

The InfraRed Absorption of Carboxylic Acids in Solution II. Intensities

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The Infra-Red Absorption of Carboxylic Acids in Solution

II. Intensities

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The integral absorption of the monomeric OH band has been measured for solutions of acetic, benzoic and lauric acids in CCl_4 at various concentrations and temperatures. At any given temperature the results indicate that the integrated intensity is roughly proportional to the amount of the monomer present, assuming that there is a monomer \rightleftharpoons dimer equilibrium. The temperature variation of the integrated absorption gave values for the heat of association varying from 6000 to 10,000 cal./g mole, which is considerably below the accepted value of 15,000 cal./g mole. This difference is attributed to the variation in the absorption coefficient with temperature. Equally anomalous results were obtained from measurements on the intensity of the monomeric C=O band. The variation of the absorption coefficient with concentration and with temperature was checked independently on solutions of cetyl alcohol in CCl_4 .

A QUALITATIVE relationship between the appearance of certain absorption bands and the degree of association of the acid having been established, an attempt was made to put that relationship on a quantitative basis. Accordingly, the intensities of the monomeric bands at 2.83μ and 5.65μ were measured at varying concentrations and at two or more temperatures. The method of measuring the intensity has already been explained. (See Paper 1.) If the assumptions are correct, then the integral absorption is a direct measure of the number of absorbing centers provided the transition probability does not alter with concentration or with temperature. As we shall see, the latter conditions do not appear to be fulfilled, although the variation with concentration does not seem to be nearly so serious as that associated with temperature. It should be noted that in all the results now to be presented a constant absorption path-length of 6.02 mm was employed. The class mark provides an indication of the estimated uncertainty involved in determining the areas, this being largely dependent on the steadiness of the background absorption. When this uncertainty is less than 5 percent an α is used; for an uncertainty of 5 percent to 12 percent, β ; and where greater than 12 percent, γ . The figures (1 and 2) illustrate typical examples of the procedure.

In Tables I-III c = total concentration of acid in g moles/liter, while m = computed integral

absorption $\int \delta d\lambda$ for the band in question in arbitrary units maintained at the same dimension throughout. If we have a monomer \rightleftharpoons dimer equilibrium and α is the fraction of solute as monomer, for a total concentration of c g moles per liter, then

$$2c^2\alpha^2/c(1-\alpha) = 2c\alpha^2/(1-\alpha) = K_{(\text{Assoc})}$$

or,

$$[\text{R}\cdot\text{COOH}]_{\text{monomer}} = c\alpha = \left(\frac{K}{2}c(1-\alpha)\right)^{\frac{1}{2}} \approx \left(\frac{Kc}{2}\right)^{\frac{1}{2}}$$

the final approximation being applicable when α is small compared with unity. Thus the monomer concentration, and therefore the integral absorption, should be proportional to the square root of the total concentration of acid if α is small. In Tables I to III are collected the observations on the monomer band at 2.83μ for acetic, benzoic and lauric acids at several concentrations and temperatures. (Fig. 1.)

Inspection shows that c/m^2 is very satisfactorily constant for acetic acid at 75° , but only moderately so for the other sets of observations. The only systematic variation in these values seems to be the anomalously high figures at the greatest concentrations, i.e., smaller values of m than would have been expected. A similar effect will be noted later in the case of an alcohol.

As m^2/c (proportional to $K(1-\alpha)$) gives an approximate measure, in arbitrary units, of the

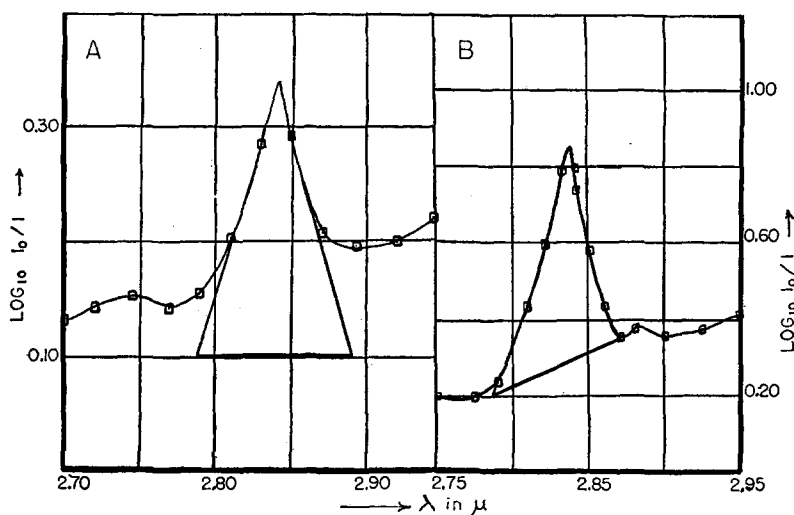


FIG. 1. A. 0.167 molar benzoic acid. Temperature: 43.0°. Area: 1458 squares \equiv 4.86 units. B. 0.167 molar benzoic acid. Temperature: 72°. Area: 945 squares \equiv 9.45 units.

association constant K , its temperature variation should allow of the heat of association being estimated. The results for acetic acid in CCl_4 give a value of $\Delta H = 9300 \pm 1000$ cal./g mole. For benzoic acid the temperature variation between 18° and 43.5° was in the wrong direction* while that between 18° and 72° gave a maximum figure of 6600 cal. per g mole. The accepted value of this heat of association, from measurements on formic and acetic acids in the gas phase, is near 15,500 cal./g mole.¹ That this value is not appreciably changed by solution in CCl_4 has been shown in the case of benzoic acid. The association of the latter was measured in CCl_4 at 19.5° by the partition method and at the boiling point by molecular weight determinations in the Cottrell apparatus.² The values for $K_{(\text{Assoc})}$ were 7.30×10^{-5} at 19.5°; 4.5×10^{-3} at 76.5°; giving $\Delta H = 14,700$ cal./g mole. The great difference between these values and those estimated from the integral absorptions can only mean that the absorption coefficient K_i in the expression $I_\alpha = I_\beta e^{-c_i K_i l}$, itself varies with temperature, actually decreasing with rise in temperature. Again, a similar effect was found for the O—H absorption in the alcohols.

* Cf. the first curve on Fig. 1 where the area taken for m considerably exceeds a normal estimate, thus giving a maximum value for m .

¹ MacDougall, J. Am. Chem. Soc. 58, 2585 (1936); Coolidge, *ibid.* 50, 2166 (1928).

² Davies, Trans. Faraday Soc. 34, 410 (1938).

In order to pursue this point, the integral absorption of the monomeric band at 5.65μ was also measured at different temperatures. This yielded a value of $\Delta H = 1000$ cal./g mole. The obvious conclusion that the variation of absorption coefficient with temperature is even greater for the C=O than for the O—H group is not, however, justified since there is considerable uncertainty in the values of m owing to the overlapping of the two bands. Allowing for all

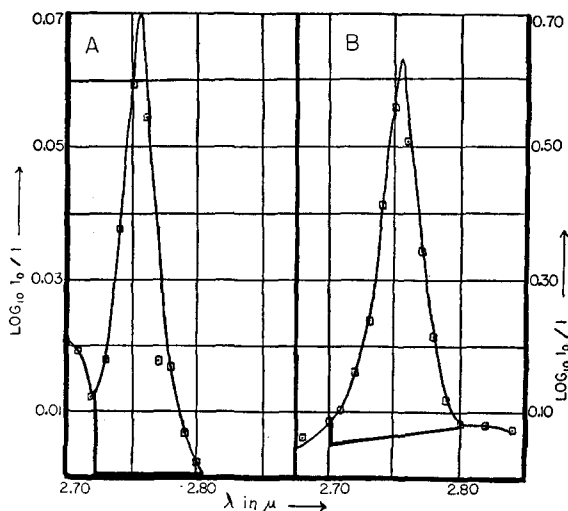


FIG. 2. A. 0.0033 molar cetyl alcohol. Temperature: 74°. Area: 1796 squares \equiv 0.90 unit. B. 0.050 molar cetyl alcohol. Temperature: 74.3°. Area: 1735 squares \equiv 8.67 units.

TABLE I.

	ACETIC ACID IN CCl_4				ACETIC ACID IN CBr_4				
	(a) At 18°		(b) At 75°		(c) At 109°				
c	0.010	0.020	0.050	0.0020	0.010	0.050	0.0038	0.0204	0.224
m	1.11	1.69	2.10	1.90	4.40; 4.19	8.50	5.20	13.3	23.0
Class	β	α	β	β	β α	α	β	γ	γ
$(c/m^2) \times 10^3$	8.12	7.00	11.3	0.55	0.52; 0.57	0.69	0.14	0.12	0.42

TABLE II.

	BENZOIC ACID IN CCl_4								
	At 18°		At 43.5°		At 72°				
c	0.00334	0.0167	0.167	0.0167	0.167	0.00334	0.0167	0.167	
m	1.31; 1.20	1.60; 1.76	4.83; 5.21	1.21	4.86	1.86	4.36	9.43	
Class	β β	β γ	β γ	γ	γ	α	α	β	
$(c/m^2) \times 10^3$	1.94; 2.32	6.52; 5.39	7.13; 6.13	11.4	7.10	0.96	0.88	1.87	

TABLE III.

	LAURIC ACID IN CCl_4 AT 74°				
	c	m	Class	$(c/m^2) \times 10^3$	
	0.0020	0.0100	0.050	0.25	
	1.06; 0.72	2.53; 2.85	6.42	7.17	
	β α	α α	β	γ	
	1.64; 3.85	1.56; 1.23	1.21	4.85	

possible sources of error, the value of ΔH found from the variation of the C=O integral absorption is no higher than that found from the O—H bands. That the present is a solvent effect on the absorption coefficient is made more certain by the observations of Badger and Bauer³ on the intensities of the O—H overtone bands in the gas phase, from which they derived a normal value of the heat of association.

A further confirmation of this effect came from a study of the OH absorption in cetyl alcohol (chosen for later use as a standard for the alcoholic OH absorption in omega-hydroxyundecanoic acid), of which a very pure sample was available. Here we measured at 18° and at 74° the monomeric OH absorption for concentrations which were always so low that the

association band was never present. The results are given in Table IV (Fig. 2).

It will be noticed that the integral absorption varies with concentration at each temperature. This is a real effect and not due to experimental error. Equally important is the variation with temperature of the integral absorption for a given concentration, which is even more pronounced than the former effect. We have tried whether a variation with temperature of the OH absorption coefficient in the acids of the above order would account for the low value of the heat of association. Although the correction is appreciable (corresponding to an increase in ΔH of 2100 cal./g mole in the case of benzoic acid) it is not nearly sufficient; indicating that the effect must be much more pronounced in the acids than in the alcohols.

From the above we see that it is not possible to use the integral absorption of the monomeric band of an associating molecule as a measure of the concentration of monomer present without making due allowance for the fact that the absorption coefficient varies both with the concentration of the absorbing centers and with the temperature. Provided due allowance is

³ Badger and Bauer, J. Chem. Phys. 5, 605 (1937).

TABLE IV.

	CETYL ALCOHOL IN CCl_4							
	(a) At 18°		(b) At 74°					
c	0.0033	0.0100	0.0033	0.010	0.0167	0.050		
m	1.22	3.23	0.90	2.67	4.40	9.52	8.67	
Class	α	α	α	α	α	α	β	
m/c	366	323	270	267	264	190	174	

made, it should be possible, however, to form a fair estimate of the concentration of free alcoholic and carboxylic OH groups in solutions of a substance the molecule of which contains one or both of these entities. The application of this to the configuration of the omega-hydroxyundecanoic acid molecule in CCl_4 solutions is considered in the next paper.

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An Infra-Red Study of Omega-Hydroxyundecanoic Acid in Carbon Tetrachloride

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An infra-red examination of a long chain omega-hydroxycarboxylic acid has provided evidence as to the inter- and intramolecular association of such molecules in solution: In particular, it is believed that the occurrence of a cyclic form of the monomeric molecules in solution has been proved.

THE examination of omega-hydroxyundecanoic acid, $\text{CH}_2\text{OH} \cdot (\text{CH}_2)_9 \cdot \text{COOH}$, was suggested by the interesting behavior in its condensation reaction which was examined in different solvents.¹ Combined with data on its molecular complexity, the kinetic analysis led to a picture of the relations of this compound in solution which may be summarized as follows:

(1) At great dilutions where the simple monomeric molecules predominate it would appear that, owing to interaction between their end-groups, these tend to assume a cyclic rather than an open-chain configuration.

(2) With increasing concentration the dissolved molecules aggregate to units of higher molecular weight, a process which occurs very readily in nonpolar solvents and which proceeds until complexes of at least three or four times the normal molecular weight represent the average degree of dispersion.

The results of the study of typical alcohols and carboxylic acids in solution (see the foregoing papers) have shown how their characteristic groups, $-\text{CH}_2\text{OH}$ and $-\text{COOH}$, when free from associative interaction with others of a similar

nature, can be separately identified and even estimated quantitatively. The essential feature of the present study lies in the measurement of the frequency of occurrence of these free individual groups in solutions of the hydroxyacid, on the basis of the integral intensities of the corresponding O—H absorption bands. It may be stated here that as a preliminary this method was applied to the examination of the occurrence of an acid-alcohol complex in mixed CCl_4 solutions of lauric acid and cetyl alcohol. The quantitative results showed that this interaction was certainly detectable but, as could be anticipated from independent estimates of its intensity,² the amount of complex so formed is very small, partly owing to the considerable self-association predominating in the case of the acid.

The present examination was confined to carbon tetrachloride solutions for this is one of the few common solvents which is free from a major absorption in the region of the hydroxyl bands. The negligible solubility of the hydroxyacid at 18°C in CCl_4 precluded measurements at room temperatures and these are accordingly confined to 74°C. The apparent molecular

¹ Trans. Faraday Soc. **34**, 410 (1938).

² Trans. Faraday Soc. **33**, 335 (1937).