[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

A Study of the Association of Some Organic Acids by Infrared Absorption Measurements[1]

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The constants for the dimer–monomer equilibra of acetic, the three chloroacetic and benzoic acids have been quantitatively determined in dilute carbon tetrachloride solutions by means of infrared absorption measurements carried out at 25 ± 1°. The constants were calculated from absorption intensity measurements of the monomer –O–H stretching frequency by combination of the Bouger–Beer law and the expression for the equilibrium constant. Values of molar extinction coefficient, ϵ_{OH}, in liter/mole cm. obtained were 97, 97, 126, 128 and 170 for acetic, monochloro-, dichloro-, trichloroacetic and benzoic acids, respectively, while the respective average equilibrium constants for dissociation of the dimer were 2.5×10^{-4}, 6.2×10^{-4}, 9.3×10^{-4}, 19×10^{-4} and 0.7×10^{-4}. The results for benzoic acid are more uncertain than those for the other acids.

Introduction

A systematic attack on the problem of determining association constants of various hydrogen bonding systems in an inactive solvent by means of infrared absorption measurements does not appear to have been reported in the literature. A number of investigators[2-10] have reported measurements on either acetic, the chloroacetic or benzoic acids in various states of aggregation and in some cases[7,10] approximate or relative values of association constants have been given. Traynard[11] reports results of his Raman spectra measurements on acetic acid from which he calculates a value of the heat of association.

In view of the somewhat limited direct quantitative attack on the problem of association by the infrared method it seemed of some interest and importance to investigate this problem and if some of the difficulties could be surmounted infrared measurements could then be used to study the associations of a variety of substances as single and mixed solutes in a relatively constant medium. Acetic, the chloroacetic and benzoic acids seemed to be a useful starting point for such an investigation and results of measurements of the association constants of this series of acids at 25 ± 1° are reported herein.

Experimental

The absorption measurements were made using an apparatus originally assembled in this Laboratory by Cobbs[12] who measured the absorption spectra of the three chloroethyl acetates and of the monofluoro- and trifluoroethyl acetate. This assembly involved a Perkin–Elmer 12B Infrared Spectrometer with a Speedomax recorder and with the wave length drive calibrated using[2,13-17] NH_3, H_2O and CO_2 in the gas phase. Other details of the equipment will be reported elsewhere.

Absorption measurements using a rock salt prism were carried out on CCl_4 solutions of the acids in concentrations ranging from 10^{-2} to 10^{-5} molar for the spectral region between 2400 and 4900 cm.$^{-1}$. Solvent was introduced into the 1-cm. and 10-cm. measuring cells through a silica gel column. The absorption occurring in the vicinity of 3537 cm.$^{-1}$ caused by the stretching mode of the OH group of the acid monomer was carefully examined as the maximum intensity of this band was used to determine concentrations of acid monomer in the solution. In this region a slit width of 0.030 mm., corresponding to a spectral region isolated of approximately 30 cm.$^{-1}$, was used. Scattered radiation and background absorption correction to the observed spectra were obtained from the relation

$$T = \frac{I - f}{I_0 - f - g} \tag{1}$$

where T is the corrected transmittance of the solution, I the apparent transmitted intensity of a solution, I_0 the apparent transmitted intensity of the pure solvent, f the false energy or scattered radiation correction and g a background absorption correction. The value of f was determined separately for the 1-cm. and 10-cm. cells by use of a glass shutter and acid solutions in the beam path. The uncorrected I_0 values for the pure solvent in the region of the —OH absorption, namely, ~3537 cm.$^{-1}$, were approximately 65 chart units. When a glass shutter was interposed this intensity was reduced to 9 and 13 chart units for the 1- and 10-cm. cells, respectively. By using the glass shutter and trichloroacetic acid solutions of increasing concentrations the lower limit of the intensity was found to approach 2 chart units for the 1-cm. cell and 5 chart units for the 10-cm. cell. Since these limits seemed to represent energy from other regions of the spectrum they were used as the f-values, or scattered radiation correction, for the respective cells.

In making absorption measurements of mixtures of each of the several acids with pyridine in CCl_4 solution it was noted that a small general absorption, proportional to the total acid concentration, occurred in the region of 3500 to 3900 cm.$^{-1}$. The atmospheric moisture bands at 3759 and 3882 cm.$^{-1}$ registered intensity changes essentially equal to the general absorption. It was thus considered feasible to use the displacement in intensity of these bands in the association studies as a measure of the general absorption caused by the acids. In view of this the average value of the intensity displacements of the 3759 and 3882 cm.$^{-1}$ bands was taken as g, or the background absorption correction. In the most concentrated acid solution, ~0.07 molar, this factor was about 3 chart units whereas I_0 was approximately 65 chart units. Thus in view of its approximate proportionality to the total acid concentration it was of little significance in

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[1] Taken in part from a thesis presented by James T. Harris, Jr., in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University.

[2] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949.

[3] A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2239 (1938).

[4] R. H. Gillette and F. Daniels, *ibid.*, **58**, 1139 (1936).

[5] E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **6**, 316 (1938).

[6] R. C. Herman and R. Hofstadter, *ibid.*, **6**, 534 (1938).

[7] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

[8] F. T. Wall and W. F. Claussen, THIS JOURNAL, **61**, 2812 (1939).

[9] M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755, 767 (1938).

[10] M. M. Davies, *Trans. Faraday Soc.*, **36**, 333, 1114 (1940).

[11] P. Traynard, *Bull. soc. chim. France*, 316 (1937).

[12] W. H. Cobbs, Ph.D. Thesis, Duke University, Durham, N.C. (1948).

[13] E. F. Barker, *Astrophys. J.*, **55**, 391 (1922).

[14] W. H. Bennett and F. Daniels, THIS JOURNAL, **49**, 50 (1927).

[15] "Infrared Spectrometer Instruction Manuals, Model 12A and 12C," Perkin–Elmer Corp., Glenbrook, Conn. (1949).

[16] R. A. Oetjen, Chao-Ian KaO and H. M. Randall, *Rev. Sci. Instruments*, **13**, 515 (1942).

[17] R. Robertson and J. J. Fox, *Proc. Roy. Soc. (London)*, **A120**, 163 (1928).

the majority of the measurements reported since they were made at concentrations of less than 0.02 molar.

The acids and solvent used were purified as indicated below.

Acetic Acid.—Merck and Co. reagent grade acid was purified by the method of Pohl, Hobbs and Gross[18] which involved fractional distillation and fractional freezing until a product of constant freezing point was obtained. The refractive index of the product, n^{20}_D, was found to be 1.3718 as compared to the literature value of 1.37182.[19]

Chloroacetic Acid.—Hooker Electrochemical Co. product was fractionally frozen twice and then recrystallized six times from dry freshly distilled benzene. The product was then stored over concentrated sulfuric acid in a vacuum desiccator to remove[18] final traces of water and benzene. The f.p. by the cooling curve method was 62.70 ± 0.05° and may be compared with 62.80° found by Michel[20] which appears to be the highest value reported[21,22] in the literature to one-hundredth degree precision.

Dichloroacetic Acid.—Eastman Kodak Company practical grade of acid was twice distilled at atmospheric pressure followed by a vacuum fractionation in which the product boiling between 102–103° at 26 mm. was collected. This fraction was redistilled under a pressure of 17–18 mm. and the fraction boiling at 95.0–95.5° was collected and stored for use. Doughty and Black[23] report a distilling temperature of 95–96° at 17 mm. for this acid.

Trichloroacetic Acid.—A sample of this acid furnished by the Hooker Electrochemical Company was purified by the methods used for chloroacetic acid. The sample used for measurements gave a freezing point by the cooling curve method of 57.40 ± 0.05°. The f.p. was constant within 0.05° until 80% of the sample had frozen at which time thermal equilibrium could no longer be maintained. Literature values for the f.p. of this acid vary from 55 to 59.4°. Pickering's[24] measurements of the f.p. of trichloroacetic acid–water mixtures indicate a continual f.p. lowering with increase in the relative water content. Our sample showed a relatively constant f.p. during the cooling process, therefore it appears that (1) if we had an impurity it was not water, (2) the high temperature of 59.4° recorded by Pickering[24] may be wrong as to its absolute value or (3) we were dealing with another crystalline modification. The thermometers used in our determination were calibrated against a certified platinum resistance thermometer.

Benzoic Acid.—A sample of standard acid obtained from the National Bureau of Standards was dried for one hour at 105° and used without further treatment.

Each acid was stored in small bottles in a desiccator so that a particular bottle was opened only the one time required to obtain a sample for measurement.

Carbon Tetrachloride.—Eastman Kodak Company white label product was purified by the methods of Williams and Krchma[25] and Fox and Martin.[26] The removal of the last traces of water and prevention of moisture absorption was effected by a silica gel column as previously indicated.

Results and Discussion

The absorption maximum for the stretching mode of the O–H group in the several acid monomers was quantitatively determined as previously outlined.

The chief absorption frequencies found for the acids in the region 2400 to 3600 cm.$^{-1}$ are given in Table I. Uncertainties in the measured frequencies are of the order of ±7 cm.$^{-1}$ for the A, or O–H monomer band and are somewhat more for the B and C bands.

TABLE I

ABSORPTION FREQUENCIES (CM.$^{-1}$)

CH_3COOH	CH_2Cl-COOH	$CHCl_2$-COOH	CCl_3-COOH	Band
3548	3539	3529	3526	A
3050	3039	3046	3046	B
2949	2938	2940	2903	
2710	2724	2720	2656	C
2651	2618	2608	2503	
2570	2551	2498		

Detailed comparison with the literature will be made only for the O–H or A band of Table I as the other bands are of less interest in the present investigation. It may be noted however that band B is attributed[3,4,9,10,27] to (1) hydrogen bonded O–H, (2) C–H stretching, and (3) slow vibrations of the acid dimer ring whereas band C is attributed[8] to the H of a hydrogen bonded structure.

The value of 3548 cm.$^{-1}$ given in Table I for acetic acid, band A, compares favorably with 3546 cm.$^{-1}$ found by Wall and Claussen[8] and Buswell, Rodebush and Roy[3] for the same acid in CCl_4 solution. Davies and Sutherland[9] find 3525 cm.$^{-1}$ for this case. The frequency in the monomer O–H region for chloroacetic acid given by Randall, *et al.*,[2] namely, 3584 cm.$^{-1}$ was determined on the solid acid in an oil paste. This value cannot be readily compared to that given in Table I. Buswell, Rodebush and Roy[3] and Davies[10] both list 3521 cm.$^{-1}$ for the O–H monomer absorption in trichloroacetic acid. This may be compared with the value 3526 cm.$^{-1}$ given in Table I. The O–H band for benzoic acid was found at 3542 cm.$^{-1}$ which compares favorably with 3546 cm.$^{-1}$ reported by Wall and Claussen[8] but not so well with 3525 and 3559 cm.$^{-1}$ reported, respectively, by Davies and Sutherland[9] and Buswell, Rodebush and Roy.[3]

The monomer–dimer equilibrium constants were calculated from the measured intensity of the OH absorptions at various acid concentrations by combination of the Bouger–Beer law, $d = \epsilon Ml$, and the expression for the monomer–dimer equilibrium constants, $K = 2M^2/(A - M)$. In these expressions d is the optical density, ϵ the molar extinction coefficient, l the absorption path length, M the acid monomer concentration and A the total acid concentration, namely, $A = 2D + M$ where D is the concentration of dimer. Combination of the above expressions and rearrangement gives

$$d = \frac{K}{2}\epsilon^2 l^2 \frac{A}{d} - \frac{K}{2}\epsilon l \qquad (2)$$

From equation 2 it follows that a graph of optical density, d, at the particular O–H absorption frequency against the ratio, A/d, of the total acid concentration to the optical density should give a straight line of slope $(K/2)\ \epsilon^2 l^2$ and intercept $(K/2)\ \epsilon l$. The data for both the 1- and 10-cm. cell are shown graphically in Fig. 1. It is evident from this figure that the assumption of a monomer–dimer equilibrium is consistent with the experi-

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(18) H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

(19) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, London, 1935, p. 43.

(20) J. Michel, *Bull. soc. chim. Belg.*, **48**, 127 (1939).

(21) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 173.

(22) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950, p. 509.

(23) H. W. Doughty and A. P. Black, THIS JOURNAL, **47**, 1091 (1925).

(24) S. U. Pickering, *J. Chem. Soc.*, **67**, 675 (1895).

(25) J. W. Williams and I. J. Krchma, THIS JOURNAL, **48**, 1888 (1926).

(26) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A174**, 234 (1940).

(27) R. H. Gillette, THIS JOURNAL, **58**, 1143 (1936).

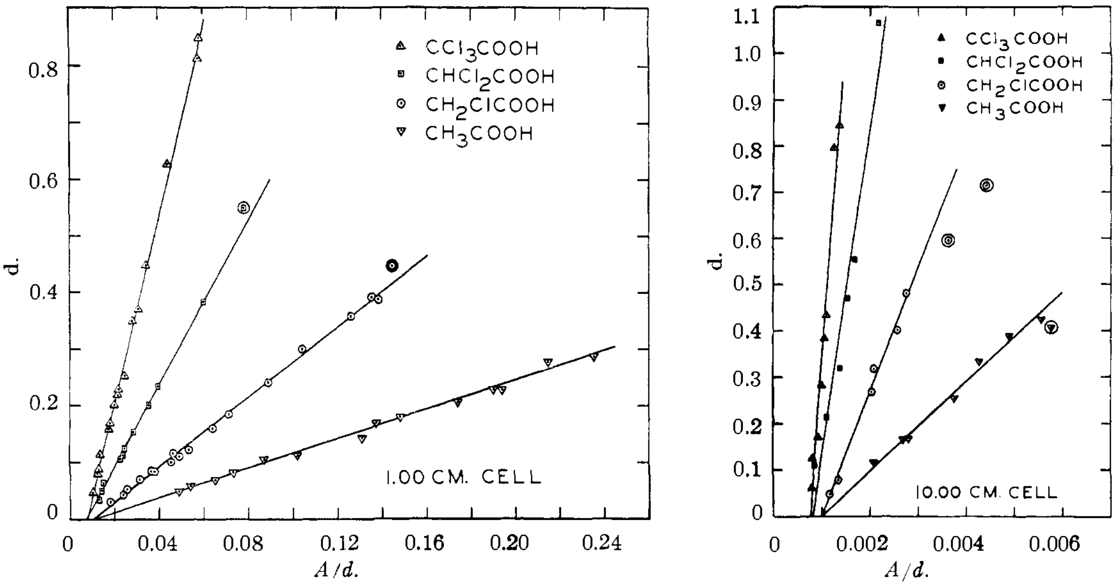

Fig. 1.—Relation of optical density, *d*, to the ratio, *A*/*d*, of the total acid to the optical density. Experimental points and least square lines are shown. Points in large circles were omitted from the least square analysis.

mental results as they are interpreted by equation 2. Points in Fig. 1 shown in the large circles were omitted from the least squares analysis of the data.

Values of ϵ and K obtained from the least squares analyses of the data for the slope and intercepts for the several acids at 25 ± 1° are recorded in Table II. The molar extinction coefficient is given in liters/mole cm. The values given for benzoic acid are somewhat more uncertain than those for the other acids since fewer measurements were made on this substance, namely, 8 concentrations, and interpretation of its spectrum in the O–H region was more complicated. The last column in Table II gives the dissociation constant for several of the acids in benzene solution at 30°

TABLE II

CONSTANTS FOR THE ACIDS

Acid	$l_{(\text{cm.})}$	$\epsilon_{(\text{OH})}$	$\epsilon_{(\text{av.})}$	K ($\times 10^{-4}$)	$K_{\text{av.}}$ ($\times 10^4$)	K_{Bz} ($\times 10^4$)
Acetic	1	92	97	1.8	2.5 ± 0.7	27[a]
	10	102		3.1		
Chloroacetic	1	95	97	6.8	6.2 ± 0.7	99[a]
	10	99		5.5		
Dichloroacetic	1	129	126	8.8	9.3 ± 0.5	
	10	122		9.7		
Trichloroacetic	1	125	128	21	19 ± 2	410[a]
	10	130		17		
Benzoic	1 + 10	(170)		(0.7)		54[b]

[a] H. A. Pohl, M. E. Hobbs and P. M. Gross, reference 18. [b] R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, 1795 (1938).

In Table II the ϵ_{OH} values found for a particular acid using the two different cells agree reasonably well with each other considering the fact that the lower limit of concentrations of the solutions used in the 10-cm. cell were usually one or two orders of magnitude below the lowest concentration in the 1-cm. cell. The values of ϵ_{OH} may be compared to average values in the range from 30 to 160 reported by Marion, Ramsay and Jones.[28]

The equilibrium constants given in Table II for the several acids in CCl_4 solution show fair agreement for the 1-cm. and 10-cm. cell except for the case of acetic acid. This acid was least dissociated and because of the limited amount of monomer present slight errors in measurement can lead to significant errors in the calculated equilibrium constants. The constants are all calculated on a concentration basis and quite possibly the agreement between the 1-cm. and 10-cm. cell would be improved if activities rather than concentrations had been used since rather different average concentration ranges were involved for measurements in the different cells. Further investigation into the equipment characteristics and the physical chemistry of the systems investigated is needed before the difference in K values for the two lengths of cell can be ascertained.

Davies and Sutherland[9] have reported a study of acetic, benzoic and lauric acids as well as cetyl alcohol in CCl_4 solutions in which an attempt was made to determine quantitatively the association constants and heats of association. In analyzing their data they used integrated areas in the O–H monomer absorption region and attempted to correct for background absorption by a careful selection of the area to be integrated. Concentrations of the order of 0.01 molar were used and only the relative constants at several temperatures were obtained. The values of the constants were not explicitly stated. For the case of benzoic acid they obtained 9300 ± 1000 cal./mole as the heat of dimerization. These investigators also determined the dimer dissociation equilibrium constant for benzoic acid in CCl_4 at 19.5° by the partition method with water and found a K value of 0.73×10^{-4}. The K value reported in Table II of this paper as 0.7×10^{-4} was actually calculated as 0.74×10^{-4} but was rounded off because of uncertainties in the measurement. The excellent agreement with Davies and Sutherlands'[9] value is regarded as fortuitous since water dissolved in the CCl_4 layer

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[28] L. Marion, D. A. Ramsay and R. N. Jones, THIS JOURNAL, **73**, 305 (1951).

in the partition method introduces a complicating factor that cannot be readily evaluated.

No data were found in the literature which could be compared unambiguously with those reported in Table II. The nearest case was the benzene solution values recorded in the last column of the table. A rough parallelism is noted in the trend of the two sets of values, and, neglecting the case of benzoic acid, the benzene values are larger by a factor of 10–20. Differences not only of the constants but of the heats of association are to be expected[29] on the basis of relative affinity of the solvent for the monomer molecules.

This study was undertaken as one phase of a program envisaging the examination of interactions of various acid–base systems in a relatively constant medium by means of the infrared absorption technique. Measurements in carbon tetrachloride on pyridine and diethyl ether with some of the acids listed above have been carried out and will be reported at a later date.

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(29) M. E. Hobbs and W. W. Bates, THIS JOURNAL, **74**, 746 (1952).

[CONTRIBUTION FROM THE INSTITUTE OF SCIENCE AND TECHNOLOGY, UNIVERSITY OF ARKANSAS]

Prediction of Cation-exchange Equilibria

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This paper offers an explanation for the selectivity of ion-exchange resins, based upon a consideration of the coulombic forces acting on the system. Herein, the resin is considered to be a series of negative point charges randomly distributed and the cations are held at an average at their closest distance of approach (which may be considered to be the sum of the radii of the "adsorbed" hydrated cation and the resin anion). Hence, the free energy change involved in the exchange of the cations, and thus K_{eq}, may be determined from the work necessary to remove each of the two types of cations involved from this distance of closest approach to infinity against the coulombic attractive forces acting between the cation and the resin anion. Calculations were made for several uni-univalent exchanges and one uni-divalent exchange, and the calculated K_{eq} was found to agree favorably with that obtained experimentally.

The exchange capacity, *i.e.*, the ability of one ion to replace another on an ion exchanger, varies according to the radii of the hydrated ions.[1] The order of absorption in general is that of the lyotropic series Cs > Rb > K > Na > Li.

Nachod and Wood[2] have compared equilibrium exchange capacities with the "a_0" values of the Debye–Hückel equation for activity coefficients which have been related to hydrated radii. They have found nearly quantitative correlation within valence types as expressed by the equation

$$R = \alpha \times 28.3 \times \text{E.E.} + \beta\,(23.5 + 5.3V)$$

where R = radius of hydrated ion, α and β are constants depending on exchanger, V = valence of entering ion, and E.E. = equilibrium exchange capacity.

Boyd, Schubert and Adamson[3] have shown that exchange constants are related to the free energies of hydration of the cations involved, and have suggested that the free energies of hydration, and thus of exchange, should be governed by electrical interactions according to Coulomb's law. They have found close correlation between free energies of hydration and exchange constants in the systems investigated.

Gregor[4] has examined the consequences of combining Donnan's equations concerning membrane equilibria with an assumed simple relationship between swelling pressure and volume of the exchange resin, wherein the stress caused by the swelling is considered to obey Hooke's law. The relationships developed in many cases have been found to describe the properties of ion exchangers rather closely.

It is a reasonable assumption that, in any completely rigid treatment of free energies or equilibrium constants of ion-exchange reactions, the variation in degree of swelling with ionic form of the exchange resin should be considered. It might also be expected that this factor should become increasingly important with increasing cross linkage and swelling pressure of the resin.

In this paper, the contribution to the free-energy difference for the exchange reaction of the change in swelling pressure for different ionic forms has been neglected. It would be expected that this assumption would be justified completely only if the amount of cross-linking is negligible. As a first approximation, it has been assumed that for moderately cross-linked exchangers this contribution, if not completely negligible, is small compared to the electrical interactions involved.

In general, it has been assumed that the ions of the resin phase may be considered to be completely disassociated, with their activities determined by interionic attractions approximately as expressed by the Debye–Hückel theory. It should not be expected, however, that this treatment would be applicable to the resin phase, inasmuch as the resin anion is attached somewhat firmly to the resin walls and a spherically-symmetrical arrangement of ions about it could hardly be expected. Also, steric or space requirements will largely rule out the attainment of a spherically-symmetrical atmosphere for the cations of the resin phase, or for the salt ions coming from the solution phase which are found in the resin phase.

(1) R. Kunin and R. J. Meyers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 22 ff.

(2) F. C. Nachod and W. J. Wood, THIS JOURNAL, **67**, 629 (1945).

(3) G. E. Boyd, J. Schubert and A. W. Adamson, *ibid.*, **69**, 2818 (1947).

(4) H. P. Gregor, *ibid.*, **70**, 1293 (1948); H. P. Gregor and J. I. Gregman, *ibid.*, **70**, 2370 (1948).