

separation factor is of the order of 35%. Because of the sensitivity of a calculated  $S$  with slight changes in overvoltage values, the converse prediction, *i.e.*, overvoltage differences from separation data, may be made with a high degree of precision. However, one qualification must be borne in mind: in overvoltage measurements the initial state of the discharged ion is isotopically homogeneous, either pure  $H_2O$  or pure  $D_2O$  being used, whereas in sepa-

ration work (particularly from dilute isotope concentrations), the ground state of one of the isotopes is considerably different. This reservation must be made in correlating overvoltage and separation measurements.

**Acknowledgment.**—The authors wish to express their appreciation to Dr. Benjamin Post for his frequent aid and advice.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## Acid-Base Reactions in Non-dissociating Solvents. Acetic Acid and Triethylamine in Carbon Tetrachloride and Chloroform

BY GORDON M. BARROW AND E. ANNE YERGER

RECEIVED MAY 10, 1954

The reactions between acetic acid and triethylamine in carbon tetrachloride and chloroform, in the acid concentration range 0.001 to 1 molar, have been studied by infrared spectroscopy. The nature of the ion-pair products is clarified. The electronic structure, and infrared spectra, are dependent on the solvent interaction. Equilibrium constants are obtained for several reactions between the acid and the base in the two solvents.

Information on the reactions of acids and bases in non-ionizing solvents can be expected to be useful in understanding, separately, the dependence of acid and basic strengths on the structure of these compounds and on the solvation of the species present in the acid-base equilibrium. Such studies have been made by Davis and co-workers<sup>1</sup> and by Bell and Bayles<sup>2</sup> using an acid with absorption in the visible region.

By using changes in the infrared spectrum to follow the acid-base reaction it was hoped to obtain, in addition to acid-base equilibrium constants, some information about the nature of the ion-pair produced in these non-ionizing, or better "non-dissociating," solvents. That such reactions lead essentially only to ion-pairs has been shown by the dielectric constant studies of Davis and McDonald,<sup>3</sup> Maryott<sup>4</sup> and by Fuoss and Kraus.<sup>5</sup> Elucidation of the type of association between the ions does however not result from such measurements, whereas some information on this is furnished by changes in the infrared spectrum.

Acetic acid and triethylamine are spectroscopically convenient for this study and the use of chloroform as a solvent, in addition to carbon tetrachloride, provides an indication of the effect of solvent interaction which, however, probably does not lead to complete dissociation of the ion-pair.<sup>6</sup>

Before considering the acid-base equilibrium constants it was necessary to identify the reaction product species present at various concentrations in the two solvents.

### Experimental

All spectra were obtained on a Baird Associates or a Beckman IR-2T instrument with rock salt optics, except for

- (1) M. M. Davis and H. B. Hetzer, *Bur. Standards, J. Research*, **48**, 381 (1952), with references to previous work.
- (2) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).
- (3) M. M. Davis and E. A. McDonald, *Bur. Standards, J. Research*, **42**, 595 (1949).
- (4) A. A. Maryott, *ibid.*, **41**, 1, 7 (1948).
- (5) R. M. Fuoss and C. A. Kraus, *This Journal*, **55**, 3614 (1933).
- (6) M. M. Davis, *ibid.*, **71**, 3544 (1949).

those of triethylammonium chloride, nitrate and picrate and the hydrochlorides of pyridine and aniline for which the latter instrument with a lithium fluoride monochromator was used. Beer's law was assumed and care was taken wherever possible to operate at fairly low absorptions so that no appreciable error would be introduced.

Cells of thickness 0.034, 0.095, 1.10 and 20.6 mm., as determined by interference effects for the thin cells and direct measurement for the thicker ones, were used for the different concentrations as follows: 1.0 molar in the 0.034, 0.5 to 0.1 molar in the 0.095, 0.02 molar in the 1.10, and 0.001 molar in the 20.6-mm. cell.

The reagents were prepared or purified in the following manner.

**Triethylamine.**—Eastman Kodak white label triethylamine was dried over KOH and distilled through a 30-cm. packed column. The product,  $n_D^{20}$  of 1.4003, was stored over KOH.

**Triethylammonium Picrate.**—Triethylamine was added to a concentrated solution of picric acid in 95% ethanol. After recrystallization from ethanol the melting point was 171–172°.

**Triethylammonium Chloride and Triethylammonium Nitrate.**—These salts were obtained by evaporation of solutions of the reagent grade mineral acid and triethylamine. The products were dried under vacuum. The hydrochloride melted at 252–253°.

**Anilinium Chloride.**—Addition of aniline to an aqueous solution of reagent grade hydrochloric acid gave a product which was recrystallized from water and dried under vacuum. The neutral equivalent was 129 and the melting point was 198°.

**Carbon Tetrachloride.**—Reagent grade  $CCl_4$  was stored over  $P_2O_5$  and subsequently filtered into a distillation pot. A center cut of constant boiling point was taken from a 30-cm. packed column.

**Chloroform.**—J. T. Baker reagent grade chloroform was stored over  $CaCl_2$  and Drierite, filtered into a distillation pot and distilled. A center cut consisting of about half the charge was taken and used immediately. Only for the very dilute solutions, 0.001  $M$  of acetic acid in chloroform was there evidence of some impurity interacting with acetic acid. The monomer-dimer equilibrium data reported elsewhere showed large deviations from the constant obtained at higher concentrations when old or not carefully distilled chloroform was used.

**I. Nature of the Intermediates and Products.**—To establish the absorption bands due to the salt, or ion-pair, formed from this acid and base the spectra of a number of salts of triethylamine were obtained. The spectra of the hydrochloride, nitrate

and picrate show split bands between 3.8 and 4  $\mu$  and can be assigned to the  $^+N-H$  stretching mode for this group associated to its anion, as suggested by Lord and Merrifield.<sup>7</sup> Our spectra were obtained in  $CHCl_3$  solution and the agreement with the results of Lord and Merrifield indicates that the association of the ion-pairs through the  $^+N-H$  bond is not different in solution from that in the crystal. Similarly the spectrum of pyridinium chloride in  $CHCl_3$  shows, as previously reported<sup>7</sup> for the solid, a broad band at 4.35  $\mu$  and a well-defined doublet at 4.78 and 5.05  $\mu$ . Anilinium chloride also shows a similar set of bands, a broad doublet at 3.59, 3.84  $\mu$  and a weaker band at about 5  $\mu$ . Although the assignment of the 5  $\mu$  band (observed also in acetic acid-triethylamine systems) has not been given, it appears reasonable to attribute it to a bending mode involving the proton in the system  $^+N-H-X^-$ . The appearance of either the 4 or 5  $\mu$  band will be taken as evidence that the proton has been transferred to the amine to form an ion-pair salt.

A detailed consideration of all the monomer and dimer bands of acetic acid is not necessary for the present purpose. These have been discussed by Sheppard and Hadzi.<sup>8</sup> A suitable band characteristic of dimer and not obscured by the monomer or triethylamine bands is the broad band at 10.7  $\mu$  attributed to a  $\delta(OH)$  mode, similarly the 7.8  $\mu$  C-O stretching band is helpful in establishing the presence of an undisturbed acetic acid dimer. The carbonyl band of the acetic acid dimer at 5.8  $\mu$  is also to be expected for a carbonyl group of acetic acid hydrogen bonded to any other molecule with approximately the hydrogen bonding strength of the acetic acid OH. Furthermore, the carbonyl of any other molecule may happen to have a carbonyl absorption band at about this frequency so the 5.8  $\mu$  band cannot be considered uniquely characteristic of the acetic acid dimer.

At most of the concentrations used the monomer appears in relatively small amounts and the monomer carbonyl band at about 5.65  $\mu$  is sufficient to determine the amount of this species.

Bands attributable to a carboxylate group found at about 6.3  $\mu$  and are generally rather broad. While it would be expected in general that a group intermediate between a carbonyl and a carboxylate might exist, the results seem to indicate that the

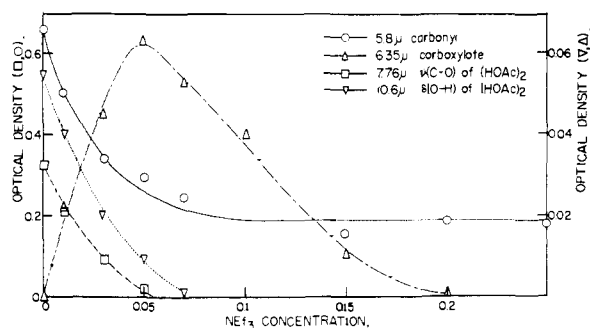


Fig. 1.—The optical density of some absorption bands in the system 0.1  $M$  acetic acid-triethylamine in  $CCl_4$ .

(7) R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

(8) Sheppard and Hadzi, *Proc. Roy. Soc. (London)*, **A216**, 247 (1953).

acetate ion in the ion-pair shows either a fairly sharp band at 5.8  $\mu$  or a broad one at 6.25 to 6.4  $\mu$ , with no intermediate types occurring. The ordinary carboxylate band is of course to be identified with a situation in which the bonding to the two oxygens from the central carbon atom is essentially the same and not necessarily with the ionization of the acetic acid molecule.

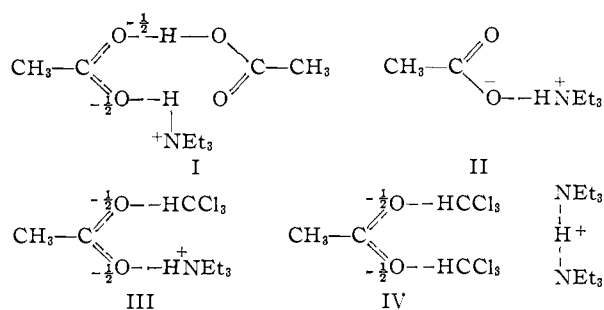
The absorption bands mentioned above are the most useful for deducing the structure of reaction products and for determining their concentrations.

**Species Present in Carbon Tetrachloride.**—Spectra were obtained, as discussed in the Experimental section of a series of solutions with a fixed concentration of acetic acid in  $CCl_4$  and a varying concentration of triethylamine. Such experiments were done with acetic acid concentrations of 1.0, 0.3, 0.1 and 0.02 and 0.001  $M$ . For the first four concentrations the proportion of monomer was small, amounting to about 10% for the 0.02  $M$  solution, and will be neglected in considering the species present during the titration.

The plot of the optical density,  $\log I_0/I$ , vs. triethylamine concentration for the 0.1  $M$  solution in a 0.1-mm. cell, Fig. 1, indicates, for all the acetic acid bands measured, a sharp change of slope or the value of zero when the acetic acid has been approximately half neutralized, *i.e.*, when triethylamine has the concentration of 0.05  $M$ . In particular, the acetic acid dimer bands at 10.6 and 7.76  $\mu$  have entirely disappeared at this concentration of triethylamine indicating a reaction to form a species  $Et_3N(HOAc)_2$ .

For the most concentrated solution, 1  $M$ , the disappearance of the dimer bands was complete at a triethylamine concentration of 0.3 or 0.4  $M$ . This is interpreted in terms of a further association of the acetic acid molecules around the ion-pair,  $Et_3N(HOAc)_2$ . For the dilute solutions 0.02 and 0.001  $M$  the plot of optical density vs. triethylamine concentration shows less abrupt changes, indicating that the equilibrium constants for the reaction are such that a stoichiometric reaction does not then occur.

The nature of the  $Et_3N(HOAc)_2$  species can be deduced from the observed spectra at about half-neutralized acetic acid. The presence of the 4 and 5.1  $\mu$  bands indicates that the triethylamine has accepted a proton from the acid dimer to form an ion-pair salt. The dimer carbonyl band has decreased only to about half its original intensity and the new species, therefore, contains a carbonyl group which must be attributed to an essentially hydrogen bonded carbonyl unless the molecule with this group is quite different from an ordinary carboxylic acid. The band at 6.35  $\mu$  is clearly due to a carboxylate group. These facts are in agreement with the structure I for this  $Et_3N(HOAc)_2$  species. The hydrogen bonding of the OH and  $NH^+$  groups on the two oxygen atoms are considered responsible for the presence of the carboxylate group. That a hydrogen bonded carbonyl band is observed indicates some association of the carbonyl oxygen of the acetic acid molecule. While a general electrostatic attraction for the positive ion may be sufficient to produce such a carbonyl band



it seems more likely that the proton is responsible for this effect and a bifurcated hydrogen bond is formed similar to that suggested by Pauling<sup>9</sup> and Albrecht and Corey<sup>10</sup> for glycine.

Further addition of triethylamine indicates that this species is only an intermediate, and the completely neutralized form is gradually achieved. Chief spectral evidence for this is the decrease of the  $6.35 \mu$  carboxylate band resulting in the essential elimination of this band when the triethylamine concentration is about twice that of the acetic acid for the more concentrated solutions. The symmetric stretching carboxylate band at about  $7.2 \mu$  and the C-O stretch at  $7.92 \mu$  appear also to be removed or shifted but the overlapping triethylamine bands obscure these effects. Although the salt band at  $4 \mu$  is partially covered by the strong CH band of the triethylamine, the  $5.1 \mu$  band shows the expected behavior; it rises sharply to the half-neutralization point and then more slowly. These results are in agreement with the expected neutralization product II, where it is postulated that the triethylammonium ion is attached, undoubtedly by a hydrogen bond, to one of the carboxylate oxygens and that this association is sufficient to cause the negative formal charge to reside essentially on the bonded oxygen. This leaves the other oxygen to form a carbonyl-like double bond to the carbon atom. That the carbonyl band has the same frequency as that of the acetic acid dimer band is a coincidence since the structure II would be expected to also give a carbonyl shifted to longer wave lengths than found for an acetic acid monomer carbonyl.

**Species Present in Chloroform.**—As in the investigation of the species present with  $\text{CCl}_4$  as a solvent, chloroform solutions of acetic acid, at fixed concentrations of 0.5 and 0.3 and 0.001  $M$ , were prepared and the spectra were obtained for various additions of triethylamine.

The initial reaction appears to follow that previously found. The  $\delta(\text{OH})$  band at  $10.7 \mu$  and the  $\nu(\text{C}-\text{O})$  band at  $7.75 \mu$  disappeared at a concentration of triethylamine equal to about half that of the acetic acid. At this concentration bands due to the intermediate I had appeared at 4, 5.1, 6.40 and  $7.97 \mu$  and the carbonyl retained an appreciable intensity. Further addition of triethylamine, however, resulted in a decrease to zero of the carbonyl band and of the  $6.4 \mu$  carboxylate band and the appearance of a new carboxylate band at  $6.20 \mu$ . At a concentration ratio of triethylamine to acetic

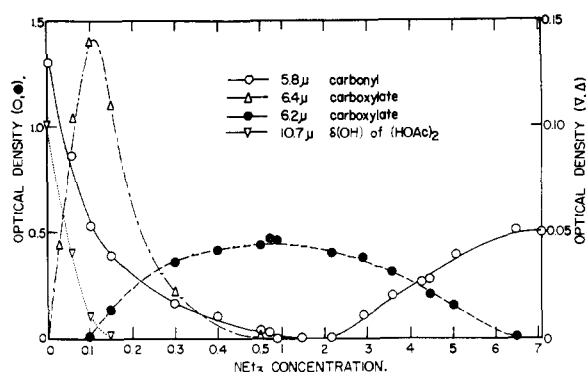


Fig. 2.—The optical density of some absorption bands in the system 0.3  $M$  acetic acid-triethylamine in  $\text{CHCl}_3$ .

acid equal to about three, the reaction to form this new species is essentially complete as shown in Fig. 2. Along with these spectral changes the  $5.1 \mu$  band appears to broaden out to a band between about 4.3 and  $5.3 \mu$ .

The great difference in the spectrum of the species formed from I by the addition of further triethylamine indicates that in chloroform the solvent is specifically participating. One explanation is that association of a solvent molecule with the oxygen which is not attached to the cation provides a sufficiently strong electron attracting influence to stabilize the resonance form with each oxygen carrying about half of the negative charge as in structure III.

This suggestion is in accord also with the spectral changes that occur when the triethylamine concentration is increased until it exceeds that of the chloroform and finally when the solution consists only of acetic acid in triethylamine, the triethylamine concentration then being 7.09  $M$ . The effect on the carbonyl and carboxylate band is also shown in Fig. 2, the remaining bands of the spectrum being rather obscured by the high triethylamine concentration. The reversal to a system having a carbonyl and no carboxylate, *i.e.*, structure I, is readily interpreted in terms of the decreasing concentration of chloroform which in this concentration range can best be considered a reactant rather than a solvent.

These spectral changes can also be interpreted, however, on the basis of dissociation of the salt to form free ions, *i.e.*, removal of the triethylammonium ion from its bonding site. Although the relatively low dielectric constants of the  $\text{CHCl}_3$  and triethylamine solutions would not be expected to lead to such dissociation, the possibility here exists of specific solvent interaction to stabilize the ions possibly in the forms  $\text{AcO}^-(\text{HCCl}_3)_2$  and  $(\text{Et}_3\text{N})_2\text{H}^+$  as indicated in structure IV. The reversal to structure I,  $\text{AcO}^-\text{HN}^+\text{Et}_3$ , would then be accounted for by the decrease in the chloroform concentration and the subsequent decrease in solvation of the acetate ion and the reassociation of the ions into ion-pairs.

This explanation seems less likely than the previous alternative and equilibrium constants will therefore be based on the assumption of III. It is hoped that further evidence on this question will be reported shortly.

(9) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 286.

(10) G. Albrecht and R. B. Corey, *THIS JOURNAL*, **61**, 1087 (1939).

## II. Determination of Equilibrium Constants

Once the species present in the system of acetic acid and triethylamine in  $\text{CCl}_4$  and in  $\text{CHCl}_3$  have been established, it is of interest to attempt to obtain the equilibrium constants for the reactions between these species.

Before considering the acid-base equilibrium it is necessary to have data on the constants for the acetic acid dimerization in carbon tetrachloride and in chloroform and also the constant for the association of triethylamine with chloroform. The acetic acid dimerization equilibria are reported separately.<sup>11</sup> The equilibrium constant for the dimerization in carbon tetrachloride and in chloroform are found to be 2000 and 250, respectively, at concentrations of about 0.001  $M$ .

Likewise the equilibrium constant for the formation of a triethylamine-chloroform complex is reported.<sup>12</sup> The value of 0.36 obtained for approximately 1  $M$  solutions is used in the present discussion. It is necessary to assume that solvent effects due to the decrease in molar concentration and the use of solvents other than  $\text{CCl}_4$  would not greatly affect this equilibrium.

**Acid-Base Equilibrium Constants in Carbon Tetrachloride.**—In  $\text{CCl}_4$  the formation of the first reaction product of triethylamine with the acetic acid dimer, as observed in the more concentrated solutions, 0.1 to 1.0  $M$ , leads to at least a stoichiometric removal of the acetic acid dimer.

The further reaction of I to lead to the final neutralization product II proceeds with a much smaller equilibrium constant. With the assumption that at a triethylamine concentration of half the acetic acid concentration all the acetic acid is present as the intermediate, the fall off of the  $6.35 \mu$  carboxylate band can be used to estimate the equilibrium constant for the formation of II. From the intensity of the  $6.35 \mu$  band at half-neutralization a value of  $\alpha I = 1.2$  is thus obtained in the equation  $\alpha I = 1/C_I \log I_0/I$  and this can be used to estimate the equilibrium constant as indicated in Table I. ( $M$  is used here, and in the following tables, as the total molarity of the component added to the solution, whereas  $C$  refers to the actual concentration of a particular species present at equilibrium.) The weakness of the carboxylate band permits only a very approximate determination of this constant.

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE REACTION  $\text{Et}_3\text{N} \cdot (\text{HOAc})_2 + \text{NEt}_3 \rightleftharpoons 2(\text{Et}_3\text{NHOAc})$  IN  $\text{CCl}_4$  SOLUTION

$M_{(\text{HOAc})_2}$	$M_{\text{NEt}_3}$	$(\log I_0/I)_{6.35}$	$C_{\text{Et}_3\text{N}(\text{HOAc})_2}$	$C_{\text{Et}_3\text{NHOAc}}$	$K$
0.15	0.15	0.17	(0.15)	...	..
.15	.30	.12	.10	0.10	1.0
.15	.35	.063	.073	.123	1.7
.15	.40	.088	.066	.166	1.5
.15	.45	.079	.060	.180	1.4
.15	.50	.072	.053	.194	2.7
.05	.05	.063	(.05)	...	..
.05	.10	.037	.031	.038	1.5
					Av. 1.6

(11) G. M. Barrow and E. A. Yerger, *THIS JOURNAL*, **76**, 5248 (1954).

(12) G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5247 (1954).

A value of 1.6, however, agrees with the assumption that the acetic acid will be almost completely present as the intermediate at half-neutralization.

In the more dilute  $\text{CCl}_4$  solutions, 0.001  $\mu$  in acetic acid, the intermediate carboxylate band fails to appear and the neutralization therefore leads directly to the final product II. This reaction can be followed fairly satisfactorily in terms of the carbonyl band of the acetic acid monomer at  $5.64 \mu$ . The carbonyl band of the salt formed coincides almost exactly with the acetic acid dimer band but does not interfere seriously with the monomer band. Duplicate sets of measurements were made using the Beckman and Baird spectrometers. The results are shown in Table II. Using the acetic acid dimerization equilibrium constant of 2000 the concentrations of the monomer and the dimer in a 0.001 acetic acid solution were calculated. From the observed optical densities of this solution values of  $\alpha I$  for the monomer were obtained. In the solutions containing triethylamine the monomer concentration was then determined from the carbonyl absorption band, the dimer from the dimer dissociation equilibrium constant, and the salt and free triethylamine from the stoichiometry. The accuracy of the measurements is probably not sufficient to allow the apparent trend to be given much significance. The equilibrium constant may, however, be somewhat disturbed by the farther association of triethylamine with the salt, but the spectra shows no evidence of this reaction which has been suggested for other systems.<sup>1</sup>

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE REACTION  $\text{HOAc} + \text{NEt}_3 \rightleftharpoons \text{Et}_3\text{NHOAc}$  IN  $\text{CCl}_4$  SOLUTION (ACETIC ACID EQUAL TO 0.001  $M$ )

$M_{\text{NEt}_3}$ Beckman	$(\log I_0/I)_{5.64}$	HOAc	$(\text{HOAc})_2$	$\text{Et}_3\text{NHOAc}$	$C_{\text{NEt}_3}$	$K$
..	0.37	(3.9)	(3.0)	..	.....	..
0.003	.23	2.3	1.06	5.6	0.0024	1000
.010	.106	1.07	0.23	8.5	.0091	870
.025	.060	0.60	0.07	9.2	.024	640
Baird						
..	0.43	(3.9)	(3.0)	..	.....	..
.001	.37	3.3	2.2	2.3	.00077	910
.003	.265	2.35	1.01	5.6	.0024	970
.010	.142	1.26	0.32	8.1	.0092	700
.025	.075	0.66	0.09	9.2	.024	570
					Av.	800

### Acid-Base Equilibrium Constants in Chloroform.

—In the more concentrated chloroform solutions also, the initial reaction of triethylamine with the acetic acid dimer to yield I is effectively stoichiometric and the equilibrium constant can only be classified as large. The subsequent reaction, however, to give III can be followed by the growth of the  $6.20 \mu$  carboxylate band and the decrease of the acetic acid dimer carbonyl band (Fig. 2). Table III shows the values of the optical density of these bands and the concentrations of the species in the equilibrium. The values of  $(\log I_0/I)_{5.85}$  are used only as a check on the acetic acid dimer concentration obtained from the stoichiometry. The concentration of the salt III is determined by comparison of  $(\log I_0/I)_{6.20}$

with the value of this quantity for complete reaction to III, as indicated by the absence of the carbonyl band. The somewhat larger value of the equilibrium constant with  $\text{CHCl}_3$  as solvent as compared to the value of the same reaction in  $\text{CCl}_4$  can be attributed to a greater interaction of  $\text{CHCl}_3$  with the salt, as in III, than with triethylamine itself.

TABLE III

THE EQUILIBRIUM CONSTANT FOR THE REACTION  $\text{Et}_3\text{N}(\text{HOAc})_2 + \text{NEt}_3 \rightleftharpoons 2(\text{Et}_3\text{NHOAc})$  IN CHLOROFORM (ACETIC ACID EQUALS 0.3 M)

$M_{\text{NEt}_3}$	$\log I_0/I$		$C_{\text{Et}_3\text{NHOAc}}$	$C_{\text{Et}_3\text{N}(\text{HOAc})_2}$	$C_{\text{NEt}_3}$	$K$
	$D_{6.20}$	$D_{6.85}$				
0.15	0.10	0.32	0.06	0.12	...	..
.25	.32	.21	.20	.05	...	..
.30	.36	.15	.22	.04	0.04	22
.40	.41	.11	.25	.025	.125	20
.50	.44	.05	.27	.015	.21	23
.80	.47	(.01)	.29	(.005)	.50	(34)

As before dilute solutions can be used to obtain information on the direct formation of III from the acetic acid monomer since again the intermediate carboxylate band is absent in the titration with acetic acid at 0.001 M. The results of measurements at such a dilution are given in Table IV. Here the concentrations of the acetic acid monomer, of the dimer, and of the salt III can be directly obtained from the absorption bands at 5.69, 5.85 and 6.05  $\mu$ . The 6.05  $\mu$  wave length does not correspond to the carboxylate maximum because with triethylamine in chloroform at the dilution an interfering band made the accurate estimation of the band maximum difficult. The equilibrium constants are satisfactory and again the larger values here as compared to the  $\text{CCl}_4$  solutions are to be attributed to the stabilization by chloroform of III.

TABLE IV

THE EQUILIBRIUM CONSTANT FOR THE REACTION  $\text{HOAc} + \text{NEt}_3 \rightleftharpoons \text{Et}_3\text{NHOAc}$  IN CHLOROFORM (ACETIC ACID EQUAL TO 0.001 M)

$M_{\text{NEt}_3}$	$\log I_0/I$			$C \times 10^4$				$K$
	HOAc	$(\text{HOAc})_2$	6.05 $\mu$	HOAc	$(\text{HOAc})_2$	III	NEt <sub>3</sub>	
0	0.606	0.338	...	7.0	1.7	..	...	..
.0005	.433	.220	0.097	4.47	1.1	3.13	1.87	3700
.001	.324	.154	.140	3.77	0.77	4.51	5.49	2200
.002	.162	(.068)	.215	1.86	(0.34)	6.93	13.1	2900
.005	.063	...	.282	0.73	..	9.42	40.6	3200
.010	(.024)	...	.304	(0.28)	..	9.82	90.2	(3900)
							Av.	3000

### Discussion

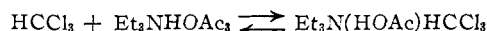
The study of acid-base reactions in non-ionizing, or "non-dissociating" solvents by means of the infrared absorption spectra gives further information about the nature of the resulting ion-pairs. That relatively concentrated solutions of the acid should lead to species involving primarily the acid dimer with one molecule of base was probably to be expected. The exact nature of this intermediate, I, and also of the final neutralization products, II and III, however, could not have been foreseen.

The species resulting from the reaction of an isolated, or free, pair of molecules, acetic acid and triethylamine, results in ionization but does not appreciably alter the electronic structure of the car-

bonyl group from that of the un-ionized acetic acid. While an essentially carboxylate group might have been anticipated it is clear that the interaction of the triethylammonium ion with the acetate ion is not a general electrostatic one but, probably because of the hydrogen bond, is a specific attachment to one oxygen of the acetate ion.

This unsymmetric carboxylate group, however, is susceptible to attachment on the carbonyl oxygen and the presence of a hydrogen bond there from chloroform or another acetic acid molecule is sufficient to produce an essentially normal carboxylate ion with effectively equivalent oxygens. Apparently intermediate configurations leading to absorption bands in the region 5.9 to 6.2  $\mu$  do not occur in these systems.

The equilibrium constants for the reaction of triethylamine with the acetic acid monomer can be compared with the results for similar systems reported by Bell and Bayles.<sup>2</sup> The corresponding constant for the reaction in aqueous solution is about  $10^6$ . The higher result in chloroform than in carbon tetrachloride can be looked upon as the effect of solvent interaction which leads, for larger interaction, to the aqueous value. The interaction of chloroform with the free ion-pair



can be estimated on the basis of two different assumptions. First, if the effect of solvent on the acetic acid monomer-dimer equilibrium is attributed entirely to interaction with the monomer than from constants given previously the above equilibrium constant can be estimated as 4. Secondly, and less reasonably, if the intermediate I is assumed to be relatively unaffected by the different solvents the above equilibrium would be expected to have a constant of 0.6. Although the disagreement is

rather large the indications are that the above solvent interaction which changes the spectrum from one with a carbonyl band to one with a carboxylate band is just that of a strong hydrogen bond. These values can be compared, for instance, to the dimerization constants for a number of alcohols of about 1.5 obtained by Coggeshall and Saier,<sup>13</sup> or with the value of 0.36 for the triethylamine-chloroform dimerization.<sup>12</sup>

The determination of acid-base equilibrium constants by these means will be used to determine the relative basicities and acidities of compounds not susceptible to measurement by means of visible or

(13) N. D. Coggeshall and E. L. Saier, *THIS JOURNAL*, **73**, 5414 (1951).

ultraviolet spectra. Such results should provide further useful data for confronting acid-base theories. Also it will be of interest to compare the

structures of the neutralization products for bases of different basic strength and steric requirements.

EVANSTON, ILLINOIS

[CONTRIBUTION NO. 1223 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

## Diffusion Coefficients for Aqueous Solutions of Calcium Chloride and Cesium Chloride at 25°

BY PHILIP A. LYONS AND JOHN F. RILEY

RECEIVED JUNE 4, 1954

Diffusion coefficients, molal refractive increments and supplementary densities and relative viscosities are reported for calcium chloride solutions from  $c = 0.03$  to  $c = 6$ , and for cesium chloride solutions from  $c = 0.06$  to  $c = 6$ . In agreement with results available from the conductance method diffusion coefficients for cesium chloride approach the values predicted by the Onsager-Fuoss relation at low concentration. At higher concentrations the deviation from theory is positive. Data reported for calcium chloride solutions supplement existing data indicating a negative deviation from the Onsager-Fuoss theory but the values presented are not consistent with the conductometric results which are at present available. Evidence is presented which suggests that Gouy diffusometry, as currently employed, yields data for very dilute electrolyte solutions which are inaccurate and define an upper bound to the correct values.

### Introduction

Diffusion coefficients for dilute aqueous calcium chloride solutions have been of considerable interest because of the large negative deviations from theory which have been observed for this system. These data<sup>1</sup> were obtained using the conductometric method of Harned. It has been shown that under certain conditions the conductance technique and Gouy diffusometry yield the same values<sup>2,3</sup> within the experimental errors involved. The work here reported supplements existing data<sup>4-6</sup> with which the conductance data can be compared. Results presented for aqueous cesium chloride solutions provide a reasonable confirmation of the conductometric work for this system.<sup>7</sup>

The investigation was extended into regions of high concentrations for several reasons: first, to permit a comparison of concentration diffusion data with existing ionic self-diffusion values<sup>8</sup>; secondly, to provide data for 1-1 and 2-1 salts at high concentrations which should be suitable for the calibration of other diffusion devices for electrolytes in these regions.

### Experimental

**Preparation of Solutions.**—Following the procedure of Shedlovsky and Brown<sup>9</sup> stock solutions of calcium chloride were prepared from C.P. calcium chloride which had been recrystallized three times. These stock solutions were analyzed and used for the preparation of the solutions of low concentration. The more concentrated solutions were prepared by addition of water to the recrystallized salt. Direct analysis of the latter solutions provided the concentration data which are reported.

Cesium chloride solutions were prepared by transferring weighed amounts of dried cesium chloride into calibrated volumetric flasks. The cesium chloride used was, spectrochemically, the purest sample available. The same sample

had been used to establish the limiting equivalent conductance for this salt<sup>10</sup> and also for the conductometric determination of diffusion coefficients at very low concentrations.<sup>7</sup> The salt was recrystallized several times from water and vacuum dried first at room temperature and finally at 50°.

**Diffusion Procedure.**—Equipment similar to that used for this work has previously been described.<sup>3,11,12</sup> One modification has been made in the design of a cell holder for use with a large Tiselius cell (92 × 5 × 50 mm. channel).<sup>13</sup> Measurements were made with this cell at low concentrations. In the new cell holder appropriate masking devices were inserted into slots immediately in front of the Tiselius cell which placed the cell and masks much closer than was the case for the conventional arrangement.

Boundary formation, movement of the boundary to the optic axis, and sharpening of the boundary by siphoning were accomplished in the usual fashion. During sharpening the positions of fringe minima in the focal plane were observed visually with the aid of a calibrated eye-piece. Following the suggestion of Longworth<sup>14</sup> these readings were used to estimate a time correction which compensates for a finite boundary thickness at the start of the experiment. If the siphoning operation is interrupted temporarily the Gouy pattern which appears can also be observed visually in the same manner. During the period of interruption the following experiment was performed several times using the large cell holder. After the withdrawal of the siphoning needle and the appearance of the pattern, a fine wire cross-hair which was the optic axis reference for this unit was moved slightly with respect to the boundary. By careful positioning, the cross-hair could be arranged so as to just blur the lowest fringe in the pattern while the boundary was still thin. At any other position of the cross-hair a blurring of fringes at higher values of  $j$  was observed. If the position of the maximum in the index of refraction gradient were invariant as would be required for ideal diffusion the lowest fringe should remain blurred. If the maximum in the gradient moved with respect to the optic axis during diffusion the blurring of fringes should be noticed at higher values of  $j$ .

The fractional values of  $j_m$  were determined in the usual way<sup>15</sup> by using the equipment as a modified Rayleigh interferometer. With a good cell and careful alignment the  $\delta$ -values (corrections for displacement of the Rayleigh bundle by the cell in the absence of the gradient of refractive index produced by the boundary) can be made quite small, and equal, for both the open and closed cell positions. A preliminary set of data for calcium chloride assuming that

- (1) H. S. Harned and A. L. Levy, *THIS JOURNAL*, **71**, 2781 (1949).
- (2) H. S. Harned and R. L. Nuttall, *ibid.*, **71**, 1460 (1949).
- (3) L. J. Gosting, *ibid.*, **72**, 4418 (1950).
- (4) E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9**, 152 (1941).
- (5) R. A. Robinson and C. L. Chia, *THIS JOURNAL*, **74**, 2776 (1952).
- (6) J. R. Hall, B. F. Wishaw and R. H. Stokes, *ibid.*, **75**, 1556 (1953).
- (7) H. S. Harned, M. Blander and C. L. Hildreth, Jr., *ibid.*, **76**, 4219 (1954).
- (8) J. H. Wang, *ibid.*, **75**, 1769 (1953).
- (9) T. Shedlovsky and A. S. Brown, *ibid.*, **56**, 1066 (1934).

- (10) W. E. Voisenet, Jr., and B. B. Owen, private communication.
- (11) L. G. Longworth, *THIS JOURNAL*, **69**, 2510 (1947).
- (12) L. J. Gosting, E. M. Hansen, G. Kegeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).
- (13) Cell made by Pyrocell Mfg. Co., New York, N. Y.
- (14) L. G. Longworth, private communication.
- (15) L. J. Gosting and M. S. Morris, *THIS JOURNAL*, **71**, 1008 (1949).