

Fig. 2.—Concentration dependence of the diffusion coefficient: O, D,L- α -alanine, Gouy method, this study; \square , L- α -alanine, Gouy method, this study; \blacksquare , D- α -alanine, Gouy method, this study; \blacktriangle , D,L- α -alanine, L. G. Longsworth, Rayleigh fringes; —, exptl. least square; - - - - , $D_0[1 + c \partial \ln \gamma/\partial c]$; $D_0[1 + c \partial \ln \gamma/\partial c][\eta^0/\eta]$; $D_0 = 91.460 \times 10^{-7}$ (extrapolated).

to 25° are about 12% lower than ours, even after correcting their cell calibration by adjusting their 25° value for sucrose to the value obtained at the

same median concentration by Gosting and Morris. The values of Polson²⁵ at 20° using the Lamm scale method²⁶ have been extrapolated to 25° using the relation $D\eta^0/T = \text{const.}$ and appear to lie a few per cent. above ours. Included in Fig. 2 is one unpublished value of Longsworth,²⁷ employing the vertical axis cylindrical lens type of Rayleigh interferometer,²⁸ in which his experimental diffusion coefficient value at 0.3166% DL- α -alanine (corrected to vacuum standard) is 9.090×10^{-6} cm.²/sec. while that calculated from our results at the same concentration using equation (5) is 9.094×10^{-6} cm.²/sec. This excellent agreement lends further confidence in the correctness of these two interference optical methods, and makes additional comparisons between them of great interest.

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(26) O. Lamm, *Nova Acta Soc. Sci. Upsal.*, **10**, No. 6 (1937).

(27) L. G. Longsworth, private communication.

(28) H. Svensson, *Acta Chem. Scand.*, **5**, 72, 1410 (1951); G. Kegeles and H. A. Sober, *Anal. Chem.*, **24**, 654 (1952); L. G. Longsworth, *THIS JOURNAL*, **74**, 4155 (1952).

BETHESDA, MARYLAND
WORCESTER, MASS.

[CONTRIBUTION NO. 1157 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

A Study of the Diffusion of *n*-Butyl Alcohol in Water Using the Gouy Interference Method

BY PHILIP A. LYONS AND C. LENNART SANDQUIST

RECEIVED APRIL 10, 1953

The diffusion coefficients, densities, viscosities and specific refractive increments for solutions of *n*-butyl alcohol in water at 1 and 25° have been determined. A limiting form for expressing the diffusion coefficient as a function of concentration in relatively dilute solutions has been suggested. The temperature and concentration dependence of the diffusion coefficient and of the relative viscosity for this system are consistent with the point of view that systems with large, positive deviations from Raoult's law will have abnormally high diffusion mobilities and relative viscosities.

Precise determinations of diffusion coefficients in solutions are now possible as a result of the development of interference methods.¹⁻³ Using one of these methods, investigations have been made on the concentration dependence of the diffusion coefficients in dilute solutions of some non-electrolytes in water.⁴⁻⁶ Among other results this work has defined the experimental limitation on the use of the change of the macroscopic relative viscosity as a measure of the change in the relative diffusion mobility. The formal limitations on this device have also been clearly outlined.⁷ For the particular class of systems which exhibits large, positive deviations from Raoult's law, it has been suggested that high diffusion mobilities might be expected.⁸

Solutions of *n*-butyl alcohol and water do show large, positive deviation from Raoult's law (there is a separation of phases before the *n*-butyl alcohol concentration reaches one molar). It was the purpose of this work to see if these large deviations are

reflected in the concentration and temperature dependence of the diffusion coefficients.

Experimental Procedure

Preparation of Solutions.—Baker's C.P. *n*-butyl alcohol was dried by shaking with anhydrous CaSO₄ before purification. After fractionation the center cut was stored over 6-mesh anhydrous CaSO₄ until use. The solutions were prepared by weighing the alcohol and adding directly into calibrated volumetric flasks. Concentrations were known to about $\pm 0.05\%$.

Densities and Viscosities.—Densities were determined at 1 and 25° using a twin-armed pycnometer of about a 20-ml. capacity.⁹

Flow times in an Ostwald viscometer were obtained to estimate the relative viscosities of the solutions used. All the viscosity data were corrected for kinetic energy losses.

Diffusion Data.—The equipment used to make the measurements reported is, with minor differences, the same as that already described.¹⁰ The cell and photographic plate masking procedure of Gosting has been used.¹¹

The mercury green line (5460.7 Å.) was used to produce the Gouy pattern. A Tiselius cell whose "a" distance, as measured by the bar and microscope method,¹² was 2.4827 cm. at 25°, was used as a diffusion cell. Bath temperatures were $1 \pm 0.01^\circ$ and $25 \pm 0.01^\circ$. The relay at 1° con-

(1) L. G. Longsworth, *THIS JOURNAL*, **69**, 2510 (1947).

(2) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

(3) L. G. Longsworth, *ibid.*, **74**, 4155 (1952).

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

(5) M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

(6) L. J. Gosting and D. F. Akeley, *ibid.*, **74**, 2058 (1952).

(7) A. R. Gordon, *ibid.*, **72**, 4840 (1950).

(8) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(9) T. Shedlovsky and A. S. Brown, *THIS JOURNAL*, **56**, 1066 (1934).

(10) L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(11) L. J. Gosting, *THIS JOURNAL*, **72**, 4418 (1950).

(12) L. G. Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

trolled a solenoid which admitted refrigerant to the cooling coil. A variable bleeder valve on the return vapor line permitted an additional control on the operating temperature of the cooling coil.

Formation of the boundary, its movement to the optic axis by siphoning and the subsequent sharpening by continued siphoning through a capillary were carried out in the usual manner.¹³ About 100 ml. of solution was removed during a 45-minute sharpening period.

The total number of fringes (j_m) in the interference pattern was measured in the conventional manner. The fractional part of a fringe was determined with the cell in both the open (sharpening) and closed (diffusing) positions. A direct count of fringe minima in the Gouy pattern gave the integral number of fringes. The extrapolation to reference marks was facilitated by the use of a filar eyepiece micrometer in the comparator microscope. In order to simplify the alignment of fringe patterns on the comparator table, the photographic plate masks were slotted in such a way that the Gouy fringe system and the bounding reference marks on either side were visible simultaneously in the field of view of the microscope.

The displacement of fringe minima from reference marks which located the position of the undeviated slit image were measured with a Gaertner comparator. The optical path length was measured to ± 0.01 cm. This "b" distance was about 209 cm. and varied slightly with refocusing which occasionally was required (changing temperature, etc.).

The method for the calculation of apparent diffusion constants for a given Gouy pattern is described completely in reference 4. Correction for initial blurring of the boundary was performed according to the method of Longworth by extrapolation of the apparent diffusion constant value to infinite time.

Results

The Gouy method was used in the "height and area approximation." Only the lower six or seven minima excluding the lowest were used in the computations. In this system, both $\Delta n/\Delta c$ and D are strongly concentration dependent. Consequently there was more than the normal drift in C_t . Each run was checked for drift in C_t for a minimum midway in the fringe pattern after diffusion had proceeded for about 20 minutes.

The value of C_t at this point was uniformly lower than the value of C_t computed from the lower fringes which was used for the calculation of apparent diffusion coefficients. The average drift for

all the runs was -0.15% , which was considered to be high but not excessive.

That the skewness of these diffusing systems does influence the accuracy of the estimated values is also evident in the difference between values of the diffusion coefficient obtained with different increments at the same mean concentration. As shown in Table I, values of 3.94×10^{-6} and 3.93×10^{-6} are obtained with increments of 0.13 and 0.26 in concentration at a mean molarity of 0.3.

Specific refractive increments were obtained from the relation $\Delta n/\Delta c = j_m \lambda / a \Delta c$. This quantity and all other data pertinent to the determination of the diffusion coefficients are collected in Table I.

Relationships representing the density and viscosity data at both temperatures have been obtained by the method of least squares and are given in Table II.

TABLE II

ANALYTICAL EXPRESSIONS FOR VARIATION WITH CONCENTRATION OF DENSITY AND VISCOSITY
1.00°C.

$$d = 0.99993 - 0.01161c + 0.0024c^2; \pm 0.002\%, c^a < 0.8$$

$$\eta_0/\eta = 1 - 0.3058c + 0.0349c^2; \pm 0.15\%, c < 0.93$$

25.00°C.

$$d = 0.99707 - 0.01205c + 0.00076c^2; \pm 0.002\%, c < 0.92$$

$$\eta_0/\eta = 1 - 0.4478c + 0.0723c^2; \pm 0.12\%, c < 0.92$$

^a G. moles/liter.

Discussion

Values of D_0 , the diffusion coefficient at infinite dilution, are listed in Table III. They were obtained by an extrapolation which assumes that the expression $D = D_0(1 + c \times \partial \ln y / \partial c) \eta_0/\eta$ is a correct limiting form. The viscosity and thermodynamic data which are required for this expression are also contained in Table III. Figure 1 is a plot of the quantity $(D/[1 + c(\partial \ln y / \partial c)] \eta_0/\eta)$ vs. c at 1°. The extrapolation seems to be reasonable as the plot is essentially linear over the greater part of the concentration interval at both temperatures. The influence of the concentration increment upon the computed values of D might also be inferred from the deviation of various values from the best line through the data.

TABLE I

\bar{c}^a	Δc^b	j_m^c	$\Delta n/\Delta c \times 10^5$	$D \times 10^6$, cm. ² /sec.	Δt^d (sec.)
1.00°					
0.0501	0.1001	35.50	780.3	4.348	22
.1000	.2000	72.02	792.3	4.243	18
.2199	.3071	113.90	816.0	4.040	19
.3001	.1326	50.08	830.9	3.941	19
.3000	.2644	99.86	831.0	3.927	21
.5002	.2535	99.42	862.9	3.657	28
.7004	.2464	98.72	881.5	3.435	19
25.00°					
0.0502	0.1004	34.31	751.9	9.557	11
.1006	.2011	69.20	757.1	9.390	12
.1424	.2849	98.57	761.3	9.248	6
.3006	.2910	102.80	777.3	8.758	8
.5001	.2775	99.74	790.8	8.147	10
.7001	.2731	98.34	792.3	7.555	5

^a Av. concn. in g. moles/liter. ^b Diff. in concn. between solutions. ^c Total no. of fringes. ^d Zero time correction for initial blurring of boundary.

(13) D. S. Kahn and A. Polson, *J. Phys. Colloid Chem.*, **51**, 816 (1947).

TABLE III

$D \times 10^6$, sq. cm./sec.	q^a	η_0/η	$\frac{D}{D_0} \times q$	$\frac{D \times 10^6}{(\eta_0/\eta)q}$, sq. cm./sec
1.00°				
0.0501	4.348	0.978	0.9778	0.9836
.1000	4.243	.972	.9559	.9658
.2199	4.040	.967	.9050	.9243
.3000	3.927	.966	.8722	.8994
.5002	3.657	.967	.7941	.8367
.7004	3.435	.980	.7219	.7755
25.00°				
0.0502	9.557	0.9797	0.9847	1.0036
.1006	9.390	.9596	.9696	1.0067
.1424	9.248	.9433	.9572	1.0086
.3006	8.758	.8864	.9112	1.0165
.5001	8.147	.8320	.8558	1.0074
.7001	7.555	.8105	.8030	0.9590

^a $q = [1 + c(\partial \ln y / \partial c)]$

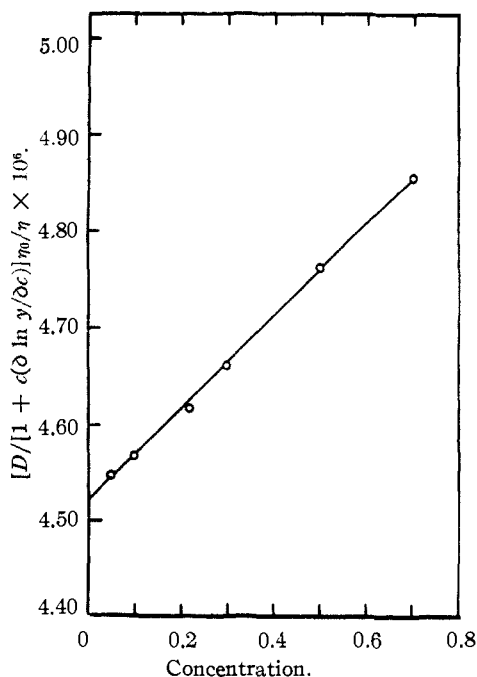


Fig. 1.—Extrapolation of 1.00° diffusion data to define D_0 .

The accuracy of this extrapolation depends upon the quality of the thermodynamic data which are employed. At 1° the extensive freezing point data which are available were used to estimate the factor $[1 + c(\partial \ln y/\partial c)]$.¹⁴ At 25°, the situation is not so favorable. No heat of dilution data are available for correcting the freezing point data upwards. A limited amount of vapor pressure data at 25° was smoothed empirically and the thermodynamic term was calculated from these smoothed data.¹⁵ A comparison of Figs. 2 and 3 will indicate that the consistency of diffusion results and thermodynamic data is poor at 25°. Use of the direct extrapolation of $D\eta$ to infinite dilution will give the same value for D_0 at 25° as obtained with the first method. This latter method of extrapolation is not feasible for the 1° data for which the plot of $D\eta$ vs. c goes through a minimum at $c \cong 0.1$ mole per liter.

With the diffusion and thermodynamic data now available the conclusion must be drawn that the value of D_0 at 25° is not as accurately defined as that at 1°.

The linearity of the plot of $(D/[1 + c(\partial \ln y/\partial c)]\eta_0/\eta)$ vs. c is not unique to the system under study. It implies the validity of a limiting equation of the form $D/[1 + c(\partial \ln y/\partial c)]\eta_0/\eta = D_0 + kc$ where $(D_0 + kc)\eta_0/\eta$ is to be identified with the mobility term $RT(\Omega/c)$ appearing in the Onsager-Fuoss expression $D = RT(\Omega/c)[1 + c(\partial \ln y/\partial c)]$. The data for sucrose,⁴ glycine⁵ and urea⁶ can also be fit extremely well over fairly large concentration intervals with the form of equation indicated. If further work shows this form of equation to be generally applicable one result of interest is obvious. By using a value of k obtained from diffusion measurements and thermodynamic

(14) W. D. Harkins and R. W. Wampler, *THIS JOURNAL*, **53**, 850 (1931).

(15) J. A. V. Butler, C. N. Ramchandani and D. W. Thomson, *J. Chem. Soc.*, **137**, 280 (1935).

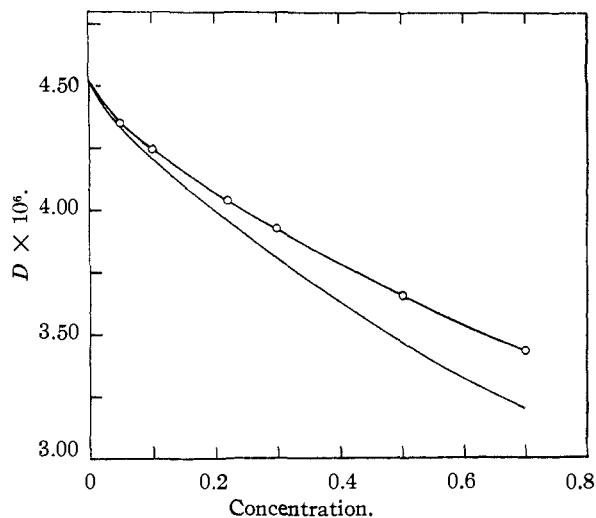


Fig. 2.— D at 1.00° vs. average concentration: \circ —, experimental; —, $D_0 [1 + c(\partial \ln y/\partial c)]\eta_0/\eta$, $D_0 = 4.52 \times 10^{-6}$ sq. cm./sec.

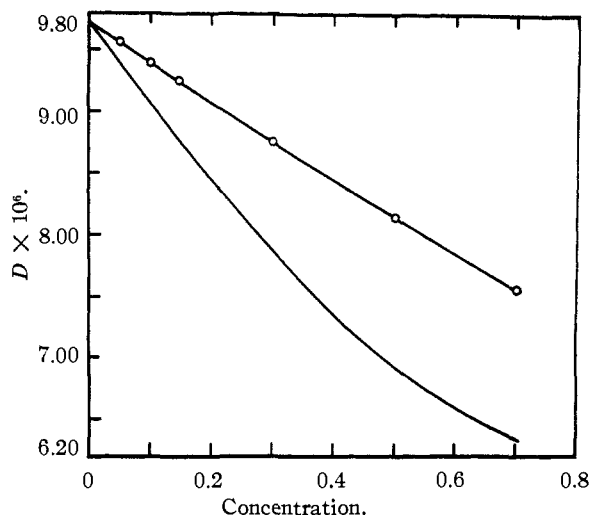


Fig. 3.— D at 25.00° vs. average concentration: \circ —, experimental; —, $D_0 [1 + c(\partial \ln y/\partial c)]\eta_0/\eta$, $D_0 = 9.72 \times 10^{-6}$ sq. cm./sec.

data in moderately dilute solutions the value for the activity of the solute could be estimated in a concentration region which might be experimentally inaccessible to some of the usual techniques, for example, vapor pressure measurements.

Alcohols in water are known to have abnormally high diffusion coefficients. This might be regarded as an anomaly common to all aqueous systems. For example, the observed diffusion coefficients in water solutions are much larger than the values available from the Eyring calculation. This behavior is in direct contrast with that in non-aqueous media. The discrepancy has been explained on the basis that the calculation neglected a contribution from rotational degrees of freedom of water in the activated state.¹⁶ This explanation is not adequate to resolve the magnitude of the anomaly of the system under study which has a very much

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 477 ff.

higher diffusion coefficient than would be expected from a comparison with other solutes in aqueous solutions. Longworth has determined the diffusion coefficients of a large number of amino acids, sugars and peptides in aqueous solutions.⁸ He has shown the relationship $D = 10.772 \times 10^{-6} / V^{2/3} - 1.450$, where D is the diffusion coefficient at a concentration of about 0.75 weight per cent. and V is the apparent molal volume, represents the behavior of these systems quite well. The measured value of D for *n*-butyl alcohol is 4.24×10^{-6} compared to the value of 3.64×10^{-6} which the relationship would give.

It has been proposed that systems which show large, positive deviations from Raoult's law would be expected to have higher diffusion coefficients than expected.⁸ Not only should D_0 be higher than expected but, as Onsager points out, the diffusion mobility should tend to increase with "local aggregation" while the same tendency to aggregate would impede viscous flow.

Thus a system showing these large, positive deviations might be expected to show a high value for D_0 , a larger than normal discrepancy between η_0/η and a computed mobility, and a marked difference in the concentration dependence of the activation energies for the viscous and diffusion processes. These effects should be more or less pronounced depending upon the magnitude of the deviations in the system.

The high value of D_0 for the *n*-butyl alcohol-water system was mentioned. Using an ingenious method for determining diffusion coefficients from surface tension measurements, data at 25° for the isomeric butyl alcohols have been obtained at a concentration of 8.2 g. per liter.^{17,18} The results are:

Alcohol	D
<i>n</i> -Butyl	8.1×10^{-6}
Isobutyl	8.0×10^{-6}
<i>s</i> -Butyl	7.6×10^{-6}
<i>t</i> -Butyl	7.3×10^{-6}

If, as is reasonable from a comparison of solubility data, the deviations from Raoult's law are in the order, deviation for *n*-butyl > isobutyl > *s*-butyl > *t*-butyl and, if it is assumed that the D_0 's would be in the same order as the reported values (the relative viscosities differ only by about

2% over the group) then Onsager's suggestion appears to be valid.

The activation energies for the diffusion and viscous processes do change with concentration as would be predicted. Figure 4 is a plot of these two quantities as a function of concentration. The activation energy for viscous flow increases monotonously with concentration while the diffusion activation energy begins to decrease at about 0.3 *M*. This behavior is in direct contrast with that of dilute aqueous sucrose solutions. In that system, the activation energies for both processes increase uniformly with concentration and with essentially the same slope. For that system, also, η_0/η was a very satisfactory substitute for a computed relative mobility over a fairly large concentration interval.

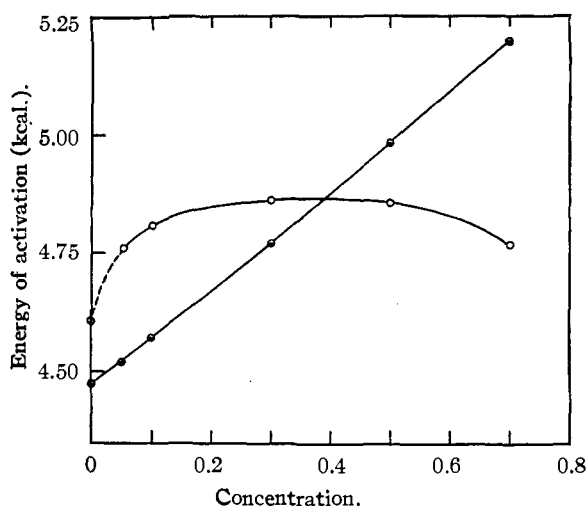


Fig. 4.—Energy of activation vs. concentration: O, diffusion; ●, viscous flow.

The authors are indebted to H. S. Harned for his interest in this problem, to L. J. Gosting for detailed designs for much of the equipment, to L. G. Longworth for several clarifying conversations and to M. S. Lyons for considerable help in initiating the work.

This investigation was supported in part by the Atomic Energy Commission under Contract AT-(30-1)-1375. The purchase of equipment was made possible by grants from the Sheffield Scientific Fund.

NEW HAVEN, CONN.

* (17) E. R. Washburn and H. N. Dunning, *THIS JOURNAL*, **73**, 1311 (1951).

(18) H. N. Dunning and E. R. Washburn, *J. Phys. Chem.*, **56**, 235 (1952).