The Diffusion of Phenylacetic Acid in Water as Measured by Changes of Surface Tension

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Phenylacetic acid has been allowed to diffuse through a column of water of known dimensions to the liquid–air interface. The surface tensions, measured after different time intervals, have been used to calculate the corresponding concentrations at the interface. The diffusion coefficient has been calculated from these values by a different, and we believe better, relationship than has been used before.

The diffusion coefficients of the butyl alcohols in dilute aqueous solutions have been determined by the observation of changes of surface tensions using a manometric capillarimeter.[2,3] Values of the diffusion coefficient were calculated from experimental data by use of an integrated expression for Fick's second law and by a method based on the solution of the analogous problem in heat transfer by Ingersoll and Zobel.[4] The latter development results in obtaining the diffusion coefficient as

$$D = L^2 z / t \qquad (1)$$

in which L is twice the observed length of the column, t is the time interval from the beginning of the experiment until the time of observation and z is evaluated from the series

$$S_{(z)} = \frac{4}{\pi} (e^{-\pi^2 z} - \frac{1}{3} e^{-9\pi^2 z} + \frac{1}{5} e^{-25\pi^2 z} -)$$

$S_{(z)}$ is determined experimentally as

$$S_{(z)} = (C_0 - C_h)/C_0 \qquad (2)$$

where C_0 is the concentration of the bulk solution and C_h is the concentration of solute at the liquid–air interface in the capillary. If equation 1 is rearranged and differentiated with respect to time, and if it is assumed that the diffusion coefficient is constant and that the length of the column does not vary during a time interval t_1 to t_2, the resulting expression is

$$D = L^2 \frac{z_2 - z_1}{t_2 - t_1} \qquad (3)$$

Equation 3 may be used to calculate diffusion coefficients on the basis of successive observations throughout an experiment. This was not possible for methods previously used.

The object of this investigation was to study further the practical and theoretical considerations affecting determinations by this method. Of particular interest were possible variations in the observed rate of diffusion brought about by varying the length of the liquid column in the capillary.

Experimental

Apparatus.—The manometric capillarimeter used in this investigation was essentially that used in previously reported work.[2,3] During studies of diffusion a small hand-operated stirrer in the capillarimeter was used to stir solutions slowly for approximately five seconds immediately after the column of water had been reduced to the desired length and again after the surface tension began to change. The purpose of this procedure was to ensure uniform mixing of the solution in the bulb with the excess water forced from the capillary. The stirring process was neither accompanied nor followed by any abrupt change in the rate at which surface tension was decreasing. While solutions were being stirred as well as at other times during a determination it was possible to maintain the desired position of the meniscus in the capillary to within ±0.002 cm.

During the work two different capillaries mounted in separate bulbs were used. Each capillary was calibrated at one-millimeter intervals throughout the working distance by observing the pressure necessary to prevent the rise of purified water. The manometric method is particularly well adapted for such calibrations. Each calibration consisted of four or more determinations with different samples of water and calibrations were repeated after the capillaries had been in use for several months. The effective radii one millimeter from the lower tips of the two capillaries were found at the time of the final calibration to be 0.02538 ±0.00001 cm. and 0.02547 ± 0.00001 cm. These values lie between the maximum and minimum values for the slightly elliptical capillaries as measured with an optical microscope equipped with an eyepiece micrometer.

The capillarimeter was mounted in an air-bath equipped to maintain automatically the temperature of the solution in the bulb at 25.0 ± 0.1°.

Duplicate determinations of the densities of solutions were made using two glass-stoppered pycnometers with capillary stems. The pycnometers were brought to constant temperature in a water-bath at 25.00 ± 0.05°.

Materials.—Eastman Kodak Co. "white label" grade phenylacetic acid was distilled three times at 140° and a pressure of 20 mm. of mercury. The product, collected on the outer wall of a water-cooled glass test-tube, was in the form of elongated crystals which melted at 76.6–76.8°.

Results

Density.—The densities of aqueous solutions of phenylacetic acid were required to calculate the concentrations of solutions in the desired terms. The densities measured for seven solutions of concentrations between zero and 0.8440 per cent. by weight are described by the empirical equation $d = 0.00158c + 0.99702$ to within ±0.00004 g./cc. Values obtained from duplicate determinations did not normally differ by more than this amount.

Surface Tension.—The surface tensions of twelve aqueous solutions of phenylacetic acid were determined by use of the manometric capillarimeter. The values obtained are described by the empirical equation $T = 72.07 - 15.71c - 19.73c^2$ at concentrations lower than 0.300% and by the equation $T = 73.27 - 28.29c + 9.61c^2$ at concentrations between this value and 1.003%. The estimated accuracy of these values is ±0.05 dyne/cm. at concentrations below 0.500% and ±0.10 dyne/cm. at concentrations above this value. Surface tensions were calculated from experimental data by

(1) Minnesota Mining and Manufacturing Company Research Fellow, 1951–1952 and 1952–1953.

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

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

(4) L. R. Ingersoll and O. J. Zobel, "Heat Conduction," McGraw-Hill Book Co., New York, N. Y., 1948, p. 127, Appendix C.

the equation of Ferguson and Dowson[5] as modified by DeWitt and Roper.[6] This equation takes the form

$$T = \frac{0.9958rg}{2}(h_{man} - h_{cap}) + 0.10 \qquad (4)$$

T = surface tension, dynes/cm.
r = radius of the capillary, cm.
g = acceleration of gravity, cm./sec.^{2}
h_{man} = vertical distance between levels of the fluid in the manometer, cm.
h_{cap} = vertical distance between the small meniscus in the capillary and the large meniscus in the bulb

for dilute aqueous solutions when water is used in the manometer, when h is small, when r is approximately 0.025 cm. and when the small meniscus is located below the large meniscus. A period of approximately ten minutes was required for surface tensions to reach their equilibrium values. During this time they normally increased by one-tenth of a dyne or less from the values which had been observed initially. The value (54.5 dynes/cm.) which we obtained for a 1.003% solution is approximately the same as that observed for a saturated aqueous solution (reported as 0.00915 g./cc.) of phenylacetic acid by Rose and Sherwin.[7] Solutions used in the present study were prepared by weight and their concentrations would not be subject to the possible error due to volatilization of the solute that might be incurred when a solution of phenylacetic acid is analyzed by evaporation of the solvent.

Diffusion.—Rates of diffusion were measured for phenylacetic acid solutions of four concentrations (0.005840, 0.007040, 0.008426 and 0.010015 g./cc.) at each of three observed column lengths (0.300, 0.400 and 0.500 cm.). Three or more determinations were made for each solution at each column length. The change of surface tension with time was recorded for each experiment until the surface tension had changed by approximately ten dynes. The concentration indicated by each recorded surface tension was determined by reference to a graph of surface tension against concentration of such a scale that one millimeter represented a concentration difference of 0.000005 g./cc. or a change of surface tension of 0.02 dyne. Results of several determinations at a single concentration and column length were averaged by finding the arithmetic mean of the surface tensions at each recorded time and then determining from the graph a single "mean" C_h for each time.

The results of a typical single diffusion experiment are tabulated in Table I. Here the change of surface tension $-\Delta T$ is recorded at ten-minute time intervals. For each value of $-\Delta T$, C_h has been determined graphically, $S_{(z)}$ has been calculated by use of equation 2 and the value of z has been obtained[4] and tabulated. Then the diffusion coefficients have been calculated by use of equation 3 for ten-minute intervals. Each value of D in Table I is recorded on the same line as the t and z which were used as t_2 and z_2 in calculating that value.

(5) A. Ferguson and P. E. Dowson, *Trans. Faraday Soc.*, **17**, 388 (1921).
(6) C. C. DeWitt and E. E. Roper, THIS JOURNAL, **54**, 446 (1932).
(7) A. R. Rose and C. P. Sherwin, *J. Biol. Chem.*, **68**, 565 (1926).

TABLE I

RESULTS OF A TYPICAL DIFFUSION EXPERIMENT

$C_0 = 0.010015$ g./cc.; $L = 2 \times 0.400 = 0.800$ cm.

t, sec.	$-\Delta T$, dynes	C_h, g./cc.	z	$D = L^2 \frac{z_2 - z_1}{t_2 - t_1}$ cm.^{2}/sec.
0	0.000			
600	.000			
1200	.097	0.000059	0.01414	
1800	.543	.000339	.02190	8.28×10^{-6}
2400	1.252	.000753	.02891	7.48×10^{-6}
3000	2.225	.001245	.03593	7.49×10^{-6}
3600	3.375	.001749	.04276	7.29×10^{-6}
4200	4.571	.002242	.04948	7.17×10^{-6}
4800	5.721	.002698	.05587	6.82×10^{-6}
5400	6.815	.003152	.06252	7.09×10^{-6}
6000	7.780	.003584	.06922	7.15×10^{-6}
6600	8.653	.004002	.07609	7.33×10^{-6}
7200	9.431	.004385	.08278	7.14×10^{-6}

The results of this experiment are typical in that the relative rate of diffusion is approximately constant during the final portion (one-half or more) of the experiment but somewhat higher during the initial stages.

The results of all studies are summarized in Table II. The values of D have been calculated for the final one-half or more of each set of experiments. Each value of z used in the preparation of this table was obtained from the "mean" C_h for three or more experiments as previously described and the values of dz/dt used were the slopes of the plots of z against time as obtained by averaging the slopes during overlapping intervals.

TABLE II

SUMMARY OF THE RESULTS OF DIFFUSION STUDIES

C_0, g./cc.	$L/2$	$D = L^2 \frac{dz}{dt}$	D_0	D_0 (mean)
0.010015	0.500	7.28×10^{-6}	8.4×10^{-6}	
	.400	7.16×10^{-6}	8.5×10^{-6}	
	.300	6.84×10^{-6}	8.6×10^{-6}	8.5×10^{-6}
.008426	.500	7.29×10^{-6}	8.4×10^{-6}	
	.400	7.08×10^{-6}	8.5×10^{-6}	
	.300	6.65×10^{-6}	8.4×10^{-6}	8.4×10^{-6}
.007040	.500	7.36×10^{-6}	8.5×10^{-6}	
	.400	7.21×10^{-6}	8.6×10^{-6}	
	.300	6.70×10^{-6}	8.4×10^{-6}	8.5×10^{-6}
.005840	.500	7.32×10^{-6}	8.4×10^{-6}	
	.400	6.98×10^{-6}	8.3×10^{-6}	
(Stirred)	.300	6.52×10^{-6}	8.2×10^{-6}	8.3×10^{-6}
(Un-stirred)	.300	6.64×10^{-6}	8.4×10^{-6}	

Included in the table are the results of three determinations at $C_0 = 0.005840$ g./cc. and $L/2 = 0.300$ cm., conducted at the conclusion of the study, in which the solution in the bulb was not stirred. For these studies z increased at a more nearly constant rate throughout the experiment. The average change during the first 60 minutes of these experiments was consistent with a diffusion coefficient of 6.8×10^{-6} while that of the corresponding stirred experiments for the same interval gave a coefficient of 7.3×10^{-6}. For the remainder of each experiment, a period of 100 minutes, the behavior in each case gave diffusion coefficients of approximately 6.5×10^{-6}. The recorded value of

D for the unstirred experiments is based upon the entire determination rather than the final portion only.

Discussion

Variation of the Apparent Diffusion Coefficient in Different Portions of Experiments.

—The decrease in the apparent diffusion coefficient with the passage of time as demonstrated by the data in Table I may be explained by one or a combination of the following three influences.

1. When the solution is stirred at the beginning of the experiment, mechanical mixing may cause some solution to be introduced to the lower portion of the diffusion column. This would cause solute molecules to arrive at the meniscus more rapidly during the early portions of the experiments than they do later in the experiments when diffusion through the entire column accounts for all transport.

2. Rapid diffusion into the column during the early parts of experiments may cause the depletion of some solute from a more or less hemispherical region below the tip of the capillary. This would lengthen the actual column during the course of the experiment causing the apparent diffusion coefficient calculated on the basis of a constant column length to decrease.

3. It is possible that solute can be transported from a region of higher concentration to a region of lower concentration in a layer adsorbed on the wall of the capillary and in so doing supplement the diffusion process. This possibility has been suggested in connection with the diaphragm cell technique by Gordon[8] and by other writers and the process was shown by Stokes[9] to occur during the diffusion of salts in dilute solutions. The influence of surface transport would be relatively greater during the earlier portions of an experiment because the rate at which solute actually arrives at the meniscus is lower than that later in the experiment and because the concentrations at different levels in the capillary and, hence, the extents of adsorption differ more widely during the initial phase.

The fact that the apparent diffusion coefficient varies less during the initial portions of experiments in which solutions are not stirred than in studies with stirring seems to indicate that one or both of the first two explanations apply. However, the excess water forced from the capillary remains visible below the tip of the capillary for a short period of time when the solution is not stirred and it is possible that this introduces an initial error which counteracts an influence such as that suggested above as the third possible explanation.

Influence of Varying the Length of the Diffusion Column.

—Examination of Table II shows that as the length of the column is increased, there is an increase in the apparent diffusion coefficient. The regularity and magnitude of this change suggest an error in the value of L used in making calculations which is independent of the value of L. If it is assumed that the true column length is given by $L_0/2 = (L + C)/2$ and the actual diffusion coefficient is given by

(8) A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 297 (1945).

(9) R. H. Stokes, This Journal, **72**, 766 (1950).

$$D_0 = L_0^2 dz/dt \qquad (5)$$

then it can be shown that

$$\frac{L}{\sqrt{D}} = L \times \frac{1}{\sqrt{D_0}} + \frac{C}{\sqrt{D_0}} \qquad (6)$$

Equation 6 indicates that a plot of $L/\sqrt{D}$ against L should give a straight line, the slope and intercept of which can be used to calculate the values of D_0 and C.

The data in Table II were plotted according to equation 6 and the slope and intercept were determined by the method of least squares to give the equation

$$\frac{L}{\sqrt{D}} = 344.3L + 25.31 \qquad (6a)$$

From the constants in this equation, D_0 is found to be $(8.44 \pm 0.14) \times 10^{-6}$ and C has the value 0 073 $\pm$ 0.008 cm. The deviations listed are calculated from the standard deviations of the slope and intercept of the straight-line equation. In obtaining these results, the observed values of D for a column length of 0.500 cm. were double-weighted because the results of studies at greater column lengths may be expected to be more reliable.

The values of C indicate that the true length of the column during the later portions of an experiment exceeds the observed length by 0.037 $\pm$ 0.005 cm. The observed length is measured as the vertical distance between the lower tip of the capillary and the lowest portion of the meniscus in the capillary. This constant error may be due to one or both of the following conditions.

1. The extension of the region of reduced concentration below the tip of the capillary would produce a column of increased length during all except the earliest parts of experiments.

2. Solute molecules probably must diffuse to a level somewhat above the lowest part of the meniscus, the point used as the top of the diffusion column in measuring its length, in order to influence capillary behavior. It was found by Antonoff[10] that the capillary behavior of a liquid is influenced by the extent of the wall of the capillary above the apparent top of the meniscus. If the solute molecules must reach or pass the apparent top of the meniscus before influencing the observed surface tension, then a difference between the effective column length and the observed column length would exist even though movement of solute particles in the surface layer may be more rapid than in the interior of the solution.

The Diffusion Coefficient of Phenylacetic Acid.

—Equation 1, in the differentiated form, and equation 5 show that for each value of D in Table II, D_0 can be calculated as $D_0 = D(L_0^2/L^2) = D \times (L + C)^2/L^2$, and calculated values of D_0 are given in that table. Each value of "D_0 (mean)" represents an integral diffusion coefficient of phenylacetic acid between C_0 and a somewhat lower concentration. All of the determined values of "D_0(mean)" lie within the standard deviation of D_0 as obtained from equation 6a. The diffusion coefficients of organic solutes in water, normally increase slightly as concentration decreases. This

(10) G. Antonoff, *Rec. trav. chim.*, **68**, 1011 (1949).

change for phenylacetic acid in the range of concentrations studied appears to be too small to be measured by this method at its present state of development.

The mean value D_0, $(8.44 \pm 0.14) \times 19^{-6}$, is thought to best represent the diffusion coefficient of phenylacetic acid in aqueous mixtures at concentrations below 0.01 g./cc. and at a temperature of 25°. The value calculated by use of the Stokes–Einstein equation based upon the viscosity of water and the mean radius of a Fisher–Hirschfelder model of the phenylacetic acid molecule is 7.7×10^{-6}. Because their molecules are disk-like rather than spherical in shape, aromatic compounds have usually been observed to diffuse more rapidly than predicted by the Stokes–Einstein equation. For example, o-hydroxybenzyl alcohol was found to have a diffusion coefficient of 7.2×10^{-6} in dilute aqueous solutions at 20°.[11] This corresponds approximately with a value of 8.3×10^{-6} at 25°, and is in good agreement with the value reported here for phenylacetic acid.

Acknowledgment.—The authors are grateful to Dr. C. E. Vanderzee for valuable suggestions pertaining to the conduct of this study.

(11) "International Critical Tables," McGraw–Hill Book Co., New York, N. Y., Vol. V, p. 71.
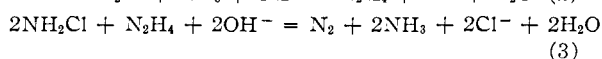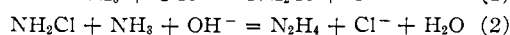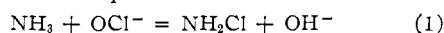
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The Raschig Synthesis of Hydrazine

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It has been possible to fit existing yield data for the Raschig synthesis by assuming simple rate laws. Hydrazine is formed by a bimolecular reaction between ammonia and chloramine and destroyed by a bimolecular reaction between hydrazine and chloramine. The latter reaction rate constant is about 18 times that of the former reaction, and therefore large excesses of ammonia are needed to make the first reaction predominate. The role of copper can be explained by assuming that copper catalyzes the destruction of hydrazine, again as a bimolecular reaction involving copper and hydrazine. In terms of these mechanisms the role of gelatin in increasing yield is that of complexing copper. This copper complex of gelatin appears to be unstable below pH 11.

Today the most useful synthesis of hydrazine is the Raschig synthesis. It consists of oxidizing excess ammonia with alkaline hypochlorite. Yields based on hypochlorite, are low unless glue or gelatin is added to the reaction mixture and even then large excesses of ammonia have to be used.

Much practical work has been done in search of conditions for maximizing yield. The qualitative conclusion reached from these are that the reaction proceeds in three steps

$$NH_3 + OCl^- = NH_2Cl + OH^- \tag{1}$$
$$NH_2Cl + NH_3 + OH^- = N_2H_4 + Cl^- + H_2O \tag{2}$$
$$2NH_2Cl + N_2H_4 + 2OH^- = N_2 + 2NH_3 + 2Cl^- + 2H_2O \tag{3}$$

The first reaction is fast and proceeds to completion rapidly. The second and third reactions are of comparable rates and the qualitative conclusions are that anything increasing the rate of the second or decreasing the rate of the third will increase the yield of hydrazine. Hence large excesses of ammonia are necessary.

The purpose of this paper is to show that the above qualitative conclusions can in fact be expressed quantitatively in terms of simple rate laws and that the role of the other variables can then be determined unequivocally.

Bodenstein[2] has measured the rate of reaction between ammonia and chloramine to give nitrogen and has found it to be first order in chloramine and ammonia. We can assume therefore that reaction 2 obeys this same rate law and if we assume that reaction 3 also proceeds as a bimolecular reaction,

first order in hydrazine and chloramine, then the rate at which hydrazine is produced will be the difference between the rate of creation by reaction 2 and destruction by reaction 3.

$$dN_2H_4/dt = k_2(NH_3)(NH_2Cl) - k_3(N_2H_4)(NH_2Cl) \tag{4}$$

and the rate at which chloramine is used up is

$$- dNH_2Cl/dt = k_2(NH_3)(NH_2Cl) + 2k_3(N_2H_4)(NH_2Cl) \tag{5}$$

Combining these two equations we get

$$- \frac{dN_2H_4}{dNH_2Cl} = \frac{1 - (k_3N_2H_4/k_2NH_3)}{1 + 2 (k_3N_2H_4/k_2NH_3)}$$

which can be integrated, assuming the ammonia concentration to remain constant, over the course of the reaction, using as limits 0 and N_2H_4 ($t = \infty$) for the hydrazine and NH_2Cl ($t = 0$) and 0 for the chloramine. This gives the implicit relation

$$\left(1 - \frac{k_3 y}{k_2 r}\right)^3 = \exp \frac{k_3}{k_2 r} (1 + 2y) \tag{6}$$

where y is the yield of hydrazine on hypochlorite and r is the ratio of the final[3] ammonia concentration to initial chloramine concentration. Figure 1

(3) In the derivation of eq. 6 the ammonia concentration is assumed constant during the course of the reaction. This assumption is valid except at low values of yield and r. The equation then reduces to

$$y = (k_2/k_3)r \text{ or } (N_2H_4)(t = \infty) = (k_2/k_3)(NH_3)$$

This is the same result if one assumes that the reaction has reached a steady state with respect to hydrazine in eq. 4

$$d(N_2H_4)/dt = 0 = k_2(NH_3)(NH_2Cl) - k_3(N_2H_4)(NH_2Cl)$$

or

$$N_2H_4 = (k_2/k_3)(NH_3)$$

so if one uses the final ammonia concentration in eq. 6, a fit is obtained in the low yield range.

(1) Institute for the Study of Metals, University of Chicago.

(2) M. Bodenstein, Z. physik. Chem., 139A, 397 (1928).