

An InfraRed Study of OmegaHydroxyundecanoic Acid in Carbon Tetrachloride

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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).

TABLE I. *Apparent molecular weights of* $\text{CH}_2\text{OH}\cdot(\text{CH}_2)_9\cdot\text{COOH}$ *in* CCl_4 *at* 76.5° .

<i>c</i> , g moles per liter:	0.037	0.074	0.112	0.153	0.234
Mol. wt. (observed):	386	420	490	526	690

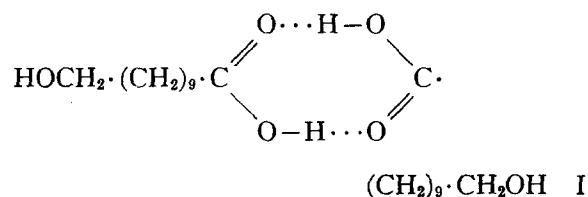
weights for $\text{CH}_2\text{OH}\cdot(\text{CH}_2)_9\cdot\text{COOH}$ (calculated = 202) determined by the elevation of the boiling point in CCl_4 are given in Table I, and show that the monomeric molecules will only predominate at very great dilutions.

Determination of the absorption spectrum of the hydroxyacid in the 2.6μ – 3.5μ region showed only the anticipated features: Distinct sharp bands with peaks at 2.755μ and 2.835μ corresponding to the alcoholic and carboxylic hydroxyl absorptions, respectively, succeeded on the long wave-length side by the band arising from the associated molecules and from the C–H fundamental. In the same manner as previously, after correction for the cell and solvent absorptions, the $\log_{10}(I_\beta/I_\alpha) \sim \lambda$ curves were plotted and the areas enclosed by each of the sharp hydroxyl bands determined. The figures illustrate typical examples of the results. In the first place the discussion will be confined to the results for the alcoholic hydroxyl ($-\text{CH}_2\cdot\text{OH}$) absorption.

The results of a systematic study of the OH absorption in cetyl alcohol at 74° in CCl_4 have been presented in the preceding paper. It was demonstrated that the integrated absorption of the 2.76μ band provides a measure of the concentration of free OH groups, the proportionality between these two factors actually being constant at dilutions greater than 0.02 molar. It must be emphasized that these similar measurements for the hydroxyacid were carried out using the same 6.02-mm absorption cell under as nearly identical conditions as those used for the alcohol. In determining the integrated absorptions it was easy to reduce these figures to the same arbitrary units as had been adopted for the alcohol. The assumption was then made that the specific absorptive power of the free alcoholic group is the same in both cetyl alcohol, $\text{C}_{16}\text{H}_{33}\text{OH}$, and in the hydroxyacid, $\text{HOOC}\cdot(\text{CH}_2)_9\cdot\text{CH}_2\text{OH}$. The similarity of the structures in which the alcoholic OH group occurs suggests this equality, while the quantitative accuracy of this assumption may be estimated by a

comparison of some results for benzyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$, with those for cetyl alcohol. In the latter case an integral absorption per g mole of solute of 350 units may be taken from the results at 18° . Under the same conditions three measurements with benzyl alcohol solutions gave a value of 300 ± 15 for this figure. The difference between these two values might safely be ascribed to the influence of the benzene nucleus in the latter molecule, in which case the practical identity of the absorptions in cetyl alcohol and the hydroxyacid would be assured. Thus, using a constant value of 270 units for the integrated absorption per g mole of free OH in dilute CCl_4 solution at 74° and interpolating, on the basis of similar values of the integral absorptions in Table IVb of the preceding paper at higher concentrations, the hydroxyacid measurements were converted into estimates of the molar concentration of free—i.e., unassociated—alcoholic hydroxyl groups. These results are summarized in Table II.

This table shows a very interesting result. Neglecting small departures which are obviously within the experimental error, the general indication is that the fraction of free hydroxyl groups, which at high concentrations is about one-half of their stoichiometric amount, at first increases with dilution but at the lowest concentrations again decreases. At the highest concentration in Table II (0.125 molar) the molecular weight data show the mean degree of association to be about 2.7. It seems very probable that the tendency to associate of the carboxyl groups, producing a dimer I, will be the first to assert itself:



This, alone, would result in no decrease in the concentration of free alcoholic hydroxyl groups, but it is certain that before association in the sense I is complete, these latter groups come into interaction either with free carboxyl groups or with other alcoholic OH groups, producing for instance, molecular aggregates of the form II.

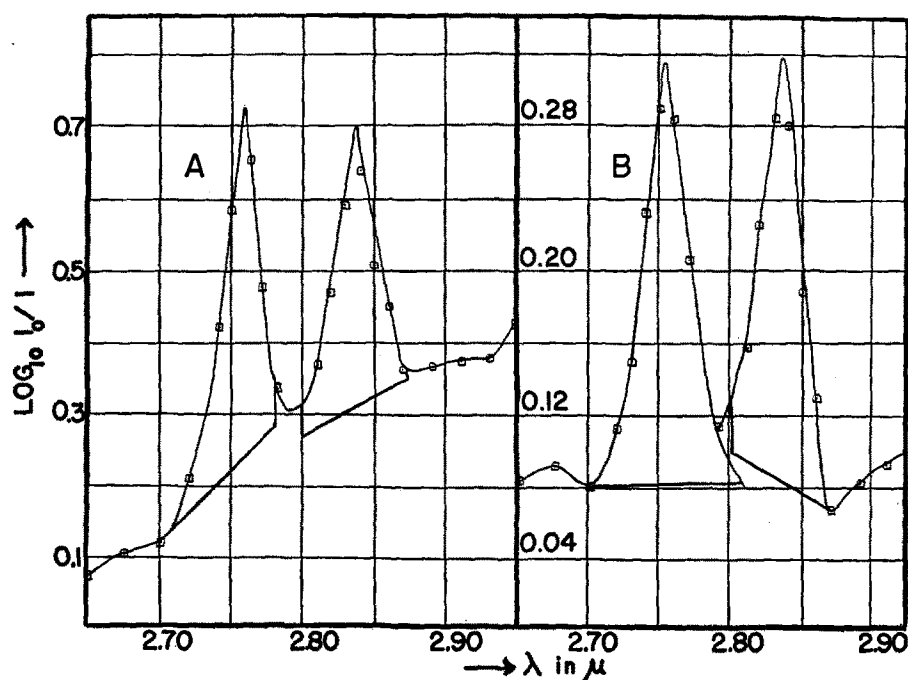


FIG. 1. Integral absorption curves. A. 0.0625 molar hydroxyacid at 74°, B. 0.0208 molar hydroxyacid at 75°.

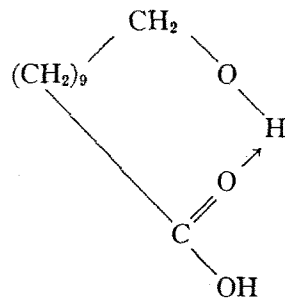
- (a) $\text{HOOC} \cdot (\text{CH}_2)_9 \cdot \text{CH}_2\text{OH} \cdot$
 $\text{HOCH}_2(\text{CH}_2)_9 \cdot \text{COOH};$ II
- (b) $\text{HOCH}_2 \cdot (\text{CH}_2)_9 \text{COOH} \cdot$
 $\text{HOCH}_2 \cdot (\text{CH}_2)_9 \cdot \text{COOH}.$

All that can be said with certainty is that type I will predominate at the dimer stage (see also a later paragraph) leaving an appreciable proportion of free alcoholic OH groups. Thus, on the arbitrary, but not unreasonable, assumption that together the two types II are as frequent as I, at the dimer stage, we should expect 63 percent of free alcoholic OH groups—which is

TABLE II. The alcoholic OH absorption in CCl_4 solutions of $\text{CH}_2\text{OH} \cdot (\text{CH}_2)_9 \cdot \text{COOH}$ at 74°.

c = TOTAL CONC. IN g MOLES PER LITER	$\int \log_{10} \frac{I_0}{I_\alpha} d\lambda$	CLASS	η = CONC. FREE ALCOHOLIC OH GROUPS	% FREE OH GROUPS $= \frac{\eta}{c} \times 100$
0.125	11.33	β	$11.33/160 = 0.071$	56
0.0625	7.01	β	$7.01/225 = 0.0312$	50
0.0500	8.06	β	$8.06/220 = 0.0366$	73
0.0208	3.58	α	$3.58/270 = 0.0132$	63
0.0070	1.21	α	$1.21/270 = 0.0045$	64
0.0050	0.40	α	$0.40/270 = 0.00148$	30
0.0035	0.28	γ	$0.28/270 = 0.00104$	30

approximately the condition found. Increasing the dilution beyond the dimer stage can only result in a rise in monomer concentration. The fact that this is not accompanied by a progressive increase in the proportion of free OH groups makes it extremely probable that intramolecular interaction of the same type occurs in the monomer: this can only be formulated as a cyclization (III).



III

It should be emphasized that the order of the variations in the last column of Table II upon which this conclusion is here based, would be even more pronounced if a constant specific absorption capacity for the free OH group had been assumed throughout. Further, a careful

examination of the possible experimental errors, including that for the solvent correction, in the result for the 0.0050 molar solution showed that their cumulative operation in one direction would hardly suffice to place the correct figure above 40 percent for the free alcoholic OH groups. The values of the two last percentages in Table II suggest that the equilibrium

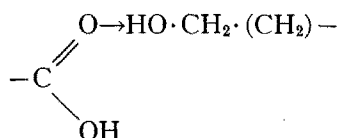
Open-chain monomeric molecules \rightleftharpoons Cyclic molecules,

under these conditions lies with about 70 percent in the cyclic form.

The whole of the previous analysis, as far as the results at 74° in the 6.02-mm cell are concerned, has been repeated for the carboxylic OH absorption. The specific integral absorption, i.e., the integral absorption per g mole of free COOH, $= 1/c \times \int \log_{10} (I_\beta/I_\alpha) d\lambda$, has been estimated for this case from the data for lauric and benzoic acids at 74°. The uncertainty in the association constants used to calculate the concentrations of monomeric molecules for these solutes undoubtedly accounts for the unsatisfactory values for this specific absorption. For lauric acid values of 1100, 580, 520, and 240 were calculated at different concentrations, while benzoic acid gave values of 1110, 965, and 590. The value of 600 chosen for this factor may thus be greatly in error, but it is important to note that we are interested not so much in the absolute values of the "free" COOH concentrations as in their variation with the total solute concentration. On this basis the following results have been obtained from the estimated integral absorptions of the 2.835 μ carboxylic OH band in omega-hydroxyundecanoic acid.

It is immediately seen that these figures essentially reproduce the results for the alcoholic OH absorption, and their interpretation may be taken in the same sense. Despite the probable error in the extinction coefficient, the very definitely lower proportion of free carboxyl than free hydroxyl groups is significant. This provides a direct confirmation that the association in the first instance predominantly involves the carboxylic groups. It must be explained that on the present interpretation the proportion of free carboxyl groups should increase on dilution only in that concentration range in which there is some proportion of solute with degree of asso-

ciation greater than that of the dimer. Thus, on the previously assumed state of affairs for a mean degree of association, $n=2.0$ (i.e., at 0.04 molar at 76.5°), there should then be 37 percent of "free" carboxyl groups. This should represent, at least approximately, a maximum value for this figure. The results, while not in quantitative agreement with this picture, nevertheless substantially confirm its essential correctness. The eventual decrease with increasing dilution of the specific absorption in the 2.83 μ band indicates that the carboxylic OH absorption in this region is also repressed when interaction with the $-\text{CH}_2\text{OH}$ group occurs: This is not obvious if the interaction is represented



as the hydroxyl group of the COOH structure is not then directly involved in the hydrogen bond. The final value for the free carboxyl groups (20 percent) should coincide, if the solute is then all present as monomer, with that of 30 percent found for the alcoholic hydroxyl groups. The difference might easily be accounted for by a small residual association involving only the carboxyl groups and/or, by the error in estimating the absolute free concentration of the latter.

One other conclusion may be drawn from these data: It appears that in the solutions examined only a small proportion of the molecules can be associated to a "parallel" dimer of the structure IV: for if this predominated, equal proportions of alcoholic and carboxylic groups should be bound in association at the dimer

TABLE III. The carboxylic OH absorption in CCl_4 solutions of $\text{CH}_2\text{OH} \cdot (\text{CH}_2)_9 \cdot \text{COOH}$ at 74°.

c = TOTAL CONC. IN g MOLES PER LITER	$\int \log_{10} \frac{I_\beta}{I_\alpha} d\lambda$	CLASS	c_f = CONC. FREE CARBOXYLIC OH GROUPS	% "FREE" COOH
0.125	9.36	β	0.0156	12.5
0.0625	5.63	α	0.0094	15.0
0.0500	4.80	α	0.0080	15.9
0.0208	3.14	β	0.0052	25.0
0.0070	1.20	α	0.0020	28.5
0.0050	0.70	α	0.0012	23.1
0.0035	0.40	β	0.00066	18.9

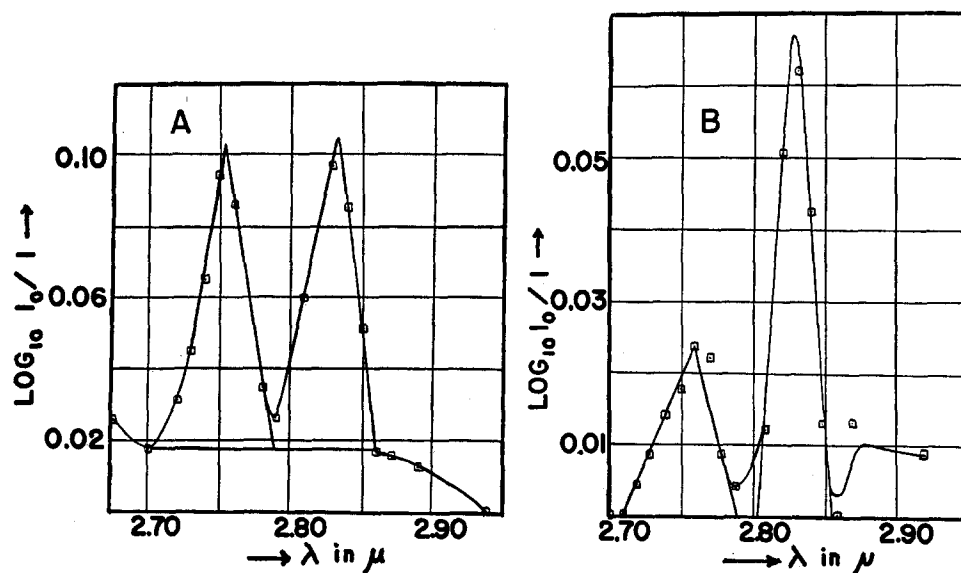
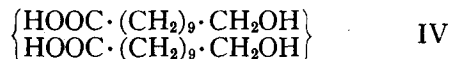


FIG. 2. Integral absorption curves. A. 0.0070 molar hydroxyacid at 74.6°. B. 0.0050 molar hydroxyacid at 74.5°.

stage. The absence of this molecular type has previously been suggested for quite different reasons.



In conclusion, it can be said that the study of the hydroxyacid by the infra-red technique has substantiated at each stage the picture of the behavior of this solute arrived at by the more indirect indications of the kinetic analysis. Further, the method used for the detection of inter- and intramolecular group interactions

would appear to be of wide applicability and its use in the present instance to establish the occurrence of ring-tied molecules of the hydroxyacid provides, we believe, a quantitative application in a very important field.

The author wishes to thank Professor E. K. Rideal for suggesting this work, Professor R. G. W. Norrish for the facilities afforded him in the Department of Physical Chemistry where the measurements were made, and Dr. G. B. B. M. Sutherland for helpful discussion.

He is also indebted to the University of Wales for a Research Fellowship.