

efficient. While there is simultaneously a decrease in the effective concentrations of fixed charges, which in itself would make for higher γ^r/γ values, the lowered activity of the *average* exchange anion more than compensates for this effect. Therefore, it is to be expected that an increasing degree of ion-pair formation will make for a lowered value of γ^r/γ as well as a small value of W_w^r .

The observed decrease in the mean activity coefficient of the diffusible or non-exchange electrolyte in ion-exchange resin systems with increasing dilution of the solution phase appears to be contrary to the normal behavior of simple electrolytes. Part of this difficulty lies in the manner in which the resin data are presented. If the mean activity coefficient of the diffusible electrolyte were plotted against the molality of the polyelectrolyte or of the resinate, curves of more normal appearance result. In Fig. 4 the reduced activity coefficient of ammonium chloride² is plotted against the molality of the corresponding ammonium resinate for three different solution phase concentrations. Here it is seen that more "normal" behavior is encountered. While it is impossible to vary the resinate concentration by dilution, the use of the same polymer having varying degrees of cross-linking accomplishes substantially the same effect. The reduced activity coefficients are depressed when $m^r_{\text{NH}_4\text{Cl}} \ll m^r_{\text{NH}_4\text{R}}$, and approaches normal behavior as $m^r_{\text{NH}_4\text{Cl}} \rightarrow m^r_{\text{NH}_4\text{R}}$, where NH_4R refers to the resinate species. However, in all instances γ^r/γ approaches unity as $m^r_{\text{NH}_4\text{R}}$ approaches zero.

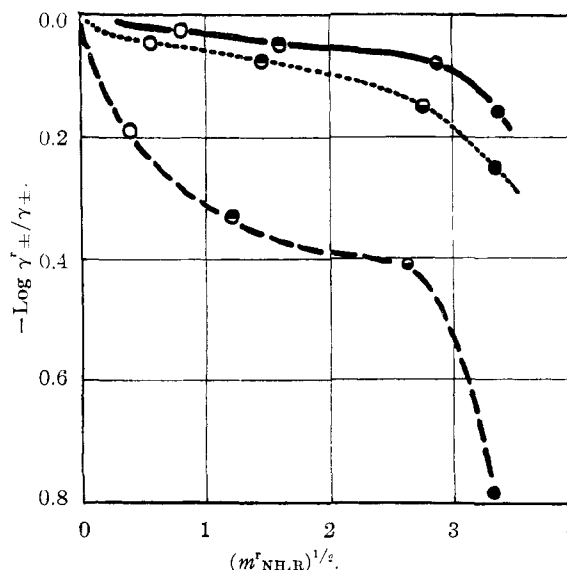


Fig. 4.—Reduced mean activity coefficients of ammonium chloride in polystyrenesulfonic acid cation exchange resins DVB 0.4 (O), DVB 2 (◐), DVB 10 (◑), and DVB 26 (●) as a function of the square root of the fixed group concentration at various solution phase concentrations: $m = 0.1$ (---); $m = 1$ (- - -); $m = 2$ (—).

The authors wish to thank the Office of Naval Research for the support given this work.

BROOKLYN, NEW YORK

[CONTRIBUTION NO. 1194 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Diffusion Coefficients for the System Biphenyl in Benzene

BY C. LENNART SANDQUIST AND PHILIP A. LYONS

RECEIVED OCTOBER 20, 1953

The diffusion coefficients, densities, viscosities and molar refractive increments for solutions of biphenyl in benzene have been determined at 25 and 35° in the concentration region 0–3 molar. Attention has been called to the significance of the overlapping of the plots of $D\eta/T$ against \bar{v} at the two temperatures. A simple and useful deviation function has been proposed for the description of this type system. The activation energies for the viscous and diffusion processes have been compared. The suggestion has been made that the data, in particular at 25°, constitute reliable standards for calibration purposes.

Recent advances in experimental techniques permit the precise determination of diffusion coefficients in the liquid state.^{1–3} In this communication one of the methods, Gouy diffusometry, has been applied to a non-aqueous system. Benzene solutions have been the subject of extensive thermodynamic studies. It was felt that biphenyl in benzene would form a particularly simple binary system for investigation being well suited to a ready correlation of its transport properties. The use of this particular system offers other advantages. Acceptable experimental materials are readily available using simple purification procedures. More important is the considerable accumulation of self-consistent vapor pressure data which are available

for the system over a wide range of concentrations and temperatures.^{4–6} These vapor pressure studies were stimulated largely by the theoretical considerations of Orr and Guggenheim,⁷ and the agreement between the predicted values for the activity coefficients and the experimental values is quite good.

In anticipation of further work on benzene solutions an effort was made to develop a satisfactory technique for work at 35°. Much of the useful vapor pressure work has been obtained at that temperature and even when possible it might not be desirable to compute activity data at temperatures widely dif-

(4) H. Tompa, *J. Phys. Chem.*, **16**, 292 (1948).

(5) D. H. Everett and M. F. Penney, *Proc. Roy. Soc. (London)*, **A212**, 164 (1952).

(6) J. H. Baxendale, B. V. Ennstun and J. Stern, *Trans. Roy. Soc. (London)*, **A243**, 23 (1950).

(7) E. A. Guggenheim, "Mixtures," Oxford University Press, 1952 pp. 215–239.

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

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

(3) C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc. (London)*, **A192**, 382 (1948).

ferent from 35°. An analysis of this situation with references to the pertinent literature is available.³

The results of the study of the biphenyl-benzene system should be useful in several ways. The work should provide information about the relationship between transport properties in solutions for which solvent effects, including the solvation of the diffusing solute, are minimized. In addition, this is one more well-defined system in which the effects on the diffusion mobility of slight associative tendencies might be observed. These effects have been discussed by Onsager for solutions showing positive deviations from Raoult's law.⁹ Calibration of other diffusion devices to be used for benzene solutions should be facilitated with the availability of data for this system.

Experimental Procedure

Preparation of Materials.—Matheson biphenyl was recrystallized three times from J. T. Baker C.P. anhydrous methanol. The melting point of the biphenyl was followed during recrystallization and changed from 68.7–68.9° to a final value of 69.1–69.2°. This is to be compared with the value of 69.1° reported by Tompa.⁴ The single final crystallization yield was dried in a vacuum desiccator for a considerable period of time by continuous evacuation and an occasional application of heat from an external heat lamp.

Baker A.C.S. grade, thiophene-free benzene, of boiling point range 79.5–81.0°, was fractionated in a 15-plate column with a reflux ratio of 1:1. The center fraction, boiling point range 80.0–80.1°, was collected in a dispensing flask which was provided with a drying train. The density of the benzene was 0.87311 ± 0.00002 as compared with the accepted value of 0.8737_0 .¹⁰ The index of refraction was $n_D^{25} 1.4975$ as compared with the accepted value of $n_D^{25} 1.4979$.¹⁰

Solutions were made up shortly before use by direct weighing into erlenmeyer flasks, which were equipped with female standard-taper caps. All weighings were corrected to vacuum. Final weighings were made immediately before the solutions were used in a diffusion experiment in order to detect any loss of benzene vapor.

A twin-armed pycnometer was used for density determinations. Flow times for the estimation of relative viscosities were measured in an Ostwald-Fenske viscometer and all viscosity results were corrected for small kinetic energy losses.

Equipment and Experimental Procedure.—Detailed descriptions of essentially the same equipment as was used in these experiments are already available.^{1,11} Minor changes in the equipment as employed in this work were mentioned in an earlier publication.¹² A General Electric AH-4 mercury vapor lamp was the source from which light of wave length 5460.7 Å. was isolated using a Wratten #77 filter. The achromatic lens in the optical train has a focal length of 100 cm. The distance along the optic axis from the center of the diffusion cell to the photographic plate, the "b" distance, was 208.72 cm. at 25° and 208.94 cm. at 35°. The channel depth, "a" distance, of the diffusion cell was 2.4827 cm.

For complete details regarding the procedure used in Gouy diffusometry reference should be made to some earlier papers.^{3,13}

For reasons of convenience, economy and safety water is the common thermostat liquid. In this experiment, since the bath fluid is an integral part of the optical path, requiring well-defined optical properties at the temperature and wave length of the experiment, accuracy also demands the

use of water in the thermostat. Since a Tiselius cell was to be used as a diffusion cell a lubrication problem had to be solved. A search for a convenient lubricant insoluble in both water and benzene was unsuccessful. Graphite, molybdenum disulfide and liquid amalgams were all unsatisfactory. Double lubrication was finally used. The central portions of the Tiselius cell end plates were coated with "Nonaq," thus surrounding the channels with a benzene-insoluble material. To the outer portions of the end plates "Lubriscal" was applied. After the lubricated cell had been clamped in the cell holder liberal amounts of a water repellent were spread over all exposed portions of the end plates. "Vaseline" was used for this purpose at 25° and, at 35°, "Gulflex Waterproof Grease" proved to be satisfactory.

The various cell-filling operations were then carried out. Both the bottom and center sections of the Tiselius cell were filled with the more concentrated solution. Transfer of solutions was accomplished by interchanging the standard taper caps on the solution flasks with a wash bottle attachment. The inlet tube was provided with an aspirator and the solutions were pumped into the appropriate cell arms. At 25° the center section was isolated in the usual way, *i.e.*, outside the bath, whereas at 35° isolation of the center section and all subsequent operations were carried out in the bath because of the large coefficient of expansion of the solutions. At 35° the flasks containing the solutions were clamped in the thermostat to allow for equilibration before use. At either temperature the excess concentrated solution in the reservoir arms was removed with a hypodermic syringe, and each arm was rinsed at least six times with benzene before finally drying with a stream of dry air.

With the center section in the isolated position several sets of the usual correction photographs were taken.¹³ After processing, the plates were examined to see if the solutions were in thermal equilibrium with the bath. This precaution, particularly at 35°, was not trivial.

When the solutions were apparently equilibrated both cell arms were rapidly filled by means of the dispenser described above and were immediately covered with "Sanitab" caps. Transfer and capping was performed speedily to minimize losses of benzene vapors. After a short interval for re-equilibration the "Sanitab" caps were replaced by similar units each provided with an opening. One of the openings allowed for the insertion of a short, #13 gage, stainless steel hypodermic needle and the other permitted the easy passage of a 10 inch, #20 gage, stainless steel hypodermic needle which was used for moving the boundary to the optic axis and for the boundary sharpening. With the exception of two important details, the remainder of the experimental procedure was the same as has already been well described. The first of these changes was the result of a suggestion by Longworth.¹⁴ Toward the end of the sharpening procedure and after the Gouy fringe pattern, which had been under visual observation at the focal plane, no longer changed under a constant siphoning rate, a two to three minute exposure of the extended fringe pattern was taken. The distance to one of the high-numbered fringe minima was related to an apparent C_1 which, with the value of the diffusion coefficient, permitted the calculation of the time correction Δt from the expression $\Delta t = \lambda^2 b^2 C_1^2 / 4\pi C_2 D$. The second detail concerned temperature control. Because of the strong temperature dependence of the density and refractive index of this system a minimum control of $\pm 0.005^\circ$ had to be maintained.

Results

In Table I are listed least-square equations for the densities and reciprocals of relative viscosity at $25 \pm 0.01^\circ$ and at $35 \pm 0.01^\circ$. The 25° data are in accord with those of Briscoe and Rinehart.¹⁵

TABLE I

25.00 \pm 0.01°	$d = 0.87314_1 + 0.024030c - 0.0001107c^2$	$\pm 0.004\%$
	$\eta_0/\eta = 1 - 0.19970c + 0.00970c^2 + 0.000519c^3$	$\pm .06\%$
35.00 \pm 0.01°	$d = 0.86245 + 0.024832c - 0.0001482c^2$	$\pm .004\%$
	$\eta_0/\eta = 1 - 0.1983c + 0.01228c^2$	$\pm .04\%$

(14) L. G. Longworth, private communication.

(15) H. T. Briscoe and W. T. Rinehart, *J. Phys. Chem.*, **46**, 387 (1942).

(8) G. Scatchard, L. B. Ticknor, J. R. Goates and E. R. McCartney, *This Journal*, **74**, 3721 (1952).

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

(10) F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons and Related Compounds," A. P. I. Research Project #44, U. S. Govt. Printing Office, Washington, D. C., 1947.

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

(12) P. A. Lyons and C. L. Sandquist, *This Journal*, **75**, 3896 (1953).

(13) L. J. Gosting and M. S. Morris, *ibid.*, **71**, 1008 (1949).

The values for the diffusion coefficients and other pertinent experimental and thermodynamic data are given in Table II.

TABLE II

i^a	Δc	j_m^b	$\frac{\Delta n/\Delta c}{\times 10^3 c}$	$\frac{D}{\text{cm.}^2/\text{sec.}} \times 10^5$	q^d	η_0/η	$\frac{D}{(q \times \eta_0/\eta)} \times 10^5$
25.00°, $D_0(25^\circ) = 1.558 \times 10^{-5}$							
0.0500	0.1000	82.81	182 ₂	1.547	1.0005	0.9900	1.562
.0852	.1704	141.38	182 ₃	1.539	1.0008	.9831	1.564
.1200	.2400	200.11	183 ₄	1.532	1.0012	.9762	1.567
.2000	.1200	99.20	181 ₃	1.513	1.0021	.9605	1.571
.4000	.1200	99.01	181 ₃	1.470	1.0048	.9217	1.587
.7001	.1216	99.64	180 ₃	1.407	1.0100	.8651	1.609
1.000	.119 ₃	98.19	180 ₂	1.342	1.0169	.8105	1.628
2.001	.120 ₇	96.58	176 ₆	1.147	1.0544	.6435	1.690
3.002	.117 ₆	90.97	171 ₁	0.977	1.1196	.5022	1.738
35.00°, $D_0(35^\circ) = 1.847 \times 10^{-5}$							
0.0600	0.1200	102.49	187 ₃	1.832	1.0008	0.9881	1.853
1.000	.120 ₆	101.01	185 ₄	1.600	1.0199	.8140	1.927
2.000	.12 ₂	97.51	17 ₈	1.381	1.0593	.6542	1.998
3.000	.12 ₈	100.06	175 ₁	1.189	1.1260	.5157	2.047

^a Av. concn. in g. moles/l. ^b Total no. fringes in pattern. ^c $\Delta n/\Delta c = j_m \lambda/\Delta c \times a$. ^d $q = [1 + c(d \ln y/dc)]$.

Discussion

The values of $\Delta n/\Delta c$ in Table II are not as self-consistent as data obtained with less volatile systems. A smooth curve through the 25° data should, however, give a fairly reliable estimate of molar refractive increments. At 35° a representative curve is best approximated by omitting the 2 molar value.

It is unlikely that for purposes of diffusion measurements highly purified materials are required. To test this assumption, one run was performed at 25° and at $\bar{c} = 0.041$ using untreated benzene and undesiccated biphenyl. The measured value of D was 1.547×10^{-5} as compared with 1.548×10^{-5} which can be obtained from interpolation.

The direct measurement of Δt proved to be a useful criterion for evaluating the reliability of some determinations, particularly at high concentrations. For every satisfactory run the values measured checked those estimated from the expression $D = D'(1 + \Delta t/t')$ to better than two seconds. Similar results were reported for measurements of the same nature which were made during experimentation with the Rayleigh fringe experimental technique.¹⁶

Limiting values of the diffusion coefficients, D_0 's, were obtained by linear extrapolations of plots of $D/[1 + c(d \ln y/dc)]\eta_0/\eta$ against concentration. A plot of this type seems to be generally linear over the low concentration range,¹² and is approximately linear over the entire range for some systems.¹⁷

The thermodynamic term, $[1 + c(d \ln y/dc)]$ was computed from the vapor pressure data of Everett and Penney whose work covers the range of temperatures 15 to 75° in ten degree intervals.⁵ Their data are consistent with the complementary values of Baxendale, *et al.*⁶ Activity coefficients derived from these measurements are in good agreement with Guggenheim's computations, based upon the assumption of a quasi-lattice structure in these

(16) L. G. Longworth, *THIS JOURNAL*, **74**, 4155 (1952).

(17) (a) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 536.

solutions.⁷ To obtain the activity coefficients at low concentrations, the smoothed measured values were fit to an empirical function of the form $\log f_1 = ax_2^2 + bx_2^3$. By means of an analytical integration of the Gibbs-Duhem equation values of $\log f_2$ were obtained and then converted to the molar scale.

The deviation of the quantity $D/[1 + c(d \ln y/dc)]\eta_0/\eta$ from constancy is a measure of the failure of the quantity $D_0\eta_0/\eta$ to represent correctly the concentration dependence of the diffusion mobility. Use of the macroscopic viscosity gives a lower value for the mobility than the apparent values available from measurements. If these apparent diffusion mobilities are not obscured by solvation effects (for which no independent correction is available) there should be a straightforward empirical relation between the deviation of $D/[1 + c(d \ln y/dc)]\eta_0/\eta$ from constancy and the percentage relative difference between the solution and solvent viscosities, $(\eta - \eta_0)/\eta \times 100$. Figure 1 contains plots of $D/[1 + c(d \ln y/dc)]\eta_0/\eta$ against $(\eta - \eta_0)/\eta$ for the 25 and 35° data. Two aspects of the plot are unusual. First the proportionality is exact and secondly it is valid within the experimental error over the entire range of concentrations (up to 50% wt. of biphenyl). The utility of this form of plot for purposes of extrapolation and interpolation is obvious. It might conceivably be argued that the linearity of the plot indicates the absolute accuracy of the molar activity coefficients as estimated at low concentrations from the analytical equation. Such an argument would, by implication, suggest the possibility of obtaining thermodynamic data from the diffusion measurements in a concentration range which is not covered by the vapor pressure measurements. This reasoning would, however, be

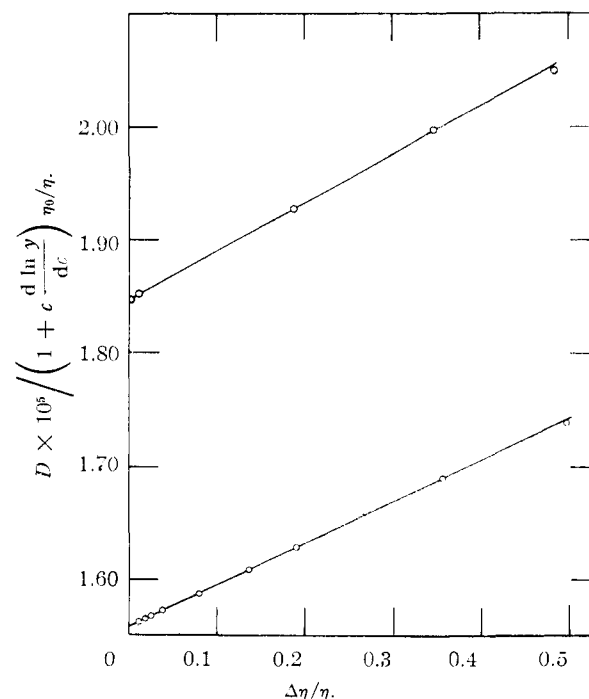


Fig. 1.— $D \times 10^5/[1 + c(d \ln y/dc)]\eta_0/\eta$ vs. $(\eta - \eta_0)/\eta$: upper line, 35°; lower line, 25°.

somewhat oversimplified. Additional precise data for benzene solutions are as yet not available to corroborate the linearity of this deviation plot. Also the magnitude of the thermodynamic term in the region involved is too small to make this system an interesting or important one for purposes of testing these ideas.

Several other aspects of simplicity are displayed in the transport properties of this system. A striking example of these is the plot of the Stokes-Einstein quantity, $D\eta/T$, against concentration for both temperatures (Fig. 2). The equality of the values at infinite dilution and the equivalence, to within approximately the experimental error, at other concentrations, was somewhat unexpected. Absolute viscosities for benzene were computed from the "International Critical Tables" relation $\eta = 14.42/[90 + t(^{\circ}\text{C.})]^{1.64}$. Since for this system adequate thermodynamic data are available at both temperatures, mobilities could be computed from the expression $\omega = D/[1 + c(d \ln y/dc)]$. If $\omega\eta/T$ is plotted against concentration a very close correlation, as before, is obtained between the two curves. For other benzene systems with larger changes in activity coefficient with temperature, it is to be expected that the product $\omega\eta/T$ would give a better, and actually a more meaningful, correlation. That there is a marked simplicity in the relationship between D and η can be readily appreciated if it is realized that by a single viscosity determination at any temperature and concentration in the interval 15 to 45°, a highly accurate estimate of the diffusion coefficient can probably be obtained from a comparison with Fig. 2.

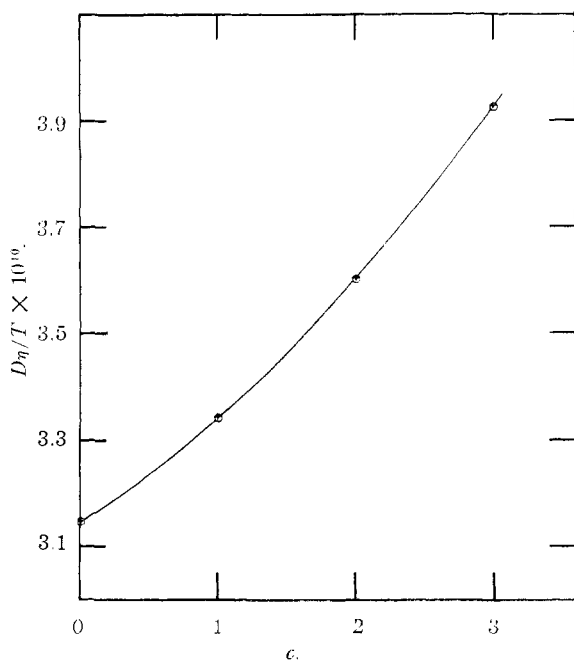


Fig. 2.— $D\eta/T$ vs. c : \circ , 25°; $+$, 35°.

The activation energies for the diffusion and viscous processes are plotted as functions of concentration in Fig. 3.¹⁸ By employing an ω defined as before, activation energies for diffusion mobilities

(18) Reference 17, pp. 482 and 524.

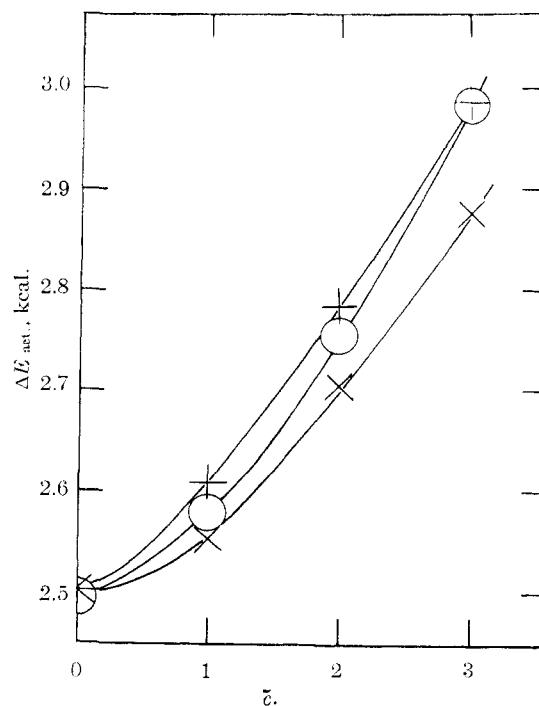


Fig. 3.—Energies of activation vs. c from the temperature dependence of: (a) D ($-\ + -$); (b) η ($-\circ-$); (c), ω ($-\times-$).

were calculated and found to be lower than those computed for uncorrected diffusion coefficients. Since the deviations from Raoult's law for the biphenyl-benzene system are positive, the observed divergence of the activation energies is roughly in accord with the prediction of Onsager that for systems with positive deviations the diffusion mobility might tend to decrease less rapidly with concentration than would be indicated by the change in macroscopic viscosity.

In Fig. 4 the diffusion coefficients of biphenyl-benzene along with $D_0[1 + c(d \ln y/dc)]\eta_0/\eta$ are plotted against concentration. Despite the fact that there seems to be little solvation of the diffusing biphenyl particles, in view of the Stokes-Einstein correlation, the change in frictional coefficient is no more directly predictable in benzene than in water.

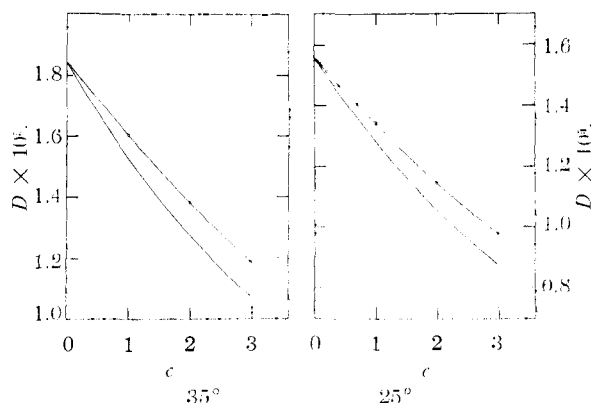


Fig. 4.— $D \times 10^5$ vs. c : D (\circ); solid curve, $D_0[1 + c(d \ln y/dc)]\eta_0/\eta$.

The Stokes' law friction coefficient $f = 6\pi\eta r$, where r is the radius of the diffusing particle, is of course in error when applied to an estimate of D_0 's for which the calculated values are some 40% below the ones obtained from extrapolation of experimental values.

The self-consistency of the diffusion data for this system, particularly at 25°, suggests that they should be of value for calibration purposes in diffusion techniques for which benzene may be used as the solvent.

Acknowledgments.—The authors have enjoyed and profited from discussions of this problem with various members of the Yale Department of Chemistry. We are also indebted to L. G. Longworth for some very fruitful advice.

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NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

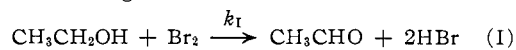
Hydrogen Isotope Effect in the Bromine Oxidation of Ethanol

BY LOUIS KAPLAN

RECEIVED APRIL 23, 1954

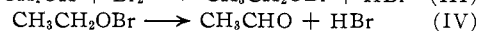
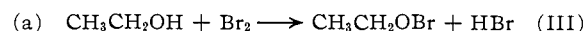
At 37.5° the rate of oxidation of ethanol-1-*t* by bromine is 0.57 times that of ethanol, corresponding to a ratio of about 0.15 for the rates of removal of tritium and hydrogen atoms from the methylene carbon. This result, taken together with the reaction kinetics, rules out the formation of ethyl hypobromite as the precursor of acetaldehyde in the oxidation, and lends support to a mechanism involving the transfer of a hydride ion from the methylene carbon to bromine.

The oxidation of ethanol by bromine has been investigated by Bugarszky¹ and more recently by Farkas, Perlmutter and Schächter.² In aqueous solutions of ethanol ranging from 1 to 76% by weight, the reaction is first order in free bromine, tribromide ion being unreactive. In 1 to 4% solutions, the reaction is also first order in ethanol. Below pH 3, the rate is independent of hydrogen ion concentration. In 76% solution, the only products are ethyl acetate and hydrogen bromide; in 41% solution acetic acid is also formed; while in 1-4% solutions very little ester is formed. In no case is there produced a significant amount of organically bound bromine. The reaction takes place in two stages

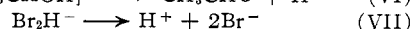
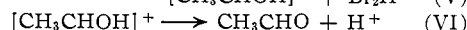
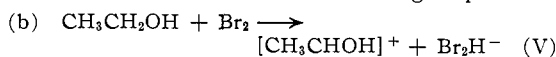


$\text{CH}_3\text{CHO} + \text{Br}_2 + \text{H}_2\text{O} \xrightarrow{k_{II}} \text{CH}_3\text{COOH} + 2\text{HBr} \quad (\text{II})$
in dilute solution at 25° the value of k_{II}/k_I is about 200.

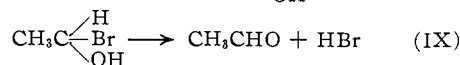
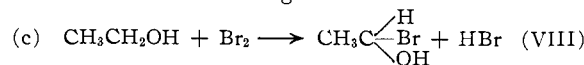
Farkas, Perlmutter and Schächter² have suggested the following three alternative mechanisms for reaction I, all of which are consistent with the reaction kinetics



with reaction III the rate-determining step.



with V rate-determining.



(1) (a) S. Bugarszky, *Z. physik. Chem.*, **38**, 561 (1901); (b) *ibid.*, **42**, 545 (1903); (c) *ibid.*, **71**, 705 (1910).

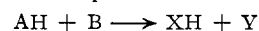
(2) L. Farkas, B. Perlmutter and O. Schächter, *THIS JOURNAL*, **71**, 2829 (1949).

with VIII rate-determining. They appear to favor mechanism (a), largely on the grounds that alkyl hypochlorites are known³ to break up into aldehyde and hydrochloric acid.

Although all three mechanisms give the same rate law, there is an essential difference between (a) on the one hand and (b) and (c) on the other. In mechanisms (b) and (c), a carbon-hydrogen bond is ruptured in the rate-determining step; in mechanism (a), this bond is ruptured in a subsequent fast reaction. The two cases can be distinguished by comparing the rate of reaction of the normal compound with that of one which has been isotopically substituted at the position of bond rupture. There is experimental evidence,⁴ as well as theoretical justification,⁵ that if a bond involving the isotope is broken in the rate-determining step of the reaction, the molecule containing the heavy isotope will, in general, react more slowly than that containing the light isotope.⁶ This paper presents the results of a study of the effect of the substitution of tritium for protium in the methylene position of ethanol on the rate of oxidation by bromine.

Calculations

Ethanol containing tracer amounts of ethanol-1-*t* was subjected to incomplete oxidation by bromine. In principle, the isotopic rate ratio for a reaction



can be determined⁷ by measuring the isotopic content of either the reaction product XH or the unreacted AH. Since, in the reaction studied,

(3) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

(4) (a) C. Reitz, *Z. physik. Chem.*, **A179**, 119 (1937); (b) F. H. Westheimer and N. Nicolaidis, *THIS JOURNAL*, **71**, 25 (1949).

(5) (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); (b) L. Melander, *Arkiv Kemi*, **2**, 211 (1950); (c) H. Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 889 (1952).

(6) For examples of isotope effects without bond rupture see (a) V. J. Shiner, Jr., *THIS JOURNAL*, **75**, 2925 (1953); (b) E. S. Lewis and C. F. Boozer, *ibid.*, **76**, 791 (1954).

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