[CONTRIBUTION NO. 1396 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Diffusion in Aqueous Acetic Acid Solutions

BY V. VITAGLIANO AND P. A. LYONS

RECEIVED APRIL 30, 1956

In this paper a method is proposed for the evaluation of diffusion coefficients for solutions of partially dissociated weak electrolytes. Measurements were made on the system acetic acid–water. They are in excellent agreement with predicted values. In order to allow a comparison of the activation energies for the various transport processes in this system measurements were made in moderately dilute solutions at two temperatures. The mobility of water in concentrated glacial acetic acid solutions can be estimated from some data obtained for these solutions at 25°.

1. Introduction

An understanding of the diffusion of weak electrolytes is a matter of some significance. It was a discussion of the general problems encountered in the diffusion of biologically important weak electrolytes which prompted this work. To the present time there has been no accurate method for interpreting diffusion data for an equilibrium mixture of a weak electrolyte and the ionic species into which it dissociates. A rigorous solution of this problem requires the accurate definition of the mobility of the undissociated species through the range of concentrations in which the degree of dissociation, α, changes from almost zero to unity. That is, the diffusion coefficient for the undissociated species must be accurately estimated in this range of concentrations. It is proposed that this may be accomplished, under certain circumstances, by a rational extrapolation of measurements relating to concentrations for which $\alpha \cong 0$. It is assumed that the limiting mobilities of the ionic species will be known from conductance measurements and that the change of ionic mobilities with concentration can be estimated from theory.

Practical considerations severely restrict the choice of a system for a study such as this. The weak electrolyte–solvent system chosen must be one for which there are good activity data and accurate values for α as a function of concentration. To have as short an extrapolation as possible, the dissociation constant should be fairly low but not so low as to prevent the collection of some data in solutions in which there is significant dissociation. For these reasons the system acetic acid–water was an obvious choice.

At 25° measurements were made over the entire range of concentrations which is accessible using the Gouy interferometric technique. Among other things these data permit an estimate of the mobility of water in the associated solvent, glacial acetic acid. Some measurements were made at 35° in moderately dilute acetic acid solutions. These data allow a comparison of the activation energies for the transport of various species in these solutions.

Experimental

Preparation of Solutions.—As a precautionary measure the acetic acid used was recrystallized several times starting with C.P. glacial acetic acid. Solutions were prepared by weighing the components directly into capped transfer flasks. All weights were corrected to vacuum.

Diffusion Measurements.—Diffusion coefficients were measured using the Gouy interferometric technique. The method is well described.[1,2] Minor modifications in the equipment and technique used in this Laboratory have previously been detailed.[3]

Extra precautions were taken to ensure precision in the results obtained at 35°. In order to avoid bubble formation in the diffusion cell the solutions were thermostated at about 40° in stoppered flasks before transferral to the cell. To improve temperature control rather vigorous stirring was used. The diffusion thermostat was lidded for the same purpose. Precision in the location of the undeviated slit image position was improved slightly by providing two reference patterns for each Gouy fringe pattern. This was accomplished by modifying the camera masking elements in such a way that after the start of the run the undeviated slit image region in the Gouy pattern could be blanked out. In this region a reference pattern was photographed. In addition, the usual reference patterns were photographed adjacent to the first. The average of the slit image position indicated by these reference patterns was used in the measurement of the Gouy fringe displacements, Y_j.

Viscosities.—A few measurements of viscosity were made using a Cannon–Fenske type viscosimeter.

Results

Table I includes the pertinent experimental results for acetic acid in water up to $\bar{c} \cong 12$ molar which were measured at 25°.

TABLE I

GOUY DATA FOR DILUTE HAc SOLUTIONS AT 25°

$\bar{c}_{\mathrm{HA_2}}$[a]	Δc_{HAc}[b]	J_m[c]	$\Delta n/\Delta c_{\mathrm{HAc}} \times 10^4$[d]	$D \times 10^5$[e]
0.04283	0.05236	10.30	42.97	$1.21\bar{2}$
.09714	.1591	31.21	42.85	1.200
.1968	.2198	42.94	42.67	1.183–1.185
.2374	.2714	52.98	42.64	1.177
.3314	.3191	62.02	42.45	1.161–1.163
.4214	.1611	31.29	42.42	1.153
.7572	.4287	82.16	41.86	$1.108\bar{5}$
1.5187	.3579	67.46	41.17	1.021
2.0030	.5429	99.80	40.15	$0.971\bar{2}$
3.0446	.2604	45.65	38.29	.877
3.6674	.2937	48.20	35.85	.821
3.6799	.4558	72.25	34.62	.817
4.9604	.2412	38.75	35.09	$.728\bar{5}$
6.0430	.1953	29.71	33.23	$.677\bar{5}$
8.0481	.2110	28.23	29.22	.611
8.9161	.1687	21.21	27.46	$.586\bar{5}$
9.7502	.2420	28.63	25.84	$.578\bar{5}$
12.4050	.3525	30.14	18.68	$.56\bar{8}$

[a] $\bar{c}$, average concentration in g. moles/liter. [b] Δc, difference in concentration across the boundary. [c] J_m, total number of fringes in the Gouy pattern. [d] $\Delta n/\Delta c = (J_m/\Delta c)(\lambda/a)$ where a = length along the optical axis of the diffusion cell and λ = 5460.7 Å. [e] D, diffusion coefficient at $\bar{c}$ in cm.^{2}/sec.

Table II lists similar data for 35°.

Table III is a tabulation of the less precise data obtained in concentrated acetic acid solutions at 25°.

---

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

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

[3] L. Sandquist and P. A. Lyons, *ibid.*, **76**, 4641 (1954).

TABLE II

GOUY DATA FOR DILUTE HAc SOLUTIONS AT 35°

$\bar{c}_{HAc}$ [a]	Δc_{HAc} [b]	J_m [c]	$\Delta n/\Delta c_{HAc} \times 10^4$ [d]	$D \times 10^5$ [e]
0.1769	0.2166	40.28	40.62	$1.51\bar{5}$
.4200	.3251	60.12	40.39	1.464
.4236	.3226	59.49	40.28	1.464
.6636	.3217	58.98	40.05	1.424
.9816	.3069	55.74	39.67	1.377
1.7780	.3703	65.48	38.63	1.270

TABLE III

GOUY DATA FOR CONCENTRATED HAc SOLUTIONS AT 25°

$\bar{c}_{HAc}$ [a]	$\bar{c}_{H_2O}$ [a]	Δc_{H_2O} [b]	J_m [c]	$\Delta n/\Delta c_{H_2O} \times 10^4$ [d]	$D \times 10^5$ [e]
17.3504	0.1946	0.2868	28.32	21.569	$1.07\bar{5}$
17.3258	.3153	.6888	61.61	19.537	1.020
17.3047	.4179	.6865	60.80	19.345	1.013
17.2826	.4640	.7165	59.09	18.014	$0.968\bar{6}$
17.1975	.8468	.7237	55.73	16.821	$.94\bar{7}$
17.0938	1.5114	.8429	51.23	13.276	.825
16.8918	2.1207	1.0567	48.64	10.054	.762
15.8642	5.9926	0.8174	13.02	3.479	.556

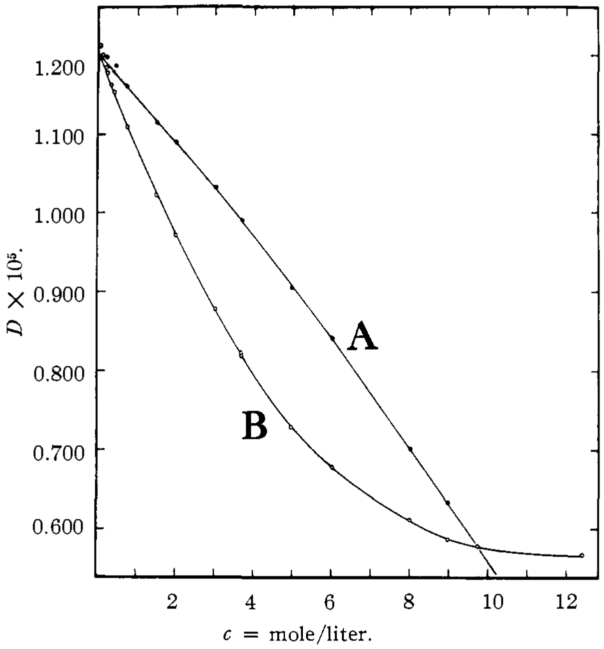

Fig. 1.—Diffusion coefficients against concentration at 25°: —○—(B) experimental data, D = cm. sec.$^{-1}$; —●—(A) $D/(1 + c(\mathrm{d} \log y)/\mathrm{d}c)$.

Individual values for the diffusion coefficients should be good to ±0.1–0.2% for all the data except those in concentrated acid solutions with the 25° data being somewhat more precise than the data at 35°. The specific refractive increments, $\Delta n/\Delta c$, listed are fairly precise, with a smooth curve through the data being good to about 0.1%.

The refractive increment data for concentrated solutions are not very precise and should be used with discretion.

Figure 1 is a plot of the 25° data. In addition the figure gives a plot of the diffusion coefficient divided by the thermodynamic term. The curves through these data are extrapolated to the limiting value of the diffusion coefficient of undissociated acetic acid which, as will later be evident, can be precisely established.

Discussion

The primary purpose of this paper was to determine the mobility of undissociated acetic acid as a function of concentration. Making use of existing complementary data, the computation of the diffusion coefficient of the equilibrium mixture, HAc ⇄ H$^+$ + Ac$^-$, in dilute solutions could then be accomplished.

Thermodynamically, this equilibrium mixture constitutes one component. If equilibrium is established fairly rapidly it may be inferred from transport process theory that the interdiffusion of water and acetic acid will be characterized by a single diffusion coefficient at a given concentration.[4] In consequence, the acetic acid equilibrium mixture may be considered to have a single, well-defined frictional coefficient.

Let us assume (following Nernst) that the frictional coefficient is the number average of the coefficients for the three species and define the diffusion coefficient for the system in the usual fashion

$$D = RT/f_{av} \qquad (1)$$

where

$$f_{av} = \frac{\alpha(f_{H^+} + f_{Ac^-}) + (1 - \alpha)f_{HAc}}{(1 + \alpha)} \qquad (2)$$

in which expression α is the degree of dissociation of HAc. Let us identify the various frictional coefficients with physically accessible quantities.

$$\begin{aligned} f_{H^+} &= \frac{N}{w_{H^+}} = \frac{F^2}{\lambda_{H^+}} 10^7 \\ f_{Ac^-} &= \frac{N}{w_{Ac^-}} = \frac{F^2}{\lambda_{Ac^-}} 10^7 \\ f_{AcH} &= \frac{1}{w_{HAc}} = \frac{RT}{D_{HAc}} \end{aligned} \qquad (3)$$

In these expressions the w's are mobilities, λ's are equivalent ionic conductances, D_{HAc} is the diffusion coefficient of undissociated HAc, and F is the Faraday (f's are molar quantities).

Introducing these quantities in equation 2 gives

$$D = \frac{(1 + \alpha)\lambda_{H^+}\lambda_{Ac^-}D_{HAc}}{(1 - \alpha)\lambda_{H^+}\lambda_{Ac^-} + \frac{F^2}{RT}\alpha D_{HAc}(\lambda_{H^+} + \lambda_{Ac^-})} \qquad (4)$$

with R in joules mole^{-1}deg.$^{-1}$.

Applying the Hartley thermodynamic correction gives

$$D = \frac{(1 + \alpha)\lambda_{H^+}\lambda_{Ac^-}D_{HAc}}{(1 - \alpha)\lambda_{H^+}\lambda_{Ac^-} + \frac{F^2}{RT}\alpha D_{HAc}(\lambda_{H^+} + \lambda_{Ac^-})}\left(1 + c\frac{\mathrm{d} \log y_i}{\mathrm{d}c_i}\right) \qquad (5)$$

where y is the activity coefficient of the Gibbs component i on the c scale.

The λ's appearing in equation 5 are given by the Onsager theory.[5]

$$\lambda_i = \left(\lambda_i^\circ - \frac{1.546 \times 10^7}{6\pi\eta}|z_i|\frac{\kappa}{1 + \kappa a}\right); \kappa = \left(\frac{8\pi Ne^2}{1000\epsilon kT}\right)^{1/2}\sqrt{I} \qquad (6)$$

---

[4] L. Onsager, *Ann. N. Y. Ac. Sci.*, **XLVI**, 241 (1945).

[5] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

In equations 6 the time of relaxation correction is omitted since electrolyte diffusion is being considered and I is the *actual ionic strength*, $I = \alpha c$.

At infinite dilution $[(\alpha = 1);\ (1 + c\,\mathrm{d}\log y/\mathrm{d}c = 1)]$ the equation reduces to the Nernst equation for the limiting diffusion coefficient of this electrolyte.

$$D^0 = 2\frac{RT\lambda^0_{\mathrm{H}^+}\lambda^0_{\mathrm{Ac}^-}}{F^2(\lambda^0_{\mathrm{H}^+} + \lambda^0_{\mathrm{Ac}^-})} \qquad (7)$$

When $\alpha \cong 0$ (at high concentration) equation 6 reduces to the familiar, but not particularly useful, expression for non-electrolyte diffusion

$$D = D_{\mathrm{HAc}}\left(1 + c\frac{\mathrm{d}\log y}{\mathrm{d}c}\right) \qquad (8)$$

It is not very useful because it does not explicitly describe the concentration dependence of D_{HAc}. Gordon has proposed a useful function which assumes mobilities to be inversely proportional to the macroscopic relative viscosity.[6]

$$D = D^0{}_{\mathrm{HAc}}\left(1 + c\frac{\mathrm{d}\log y}{\mathrm{d}c}\right)\eta_0/\eta \qquad (9)$$

where $D^0{}_{\mathrm{HAc}}$ is the diffusion coefficient at infinite dilution and η_0 and η are the viscosities of solvent and solution, respectively. Gordon has also called attention to the limitations of this expression.[7] The use of this viscosity correction normally results in an overcorrection which is approximately proportional to the difference between the viscosity of the solution and that of the pure solvent.[3] When this is true, the extrapolation of diffusion data is quite direct and the self-consistency of transport properties and thermodynamic data for a system becomes strikingly evident. A plot of the quantity $D/(1 + c(\mathrm{d}\log y/\mathrm{d}c)\eta_0/\eta$ against $(\eta - \eta_0)/\eta$ under these circumstances should be linear.

In Fig. 2 there is a plot of the quantity $D/(1 + c(\mathrm{d}\log y/\mathrm{d}c)\eta_0/\eta$ against $(\eta - \eta_0)/\eta$. A linear extrapolation has been made through the data at higher concentrations for which $\alpha = 0$, which correspond to the diffusion of undissociated acetic acid. This line extrapolates to $D^0{}_{\mathrm{HAc}} = 1.201 \times 10^{-5}$, the hypothetical diffusion coefficient of undissociated acetic acid at infinite dilution. At finite, but low, concentrations the experimental points are above the linear plot since in this region some of the faster moving ionic species are present. Equation 5 may be used to compute values of D_{HAc} for this region. If these latter quantities are multiplied by the relative viscosity, they should be consistent with the extrapolation. The filled circles in Fig. 2 correspond to these quantities. The agreement is excellent.

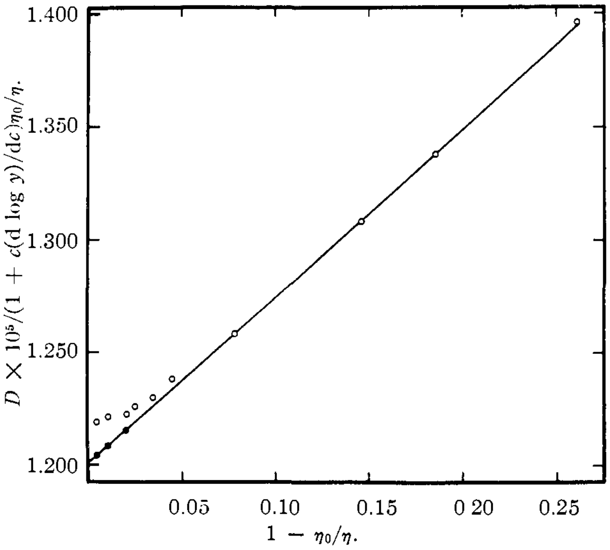

Fig. 2.—Graph for estimating diffusion coefficients of undissociated acetic acid at lower concentrations.

Three things are evident from Fig. 2. First, the problem of establishing the limiting mobility of undissociated acetic acid is apparently precisely solved. Secondly, the quantity D_{HAc} may be accurately estimated from the linear plot. (In the interval between 0.0 and 0.2 molar a more convenient form is $D_{\mathrm{HAc}} \times 10^5 = 1.201 - 0.55c$ which is good to about 0.1%.) Third, equation 5 may apparently serve as an adequate guide in predicting the diffusion coefficient of acetic acid in very dilute aqueous solutions.

An additional comment may be made on Fig. 2. If association (dimerization) of the solute is obscuring the analysis of the data, it is not apparent up to $\bar{c} = 3$ molar. In any event, the extrapolation, which includes data in solutions sufficiently dilute as to preclude association, would still be valid.

In order to establish the curve in Fig. 2, a considerable number of auxiliary data were used. Values of α to be used in equation 5 are those of MacInnes and Shedlovsky.[8] They are listed in Table V, together with values for the diffusion coefficients for the equilibrium mixtures, $\mathrm{H_{Ac}}$, H^+, Ac^-, in water available from equation 5. Table IV is a résumé of the quantities which would be used in dilute solutions.

The thermodynamic term

$$\left[1 + c\frac{\mathrm{d}\log y}{\mathrm{d}c}\right] = \left[1 + N_2\frac{\mathrm{d}\log f_2}{\mathrm{d}N_2}\right]\left[1 - N_2\left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right)\right]$$

was estimated in the following way. Thermodynamic studies by Hansen, Miller and Christian provided an explicit expression[9] for the activity coefficient on the mole fraction scale, f, as a function of mol efraction.[10] This allowed direct calculation of the first factor. Density data from the I.C.T. were used to estimate values for the partial molar volumes which were needed for the second factor. As is evident from Table IV, it is imperative that the complete thermodynamic term be used, and not the approximate expression

$$1 + N_2\frac{\mathrm{d}\log f_2}{\mathrm{d}N_2}$$

Viscosities used in the preparation of Fig. 2 were obtained from the data in the I.C.T. The I.C.T. equation

$$\eta/\eta_0 = 1 + 0.1104C + 0.00208C^2 \pm 0.002$$

---

[6] A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

[7] A. R. Gordon, THIS JOURNAL, **72**, 4840 (1950).

[8] D. A. MacInnes and T. Shedlovsky, *ibid.*, **54**, 1423 (1932).

[9] The activity coefficient f or y appearing in the last expression must not be confused with mean ionic activity coefficients, $f_\pm$, $y_\pm$.

[10] L. S. Hansen, F. A. Miller and S. D. Christian, *J. Phys. Chem.* **59**, 391 (1955).

TABLE IV

PERTINENT PARAMETERS USED IN THE ANALYSIS OF DIFFUSION DATA AT 25°[a]

c	$1 + N_2\frac{d \log f_2}{2dN_2}$	$1 - N_2\left[1 - \frac{\bar{V}_1}{\bar{V}_2}\right]$	$1 + c\frac{d \log y}{dc}$	η/η_0	$1 - \eta_0/\eta$	$D/\left(1 + c\frac{d \log y}{dc}\right)$	$D/\left(1 + c\frac{d \log y}{dc}\right)\eta_0/\eta$
0.04283	0.99581	1.001437	0.99724	1.004728	0.004706	1.2134 × 10^{-5}	1.2191 × 10^{-5}
.09714	.99071	1.003260	.99394	1.01074	.010626	1.2073	1.2203
.1968	.98149	1.006607	.98798	1.02181	.021344	1.1984	1.2245
.2374	.97784	1.007972	.98564	1.02622	.025550	1.1942	1.2255
.3314	.96921	1.01125	.98011	1.03661	.035317	1.1856	1.2290
.4214	.96101	1.01442	.97487	1.04689	.044790	1.1827	1.2384
.7572	.93120	1.02642	.95580	1.08478	.078154	1.1598	1.2581
1.5187	.86787	1.05444	.91512	1.17246	.147092	1.116	1.308
2.0030	.83079	1.07364	.89197	1.22847	.185979	1.0888	1.3376
3.0446	.76011	1.11834	.85006	1.35448	.261709	1.0311	1.3966
3.6674	.72376	1.14736	.83041	1.42993	.300665	0.9887	1.4138
3.6799	.71951	1.14794	.82595	1.43146	.301413	.9892	1.4160
4.9604	.66400	1.21313	.80552	1.58978	.370982	.9044	1.4378
6.0430	.63101	1.2776	.80615			.8404	
8.0481	.61168	1.4246	.87139			.7012	
8.9161	.61887	1.4969	.92638			.6331	
9.7502	.63571	1.5743	1.00079			.5780	
12.4050	.71172	1.9143	1.36240			.4169	

[a] Nearly all the computed quantities in this table could be rounded off to about 0.1% for practical use.

TABLE V

COMPUTED HAc DIFFUSION COEFFICIENTS AT 25° IN VERY DILUTE SOLUTIONS

c[a]	α[b]	$D/\left(1+c\frac{d \log y}{dc}\right)$
.00002801	0.5393	$1.640\bar{8}$
0.00000000	1	$1.949\bar{9}$ × 10^{-5}
.00002801	0.5393	$1.640\bar{8}$
.00011135	.3277	$1.479\bar{8}$
.0002184	.2477	$1.415\bar{2}$
.0010283	.12375	$1.310\bar{5}$
.002414	.08290	$1.274\bar{8}$
.005912	.05401	$1.249\bar{0}$
.02	.02987	$1.225\bar{0}$
.05	.01905	$1.215\bar{2}$
.10	.013493	$1.207\bar{5}$
.20	.009494	$1.198\bar{4}$

[a] c = concentration of acetic acid in g. moles/liter. [b] α = degree of dissociation of acetic acid.

is valid up to $c = 3$. Above 3 molar the equation

$$\eta/\eta_0 = 1 + 0.1125C + 0.00129C^2$$

is the least squares fit.

Extrapolation of the 35° data was carried out in the same way. The concentration dependence of the ionization constant given by MacInnes and Shedlovsky for 25° was assumed to be nearly the same at 35°. The temperature dependence of the ionization constant at finite concentration was assumed to be the same as at infinite dilution. The latter quantity was reported by Harned and Ehlers.[11] The thermodynamic correction at 25° was used for the 35° extrapolation. Because of the variety of approximations which were involved in treating the 35° data, it must be assumed that the limiting value, D^0_{HAc}, was not as accurately established as at the lower temperature.

D^0_{HAc} at 35° was estimated to be 1.530 × 10^{-5}, which is slightly lower than the Stokes–Einstein prediction based on the 25° data. Assuming $D\eta/T$ to be constant would give a value of 1.535 × 10^{-5}.

Since the mechanism of the diffusion processes is different for the dissociated and undissociated species it is to be expected that the activation energies for the various transport processes differ considerably. The activation energies for the relevant processes at infinite dilution are:

		$E_{\text{act.}}$ (25–35°), cal.
1.	For diffusion of undissociated HAc	3817
2.	For diffusion of dissociated HAc	3684
3.	For limiting H^+ conductance	3230
4.	For limiting Ac^- conductance	4590
5.	For viscous flow of water	3882

In keeping with expectations,[12] 1 and 5 are nearly the same. Since the mobility of H^+ is abnormally high due to the phenomenon of proton jumps, 3 is much lower than 4, and 2 is considerably lower than 1.

The data for concentrated acetic acid solutions at 25° are not too valuable, being rather inaccurate due to lubrication difficulties encountered in these solutions. In addition, the thermodynamic data for this region do not permit an accurate extrapolation, with the scatter in a plot of $D/(1 + c(d \log y/dc))$ against $\bar{c}$ being much worse than the scatter in the original, poor diffusion data. The values are listed merely to give approximate values for the diffusion of H_2O in an associated solvent. Lamm[13] some time ago reported on an amazingly low effective Stokes' radius for H_2O diffusion in glycerol, $r_{H_2O} = 0.19 \times 10^{-8}$. In acetic acid the value is more nearly normal, $r_{H_2O} \cong 2.1 \times 10^{-8}$.

Data at 35° for concentrated acetic acid solutions were not collected. The magnification of experimental errors at this temperature and the hypothetical nature of the extrapolation proced-

---

[11] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 625 (1933).

[12] L. G. Longsworth, *J. Phys. Chem.*, **58**, 770 (1954).

[13] O. Lamm and G. Sjöstedt, *Trans. Faraday Soc.*, **XXXIV**, 1158 (1938).

ure at these concentrations would remove most of the significance which might be attached to the temperature coefficient of the diffusion process in glacial acetic acid.

A gap in the 25° data, about $\bar{c} = 14$, exists because in this region both the density and refractive index of this system go through a maximum.

Acknowledgments.—This investigation was the direct result of a general discussion with Professor J. G. Kirkwood and Dr. I. Tinoco of the relationship between the transport and thermodynamic properties of partially dissociated proteins. Our thanks are due also to Professor H. S. Harned for some pertinent comments on this problem. The work was supported in part by Atomic Energy Commissions contract AT (30-1)-1375. V. Vitagliano is indebted to the Fondazione A. Beneduce, Napoli, for a foreign study fellowship.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM AND HAAS COMPANY]

The Kinetics and Mechanism of the Aminolysis of Ethyl Formate with *n*-Butylamine

BY WARREN H. WATANABE AND LESTER R. DEFONSO

RECEIVED APRIL 9, 1956

The kinetics of the reaction of *n*-butylamine with ethyl formate to give *n*-butylformamide and ethanol have been measured in approx. 4 *M* ethylene glycol in dioxane, and in absolute ethanol. In both solvents the initial rates are represented to a good approximation by the rate equation $-d[\text{Amine}]/dt = k[\text{Amine}]^{3/2}[\text{Ester}]$. This result is shown to correspond to a mechanism in which the sole reaction is between the anion of the amine, RNH^-, and the ester. Abnormally high positive neutral salt effects have been observed in both solvents. The strong retarding effect of *n*-butylamine hydrochloride at constant ionic strength on the reaction in ethanol supports this mechanism; however there is still a residual rate at extrapolated infinitely high concentration of the amine acid salt. This residual rate indicates that a reaction of molecular amine with ester provides a minor but nevertheless distinct portion of the over-all reaction. The complete rate equation is thus shown to be $-d[\text{Amine}]/dt = k[\text{Amine}]^{3/2}[\text{Ester}] + k'[\text{Amine}][\text{Ester}]$ in harmony with the mechanism of ammonolysis first proposed by Betts and Hammett. The relationship of the present results with those of previous investigators, notably Hawkins, is discussed.

Of the large variety of reactions into which amines enter as nucleophilic reagents, perhaps the most thoroughly studied from the standpoint of kinetics and mechanism are those of aminolysis, in which an amine and an ester react to form an amide and an alcohol. It is therefore the more surprising that with but two recent exceptions,[1] none of these studies have dealt with the detailed kinetics of a single such aminolysis reaction, although in most of the earlier reports there have been strong indications that the rate of aminolysis does not follow the simple second-order kinetics so often assumed. Previous studies have dealt with the effect of structure on reactivity in aminolysis,[2] on the effect of solvents on rates,[3,4] on the effect of base[3] and of acid salts,[3,5] and on the accelerating influence of water[6] and hydroxylic solvents.[2] In this earlier work it has been the practice to calculate rate constants as over-all second order, first order in amine and first order in ester. Hawkins has shown, however, that in the simultaneous aminolysis and hydrolysis of ethyl thioacetate and β-acetaminoethyl thioacetate in water with *n*-butylamine[1a] the only term in the rate equation attributable to aminolysis is

$$\text{Rate} = k[RNH^-][\text{Ester}] \qquad (1)$$

and in the simultaneous aminolysis and hydrolysis of α-naphthyl acetate in water with *n*-butylamine[1b] there are two terms in the rate equation describing the aminolysis

$$\text{Rate} = k[RNH^-][\text{Ester}] + k'[RNH_3^+][\text{Ester}] \qquad (2)$$

In the fundamentally important study of the ammonolysis of methyl phenylacetate in anhydrous methanol carried out by Betts and Hammett[7] the rate equation was found to contain two terms

$$\text{Rate} = k[NH_3][\text{Ester}] + k'[NH_2^-][\text{Ester}] \qquad (3)$$

Thus the only relevant detailed investigations have shown that the order with respect to the amine (or ammonia) is greater than one, and that the rate must then be a function of the amine concentration if the rate constant is calculated as first order in amine.

The present study of the kinetics of aminolysis was undertaken as a preliminary to a determination of the effects of certain metal salts on the rate of a typical nucleophilic reaction of an amine.[8] For this purpose the aminolysis of ethyl formate with *n*-butylamine was chosen as the model reaction both

$$n\text{-}C_4H_9NH_2 + HCOOC_2H_5 \longrightarrow n\text{-}C_4H_9NHCHO + C_2H_5OH \qquad (4)$$

because of its high rate, which would allow measurements to high conversion, and its presumed freedom from complicating side reactions. As solvents were used 4.137 *M* ethylene glycol in dioxane, claimed to be a particularly good solvent mixture for aminolyses by primary amines,[2] and absolute ethanol, in which it was found rates were also rapid. Our kinetic results substantiate those of

---

[1] (a) P. J. Hawkins and D. S. Tarbell, THIS JOURNAL, **75**, 2982 (1953); (b) P. J. Hawkins and I. Piscalnikow, *ibid.*, **77**, 2771 (1955).

[2] E. M. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950); **73**, 5393 (1951).

[3] R. Baltzly, I. M. Berger and A. A. Rothstein, *ibid.*, **72**, 4149 (1950).

[4] M. Grunfeld, *Ann. chim.*, **20**, 351 (1933).

[5] P. K. Glasoe, J. Kleinberg and L. F. Audrieth, THIS JOURNAL, **61**, 2387 (1939).

[6] P. K. Glasoe, L. D. Scott and L. F. Audrieth, *ibid.*, **63**, 2965 (1941).

[7] R. L. Betts and L. P. Hammett, *ibid.*, **59**, 1569 (1937).

[8] This work will be the subject of a future communication.