moderately small values of ΔC.

$$z_* = (\Delta C/2)z_1 + (\Delta C/2)^2z_2 + (\Delta C/2)^3z_3 + \ldots \quad (53)$$

The coefficients z_1, z_2, etc., are determined as follows. First, all Ψ_i's ($i \geqslant 0$) are expanded in powers of z and derivatives of the resulting expressions are substituted in equation 49. The value of dn/dz, obtained from equation 49, is then inserted in equation 52 to give an expression which, after substituting equation 53 for z, may be arranged in powers of $\Delta C/2$. Each coefficient in that series is equated to zero, giving a system of equations which may be solved successively for z_1, z_2, etc. This procedure yields

$$z_* = \frac{\Delta C}{2\sqrt{\pi}}\left\{(2a_1 - k_1) + \frac{(\Delta C)^2}{16\pi}[96a_2a_1 - (72 - 12\pi)a_2k_1 - 96a_1^3 + (96 - 8\pi)a_1^2k_1 - (24 + 8\sqrt{3} - 8\pi/3)a_1k_2 - (12 - 6\sqrt{3} + 2\pi)a_1k_1^2 + (40 + 4\sqrt{3} - 16\pi/3)k_1k_2 - (6 + 3\sqrt{3} - 3\pi)k_1^3] + O[(\Delta C)^4]\right\} \quad (54)$$

Longsworth's statement[9] that the two sources of skewness may partially compensate each other for some systems is supported by this relation; in fact, if $k_1 = 2a_1$ there is no first-order shift in the position of the maximum refractive index gradient from the initial boundary ($x = 0$).

By inserting equation 54 in equation 49 we obtain

$$\left(\frac{\partial n}{\partial x}\right)_{\max} = \frac{R\Delta C}{2\sqrt{\pi D(\bar{C})t}}\left\{1 + \frac{(\Delta C)^2}{16\pi}P + O[(\Delta C)^4]\right\} \quad (55)$$

where

$$P = 16a_1^2 - (24 - 4\pi)a_1k_1 + (6 + 3\sqrt{3} - 3\pi)k_1^2 + (4 - 4\sqrt{3} + 4\pi/3)k_2 \quad (56)$$

Substitution of equations 51 and 55 into equation 50 yields the desired relation

$$\mathfrak{D}_A = D(\bar{C})\,\{1 - K(\Delta C)^2 + O[(\Delta C)^4]\} \quad (57)$$

with K given by[20]

$$K = \frac{1}{24\pi}[48a_1^2 - (72 - 12\pi)a_1k_1 + (18 + 9\sqrt{3} - 9\pi)k_1^2 + (12 - 12\sqrt{3} + 4\pi)k_2 - 12\pi a_2] \quad (58)$$

Equation 57 indicates that $\mathfrak{D}_A$ for a given $\bar{C}$ varies linearly with $(\Delta C)^2$ for sufficiently small values of ΔC. The intercept at $\Delta C = 0$ and the slope of this straight line permit direct determination of $D(\bar{C})$ and K.

The reduced second moment, $\mathfrak{D}_{2m}$, of the refractive index gradient curve is defined by

$$\mathfrak{D}_{2m} = \frac{1}{2t(n_B - n_A)}\int_{-\infty}^{\infty}\frac{\partial n}{\partial x}x^2\,\mathrm{d}x \quad (59)$$

It will be recalled that $x = 0$ is defined as the position of the initial boundary. Substitution of equations 49 and 51 then leads to

$$\mathfrak{D}_{2m} = D(\bar{C})\,\{1 - L(\Delta C)^2 + O[(\Delta C)^4]\} \quad (60)$$

where[21]

$$L = \frac{1}{12}[-2a_1k_1 - k_2 - (6\sqrt{3}/\pi)a_2] \quad (61)$$

Thus, for sufficiently small values of ΔC, $\mathfrak{D}_{2m}$ at a given $\bar{C}$ also varies linearly with $(\Delta C)^2$. The intercept at $\Delta C = 0$ and the slope of this straight line permit direct evaluation of $D(\bar{C})$ and L.

Methods for Determining the Diffusion Coefficient *versus* Concentration Relationship.—On the basis of the theoretical relations obtained above we now propose two methods for determining the dependence of the diffusion coefficient on concentration for a given system from measurements of $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$.

a. **First Method.**—From equations 57 and 60 it is seen that the value of D corresponding to a

(20) For purposes of computation, equation 58 is written in the form

$$K = 0.63662a_1^2 - 0.45493a_1k_1 + 0.07048k_1^2 + 0.05016k_2 - 0.50000a_2 \quad (58a)$$

(21) This equation may also be written

$$L = -0.16667a_1k_1 - 0.08333k_2 - 0.27566a_2 \quad (61a)$$

particular concentration, $C = \bar{C}'$, can be obtained by performing several experiments with different values of ΔC but with each value of $\bar{C}$ equal to $\bar{C}'$. A plot of *either* $\mathfrak{D}_A$ or $\mathfrak{D}_{2m}$ against $(\Delta C)^2$ should be a straight line, which may be extrapolated to $(\Delta C)^2 = 0$ to obtain the value of D at $\bar{C}'$. Repetition of this procedure for several different values of $\bar{C}'$ yields the correct graph of D *versus* C without knowledge of the refractometric constants R, a_1, a_2, etc.

Because of the large number of experiments required, this procedure might be very laborious. Provided that sufficiently small values are used for ΔC, approximate data for the dependence of D on C may be obtained by performing only one experiment at each of several mean concentrations, $\bar{C}$. The resultant error is seen from equations 57 and 60 to be of the order $K(\Delta C)^2$, or $L(\Delta C)^2$, compared with unity. It should be remembered that for a constant value of ΔC this error may vary throughout the concentration range because in general both K and L depend on the value of $\bar{C}$.

b. Second Method.—In this method the desired D *versus* C relationship is calculated from equation 4, after using $\mathfrak{D}_A$ and $\mathfrak{D}_{2m}$ to evaluate its coefficients at a particular concentration. For this purpose some concentration, $\bar{C}'$, is selected in the central part of the concentration range of interest, and several experiments with $\bar{C} = \bar{C}'$ but with different values of ΔC are performed. The values of $\mathfrak{D}_A$ and of $\mathfrak{D}_{2m}$ from these experiments are plotted against $(\Delta C)^2$ in order to determine the limiting slopes, K and L, of equations 57 and 60. A separate value of $D(\bar{C}')$ is provided by each graph; the two results should be identical. Substitution of these values for K and L into equations 58 and 61 allows solution for k_1 and k_2, provided a_1 and a_2 are known from independent data. It should be noted that all of these values correspond to concentration $\bar{C}'$; in general they are all concentration dependent. Equation 51 may be of use to determine the value of a_2, because it indicates that a plot of $(n_B - n_A)/\Delta C$ *versus* $(\Delta C/2)^2$ for experiments at a given mean concentration should have an intercept equal to R at $\Delta C = 0$, and a limiting slope of Ra_2. Substitution into equation 4 of the values of k_1, k_2 and $D(\bar{C})$ thus determined at concentration $\bar{C}'$ permits calculation of D as a function of C throughout the range in which terms of order higher than $(C - \bar{C}')^2$ may be neglected in comparison with unity.

Experimental

All experiments were performed with the Gouy diffusiometer described previously,[22,23] using the 5460.7 Å. mercury line isolated from a General Electric Co. A-H4 lamp with a Wratten 77A filter. The diffusion cell was of a fused silica Tiselius type,[24] 9 cm. in height, having an optical path, **a**, of 2.506_2 cm. and an optical lever arm, b, of 306.86 cm. referred to the refractive index of air as unity. This cell was mounted[25] so that when opening the cell its center section remained fixed relative to the cell holder and masks. To determine the small permanent displacement,[26,27] δ, of the reference fringes relative to fringes formed from light coming through the central part of the cell, five sets of special photographs were taken for this purpose in each experiment and the data averaged. Because these average values fell within a range of only 3 μ, an over-all average value of $\delta = +7\ \mu$ was applied to measured displacements of Gouy fringes from the reference pattern in every experiment to obtain the corrected Gouy fringe displacements, Y_j (j denotes fringe minima 0, 1, 2, etc., counting upward along the Gouy pattern). A similar correction, $\delta' = +8\ \mu$, was measured and used in evaluating the Rayleigh fringe data to obtain the fractional part of the total number of fringes, j_m.

The methods used to analyze the Gouy fringe data were essentially the same as those used previously[26,28] when the concentration dependence of the diffusion coefficient was neglected. However, the former notation based on the variable $z = x/(2\sqrt{Dt})$ is not rigorously applicable to the present experiments because the refractive index gradient curves are known to be appreciably skew[9,10] Therefore we write the interference condition for fringe minima as[29,30]

$$\mathrm{f}(\zeta_j) = Z_j/j_m \qquad (62)$$

which defines the variable ζ_j for a given experiment. As before, the reduced fringe displacement, $e^{-\zeta_j^2}$, corresponding to the reduced fringe number, $\mathrm{f}(\zeta_j)$, was obtained from tables. For each photograph the ratio $Y_j/e^{-\zeta_j^2}$ was then extrapolated[29,31] to $Z_j^{2/3} = 0$ to obtain the deflection, C_t, corresponding to the maximum refractive index gradient at that time. Although this procedure was shown to be valid for symmetrical refractive index gradient curves consisting of the sum of two or more Gaussian curves, it must at present be considered an empirical procedure when applied to these skew curves. That a reasonable extrapolation can be obtained is observed from Fig. 2, which shows this extrapolation for one photograph from each of three experiments with different concentration differences, ΔC, across the initial boundary. These photographs were selected to give an approximately constant value of the ratio $C_t/(j_m)^{2/3}$; equation 31 of reference 29 then predicts equal slopes if these non-zero slopes had arisen from the presence of an impurity in the n-butanol, rather than from the concentration dependences of D and of $\mathrm{d}n/\mathrm{d}C$.

The reduced height–area ratio, $\mathfrak{D}_A$, for each experiment was calculated using equation 50 written in the form[25]

$$\mathfrak{D}_A = \frac{(j_m \lambda b)^2}{4\pi C_t^2 t} \qquad (63)$$

in which λ is the wave length of the light in air, 5460.7 Å. To correct for imperfections in the initial boundaries produced by the single-prong capillary sharpening technique, 7 or 8 Gouy fringe photographs were taken during the course of each experiment, and the measured values of $\mathfrak{D}_A$ obtained from these photographs were extrapolated to $1/t = 0$.[32] This extrapolation gave satisfactory straight lines for experiments with the smaller values of ΔC, but difficulty was encountered when ΔC was large. Long times then had to elapse before all fringes were in view so photographs could be taken, and the proper slopes of lines for extrapolating these closely grouped points were not obvious from the data. However, since the slopes for experiments with $\Delta C = -0.2$ and $\Delta C = -0.3$ corresponded to starting times of about 14 sec., this figure was arbitrarily used to guide the extrapolations for the other experiments. All other reasonable slopes would have yielded values of $\mathfrak{D}_A$ within 0.1% of the reported values.

No temperature correction of the observed values of $\mathfrak{D}_A$ was required because the constant temperature water bath surrounding the diffusion cell was maintained within 0.00_3° of 25°.

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[22] L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

[23] P. J. Dunlop and L. J. Gosting, THIS JOURNAL, **75**, 5073 (1953).

[24] Obtained from Pyrocell Mfg. Co., 207 East 84th Street, New York 28, N. Y., and referred to in ref. 25 as cell number SD.

[25] P. J. Dunlop and L. J. Gosting, THIS JOURNAL, **77**, 5238 (1955).

[26] L. J. Gosting and M. S. Morris, *ibid.*, **71**, 1998 (1949).

[27] L. J. Gosting, *ibid.*, **72**, 4418 (1950).

[28] G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

[29] D. F. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).

[30] Values of $Zj = (j + {}^3/_4 + \ldots)$ were obtained from Table I of ref. 26.

[31] Values of $Zj^{2/3}$ were obtained from Table III of ref. 29.

[32] L. G. Longsworth, THIS JOURNAL, **69**, 2510 (1947).

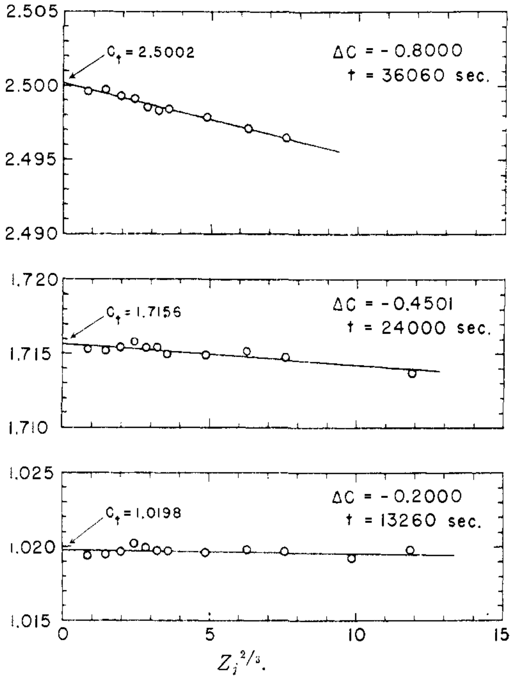

Fig. 2.—Representative extrapolations used for obtaining C_t. It is seen that $Y_i/e^{-\zeta_i^2}$ *versus* $Z_i^{2/3}$ is linear within experimental error, even though each refractive index gradient curve was known to be appreciably skewed.

Materials.—Approximately two liters of a commercially available sample[33] of n-butanol was distilled using a Oldershaw glass bubble plate column having 30 (actual) plates and equipped with an automatic liquid-dividing still-head. The first 750 ml. of distillate was discarded and the next 500 ml. of n-butanol was kept for the experiments. During collection of this sample the temperature at the top of the still-head was constant within $\pm 0.0_1°$. The density of this material at 25° was found to be 0.80570 g./ml.[34]

Doubly distilled water which had been saturated with air at room temperature was used as solvent.

Solutions.—All solutions were made up by weight. In an attempt to minimize difficulties due to evaporation, a stock solution containing $6.002_3\%$ by weight of n-butanol *in vacuo* (0.8000_4 molar) was prepared first using conditions designed to minimize exposure of the materials to the atmosphere. Density measurements on this solution yielded a value of 0.98799 g./ml. Other solutions were then prepared by adding the proper amount of solvent to weighed portions of this stock. The calculated weight % of each solution was converted to moles per liter by using the 25° density data of Lyons and Sandquist[11] and a value of 74.124 for the molecular weight of n-butanol.

Results and Discussion

Data for five experiments designed to test the above theory are presented in Table I. It will be noted that the mean concentration, $\bar{C} = (C_A + C_B)/2$, of n-butanol was made the same in each experiment, while the concentration difference, $\Delta C = C_B - C_A$, was varied. Here ΔC is negative because, to maintain gravitational stability, the upper solution, A, was made more concentrated in n-butanol than the lower solution, B. Column 1 indicates the order in which the experiments were performed, while column 5 lists the starting time corrections,[32] Δt, associated with extrapolation of the measured reduced height–area ratios to infinite time (*i.e.*, to $1/t = 0$). These extrapolated values of $\mathfrak{D}_A$ are presented in column 6, and it is seen that they vary appreciably with ΔC. That this change in $\mathfrak{D}_A$ is linear in $(\Delta C)^2$, as predicted by equation 57, is shown in Fig. 3; from the slope of the solid line a value of 0.031_7 is obtained for K.

TABLE I

DEPENDENCE OF THE REDUCED HEIGHT-AREA RATIO, $\mathfrak{D}_A$, ON ΔC FOR THE SYSTEM n-BUTANOL–WATER

$T = 25.00_0°$

1 Exp. no.	2 ΔC, moles/l.	3 $\bar{C}$, moles/l.	4 j_m	5 Δt, sec.	6 $\mathfrak{D}_A \times 10^5$, cm.²/sec.
IV	−0.2000	0.4000	72.17	14.4	0.8432
I	− .3000	.4000	108.70	14.0	.8414
III	− .4501	.4000	162.99	(14)[a]	.8391
V	− .6500	.4000	234.64	(14)	.8331
II	− .8000	.4000	288.90	(14)	.8268

[a] Values in parentheses were assumed and used to guide the extrapolation of measured reduced height–area ratios to infinite time ($1/t = 0$).

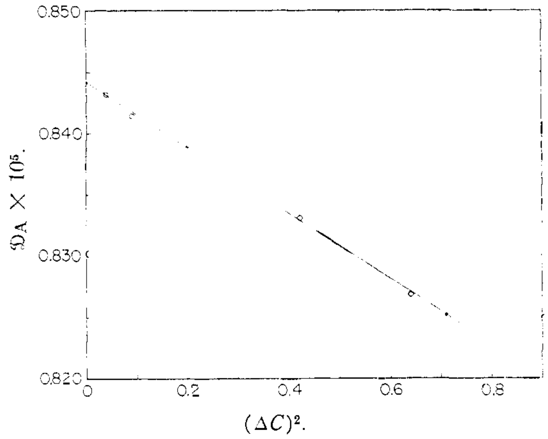

Fig. 3.—The linear dependence of the reduced height-area ratio, $\mathfrak{D}_A$, on $(\Delta C)^2$ for n-butanol in water when $\bar{C}$ = 0.4 molar. The straight line shown was drawn to represent best the experimental points and its slope was used to evaluate K, equations 57 and 58. A value of $0.844_2 \times 10^{-5}$ cm.²/sec. is obtained for D from the intercept at $(\Delta C)^2 = 0$.

According to equations 57 and 58, K is directly related to the coefficients a_1, a_2, k_1 and k_2 in equations 4 and 40. By fitting the data of Lyons and Sandquist[11] to equations 4 and 40[35] written with $\bar{C} = 0.4$, we obtain the values $k_1 = -0.360_5$, $k_2 = 0.023$ and $a_1 = 0.042$. The value so calculated for a_2 is less reliable; depending on the particular curve drawn through the experimental points, values ranging from −0.05 to −0.03 may be ob-

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(33) "Baker Analyzed" Reagent, J. T. Baker Chemical Co., Phillipsburg, N. J.

(34) Values of 0.80572 and 0.80567 were obtained for $d^{25}{}_4$ by G. Jones and S. M. Christian, THIS JOURNAL, **61**, 82 (1939), and by A. S. Brunjes and M. J. P. Bogart, *Ind. Eng. Chem.*, **35**, 255 (1943), respectively.

(35) For this calculation equation 40 was rewritten in the form

$$\frac{\Delta n}{\Delta C} - Ra_2\left(\frac{\Delta C}{2}\right)^2 = R[1 + 2a_1(\bar{C}^* - \bar{C}) + 3a_2(\bar{C}^* - \bar{C})^2 + \ldots] \quad (40a)$$

where $\Delta n = n_B - n_A$, $\bar{C}$ = 0.4 molar and $\bar{C}^*$ denotes the several values of $(C_A + C_B)/2$ corresponding to the measured values of $\Delta n/\Delta C$ in their different experiments. It will be recalled that in Lyons and Sandquist's experiments ΔC was held nearly constant while $(C_A + C_B)/2$ was varied over a wide range. The term $Ra_2(\Delta C/2)^2$ was so small that it could be neglected in fitting equation 40a to their experimental points near $C = 0.4$.

tained.[36] Since for this system the term containing a_2 in equation 58 (or 58a) contributes nearly half the value of K, this uncertainty in a_2 imposes a serious limitation on checking the validity of equation 57. A partial confirmation is obtained, however, subject to the assumption of a negligible volume change on mixing, by using the above values of k_1, k_2, a_1 and K to calculate a value for a_2. In this way we obtain $a_2 = -0.027$, which is consistent with the range of a_2 obtained from Lyons and Sandquist's refractometric data. It is hoped that a more exact test of equation 57 will eventually be possible, either by obtaining a more accurate measurement of a_2 at $\bar{C} = 0.4$ for this sytem or by studying a system for which a_2 is so small that its contribution to K is negligible.

Figure 3 illustrates part of the "first method," described at the end of the theoretical section, for obtaining the *D versus C* relationship. The intercept at $(\Delta C)^2 = 0$ yields the value $D = 0.844_2 \times 10^{-5}$ cm.²/sec. for $\bar{C} = C = 0.4$. From the slope of these data it is seen that for this system with $\bar{C} = 0.4$ the values of $\mathfrak{D}_{\mathrm{A}}$ differ from the value of D by less than $0.1_2\%$ provided that $|\Delta C| \leqslant 0.2$. If $|\Delta C| \simeq 0.3$, $\mathfrak{D}_{\mathrm{A}}$ differs from D by about $0.2_9\%$. In order to use confidently the approximate form of the "first method," whereby the *D versus C* curve is obtained by using only one experiment with a small ΔC at each value of $\bar{C}$, some knowledge of this difference between $\mathfrak{D}_{\mathrm{A}}$ and D is required.

Neither the "second method" for obtaining the *D versus C* relationship, nor the alternative part of the "first method" utilizing $\mathfrak{D}_{2\mathrm{m}}$, could be tested with the data presented above. These limitations exist because no method has been found for evaluating the reduced second moments, $\mathfrak{D}_{2\mathrm{m}}$, from Gouy fringe data for skewed refractive index gradient curves; the method[37] for obtaining $\mathfrak{D}_{2\mathrm{m}}$ from $\mathfrak{D}_{\mathrm{A}}$ and the fringe deviation graph is applicable only to symmetrical refractive index gradient curves.

The remaining data of interest from the experiments reported in Table I are contained in the fringe deviation graphs,[25,29] shown in Fig. 4. Here the reduced fringe deviations, $\Omega_j \equiv e^{-\zeta_j^2} - Y_j/C_t$, contain all of the information provided by the Gouy fringes about deviations of the refractive index gradient curves from the Gaussian shape. They are plotted against the reduced fringe numbers, $f(\zeta_j)$, equation 62. To simplify the notation the subscripts, j, are now omitted. The dots at a given value of $f(\zeta)$ represent values of Ω for a given fringe at different times, while each cross indicates the arithmetic average of these values. It is seen that the fringe deviations are largest for the largest value of ΔC and diminish as ΔC diminishes until they become nearly zero for $\Delta C = -0.3$ and $\Delta C = -0.2$. These fringe deviation graphs would have been identical had they arisen from an impurity in the n-butanol.[29] Because Longsworth[9] and Creeth[10] have demonstrated with their Rayleigh fringe measurements that n-butanol–water solutions with $\Delta C \simeq -0.2$ exhibit quite skew refractive index gradient curves, it is evident from the data in Fig. 4 that the Gouy fringes are quite insensitive to such skewness. Further studies are required to determine whether the fringe deviations for the larger values of ΔC are due to skewness or to the second order symmetrical deviations represented by $d\psi_2/dz$ and $d\psi_3/dz$, equations 33 and 34.

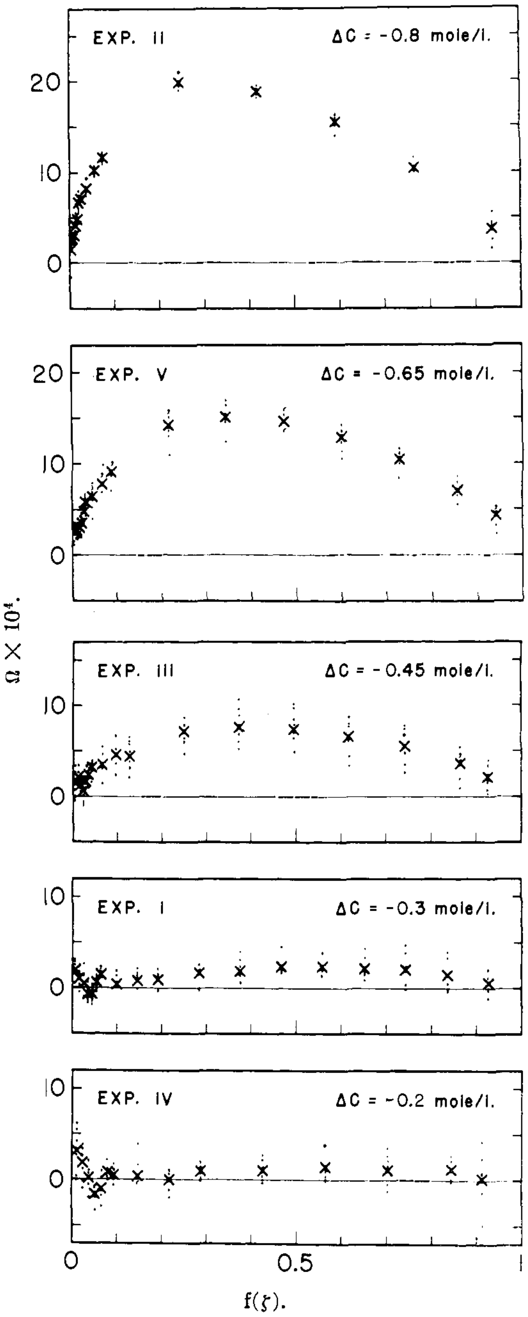

Fig. 4.—Graphs of the Gouy fringe deviations for experiments reported in Table I.

Acknowledgments.—The authors are indebted to Drs. R. L. Baldwin, P. J. Dunlop and J. W. Williams for helpful suggestions during the preparation of this manuscript.

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(36) The value of a_2 is extremely sensitive to small errors in the values for $\Delta n/\Delta C$. It was hoped that a better value of a_2 could be obtained by plotting our data for $\Delta n/\Delta C$ (obtained at $\bar{C} = 0.4$) *versus* $(\Delta C)^2$ and using equation 51 to evaluate a_2 from the slope. However, perhaps because of evaporation while filling the cell, the data showed too much scatter to yield a more reliable result.

(37) See equation 47 of ref. 25 or equation 39 of ref. 29.

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MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Potentiometric Measurement of Ion-pair Dissociation Constants. HCl, NaCl and KCl in 70% Dioxane–30% Water[1]

BY E. LEE PURLEE AND ERNEST GRUNWALD

RECEIVED OCTOBER 12, 1956

In the calculation of ion-pair dissociation constants K from potentiometric data the difficult part is the estimation of the activity coefficients, y', of the free ions. For solvents of intermediate dielectric constant, Marshall and Grunwald derived the equation, $-\log y' = 0.8686\,\{1 - [\log(1 + 2.303\,S\sqrt{\mu})]/S\sqrt{\mu}\}$, (where S is the Debye–Hückel limiting slope and μ the free ion ionic strength). The validity of this equation is now demonstrated by means of accurate potentiometric data for concentrations ranging from 8×10^{-5} M up to 0.0025 M where interionic effects of higher order than pairwise become significant. E.m.f. data accurate to 0.05 mv. even at the lowest concentrations were obtained by the following experimental techniques. The measuring cell was: glass electrode/solution X/AgCl–Ag, it having been shown that the e.m.f. of the cell: Pt–H_2/solution X/glass electrode, is constant for our solutions. The Ag–AgCl electrode was of the silver mirror-electrolytic type, equilibrated in 10–15 minutes and was free from aging effects. The ionic strengths were low enough so that different methods of extrapolation to infinite dilution led to almost identical values for the standard e.m.f. Activity coefficients for HCl were predicted without adjustable constants by means of the equation of Marshall and Grunwald and of a conductometric value of K, and agreed to ±0.06% with the measured values. The same approach led to precise values of 10^3K for NaCl (5.35 ± 0.07) and KCl (2.35 ± 0.11).

In solvents of intermediate dielectric constant where the formation of short-range ion pairs is not negligible, Bjerrum's approach to the problem of ionic activity coefficients[2] is particularly useful. In this approach, the troublesome short-range interionic effects need not be calculated explicitly; they are accounted for by the device of an equilibrium (1), between the short-range ion pairs C^+A^- and the long-range pairs or free ions. Thus, if c is

$$C^+A^- = C^+ + A^- \qquad (1)$$

the formal concentration and y the molar activity coefficient of the electrolyte, and if α is the fraction and y' the activity coefficient of the free ions, y is given by equation 2 and α by equation 3.

$$y = \alpha y' \qquad (2)$$

$$\alpha^2(y')^2c/(1 - \alpha) = K \qquad (3)$$

Since in equation 2, the factor α allows for the short-range interactions, the calculation of y' involves long-range interactions only. K in equation 3 is the ion-pair dissociation constant.

In a recent paper from this Laboratory[3] it was shown that K may be identical with the ion-pair dissociation constant deduced from conductivity data if the equations for the equivalent conductance Λ and for y' are given to a better approximation than that of the limiting laws. For uni-univalent electrolytes equation 4 was derived for y' from a plausible model for the charging process of a free ion in media where the ionic diameter is small compared to the Bjerrum distance $q = \epsilon^2/2DkT$.

$$-\log y' = \frac{\epsilon^2[\kappa q - 2.303\log(1 + \kappa q)]}{2.303\,q^2DkT} \qquad (4)$$

In this equation, ϵ is the unit of ionic charge, D the dielectric constant, k Boltzmann's constant, and T the absolute temperature. $1/\kappa$, the effective thickness of the ionic atmosphere, is defined as usual[2,4] by equation 5, where μ is the ionic strength of the free ions and N is Avogadro's number.

$$\kappa^2 = 8\pi\epsilon^2N\mu/1000DkT \qquad (5)$$

For practical calculations equation 4 reduces to the form 4a, where S, the Debye–Hückel limiting slope, is equal to $1.825 \times 10^6/(DT)^{3/2}$

$$-\log y' = 0.8686\,\{1 - [\log(1 + 2.303\,S\sqrt{\mu})]/S\sqrt{\mu}\} \qquad (4a)$$

We now report potentiometric data, accurate to 0.05 mv., for solutions of HCl and its mixtures with NaCl and KCl in 70.00 wt. % dioxane–30.00 wt. % water at concentrations as low as 0.0001 M. (This concentration is low enough to permit an unambiguous evaluation of the standard potential and hence of y.) In this solvent (D = 19.07 at 25°) the formation of ion pairs is considerable even at low concentrations, and the data furnish a good basis for the testing of equations 2, 3 and 4a. Using the conductometric value of K for hydrochloric acid,[3] the predicted values of y agree with observation within 0.06% up to 0.0025 M and are in error by no more than 2.6% at 0.01 M. For NaCl and KCl, conductometric K values are not available, but application of equations 2, 3 and 4 to the data for HCl–NaCl and HCl–KCl mixtures at ionic strengths below 0.002 M leads to highly precise values of K over several-fold variations in the solute concentrations. One may conclude, therefore, that the potentiometric method, in conjunction with equations 2, 3 and 4a, is well-suited to the precise determination of ion-pair dissociation constants.

E.M.F. Measurements and Electrode Behavior.—The cell used in this work is shown in equation 6,

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[1] This work was supported by the National Science Foundation.

[2] N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Math-fys. Medd.*, **7**, No. 9 (1926).

[3] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1950, second edition, p. 32.