730. *Infra-red Studies of the Molecular Interactions of ω-Hydroxypalmitic Acid.*

By W. J. Orville Thomas.

The end-group interactions of ω-hydroxypalmitic acid in carbon tetrachloride solutions have been studied spectroscopically. No indications of the cyclisation of the monomeric species have been obtained.

Values for the extinction coefficient of the hydroxyl bands of ethyl alcohol and propionic acid at 59° in carbon tetrachloride have been obtained.

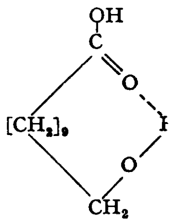
The effects of association on the infra-red absorption spectrum of carboxylic acids in solution have been examined many times (cf. Davies and Sutherland, *J. Chem. Physics*, 1938, **6**, 755). It has been shown that under suitable experimental conditions certain bands consisted of two components, one due to the monomeric and the other to the associated form of the molecule. Careful quantitative work by Kempter and Mecke (*Z. physikal. Chem.*, 1941, *B*, **46**, 229) and

Hoffmann (*ibid.*, 1943, *B*, **53**, 185) has shown that for the alcohols the monomeric molecules alone contribute to the " free " OH absorption band.

Davies and Sutherland (*J. Chem. Physics*, 1938, **6**, 767) studied typical alcohols and carboxylic acids in solution and showed that the groups $CH_2{\cdot}OH$ and CO_2H when free, could be separately identified and quantitatively estimated. Even when the two groups were present in the same molecule it was possible to follow the frequency of occurrence of the free $\cdot CH_2{\cdot}OH$ and CO_2H groups (Davies, *J. Chem. Physics*, 1938, **6**, 770). This is possible because the characteristic hydroxyl absorption for alcohols is at 2·76 μ whilst that for the carboxyl group is at 2·84 μ.

The results of an earlier study with ω-hydroxyundecanoic acid (Davies, *loc. cit.*) were interpreted as indicating that the monomeric molecules of this compound in dilute solution assumed a cyclic form (*e.g.*, as inset).

This possibility is of considerable interest. Both the entropy and energy changes for the conversion of open-chain into cyclic molecules would become available if the equilibrium distribution between these configurations could be evaluated over a range of temperatures. A particular interest attaches to such data in these structures because of the well-known Ruzicka–Stoll results on the yield of cyclic esters, etc., and their variation with the size of the ring. The present equipment, and in particular the greatly increased stability in recording spectra, suggested that the earlier observations should be confirmed and extended if possible.



EXPERIMENTAL.

Materials and Experimental Cells.—" AnalaR " carbon tetrachloride was distilled from and kept over anhydrous silica gel; absolute ethyl alcohol was dried over anhydrous silica gel and a middle fraction collected on redistillation.

Dr. E. M. Wilkinson furnished a sample of carefully purified propionic acid. The hydroxypalmitic acid used was provided by Dr. M. Stoll of Firmenich et Cie, Geneva, whom we thank for this gift. The acid had m. p. 80—82°.

Solutions were prepared at the working temperature. With the dilute solutions used in this work path lengths of up to 40 mm. were necessary. The very simple cell illustrated in Fig. 1 was used. *H* is a heating coil, *F* a filling hole, *W* a rock-salt window, *S* a securing screw, *T* a small cavity for the insertion of a copper–constantan thermocouple junction, and *C* a spacing collar whose size can be varied from 1 mm. to 40 mm. It was found that the temperature could be controlled and read to ± 1°.

When necessary the moisture content of the spectrometer could be decreased and kept at a constant level by means of a stream of dry nitrogen in conjunction with silica gel as drying agent inside the instrument. A fused silica prism was used in the spectrometer for these experiments.

Experimental Procedure.—Since the Grubb-Parsons S.3 spectrometer is a single-beam instrument it is necessary to carry out two separate runs; one with solvent to obtain the background transmission (I_β) and the other with the working solution (I_a). Curves of $\log_{10} I_\beta/I_a$ against wave-length were plotted and the areas enclosed by the sharp bands and the peak heights determined. Then,

$$\log_{10} I_\beta/I_a = kc_m l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the extinction coefficient, c_m is the monomer concentration in g.-mol./l., and l the cell-length in cm. The expression on the left of equation (1), evaluated for the peak optical density, P, gives :

$$k_p = P/c_m l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

An alternative measure, which is preferable on some grounds, and which we have also used, is the integrated intensity :

$$\int \log_{10} (I_\beta/I_a)\mathrm{d}\omega \equiv A = c_m k_A l \Delta\omega$$

$$\text{or} \qquad k_A = A/c_m l \Delta\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta\omega$ is the half-width of the band in cm.$^{-1}$. Equations (2) and (3) give the value of the extinction coefficient when c_m is known. The values were determined graphically by counting squares in an appropriate plot. Much the greatest uncertainty in this procedure consisted in the base-line drawn to represent any background absorption : errors are liable to enter owing to the variable absorptions of water in the background and the overlapping of the adjacent hydroxyl bands, *i.e.*, of the sharp monomer peaks and the broader association bands which soon appear as the concentration is raised. As being perhaps the least arbitrary procedure the base-line was obtained by joining the points of minimum absorption on either side of the sharp bands.

On these simple grounds it is seen that the peak height P, or integral absorption A, should provide a measure of the monomer concentration, c_m, provided the extinction coefficient, k, does not vary with concentration and temperature. It is, however, necessary to know the value of the extinction coefficient, k, for the particular band in question. Thermodynamic data are available for solutions of propionic acid in carbon tetrachloride (Davies, Jones, Patnaik, and Moelwyn-Hughes, *J.*, in the press) which enable the monomer concentration of propionic acid to be calculated under varying experimental conditions. The peak height and integral absorption of the hydroxyl band were obtained for propionic acid solutions of differing concentrations. Curves of peak height (P) and integral absorption (A) against monomer concentration (c_m) were drawn. Straight lines were obtained whose slopes gave a measure of the extinction coefficient, k', for the hydroxyl band of the carboxyl group of propionic acid.

The alcoholic OH band was calibrated by means of the hydroxyl band of ethyl alcohol. The peak heights and integral absorption of solutions so dilute that only the monomer was present were obtained and plotted against the concentrations, c, of the ethyl alcohol solutions. Over a certain range a straight line was obtained, the slope of which gives a measure of the absorption coefficient, k'', for the OH band of the $\cdot CH_2\cdot OH$ group.

FIG. 1.

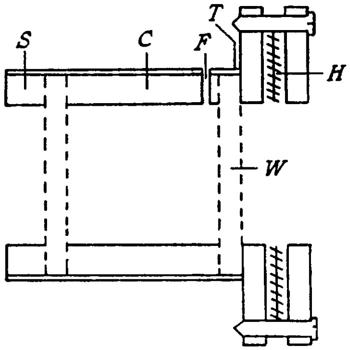


FIG. 2.

Peak height–monomer concentration curves for propionic acid and ethyl alcohol at 59°.

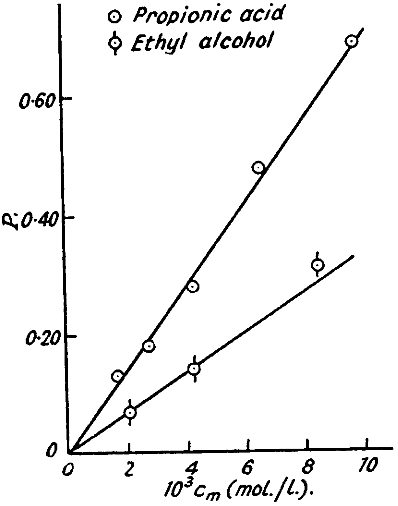
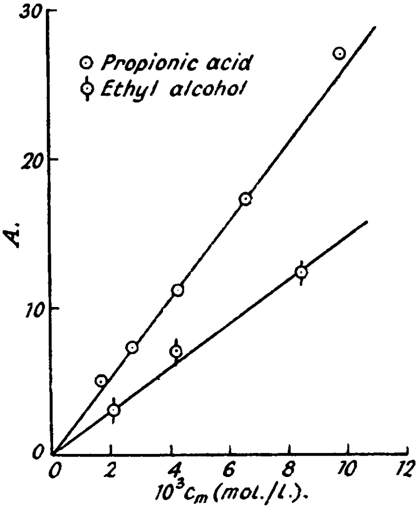


FIG. 3.

Integral absorption–monomer concentration curves for propionic acid and ethyl alcohol at 59°.



The assumption is now made that the absorption coefficients of the free hydroxyl groups present in monomeric ω-hydroxypalmitic acid have the values k'' and k'. The quantitative accuracy of this assumption is somewhat uncertain but relatively correct results should be obtained. By this means the peak heights and integral absorptions obtained for the free hydroxyl bands of the hydroxy-acid were converted directly into measurements of the monomer concentrations of these two groups. The measurements were conducted to as low a concentration as was reasonable ($5{\cdot}0 \times 10^{-4}$M) with the practical errors involved.

RESULTS.

The curves of peak height, P, and integral adsorption, A, against monomer concentration, c_m, for propionic acid and ethyl alcohol are given in Figs. 2 and 3. The results obtained for ω-hydroxypalmitic acid are given in Tables I and II (in which l is the cell length, and c_m is the monomer concentration, estimated spectroscopically, of the free hydroxyl groups at the total concentration c g.—mol./litre).

From equations (2) and (3) the values of the extinction coefficients for propionic acid and ethyl alcohol may be obtained. They are: propionic acid, k_p 70 ± 2, k_A 73 ± 2; ethyl alcohol, k_p 37 ± 2, k_A 39 ± 2.

TABLE I.

The alcoholic OH *absorption in carbon tetrachloride solutions of ω-hydroxypalmitic acid at* 62·4° ± 1°

Molar concn., 10^3c	A/l	Monomer concn., 10^3c_m	$10^2c_m/c$	Molar concn., 10^3c	A/l	Monomer concn., 10^3c_m	$10^2c_m/c$
0·956	1·444	1·00	105	2·390	3·570	2·50	105
1·338	1·802	1·25	93	5·976	8·301	5·80	97

TABLE II.

The carboxylic OH *absorption in carbon tetrachloride solutions of ω-hydroxypalmitic acid at* 62·4° ± 1°.

Molar concn., 10^2c	A/l	Monomer concn., 10^3c_m	$10^2c_m/c$	Molar concn., 10^3c	A/l	Monomer concn., 10^3c_m	$10^2c_m/c$
0·956	2·802	1·00	105	2·390	5·811	2·06	86
1·338	3·573	1·26	94	5·976	10·22	3·63	61

DISCUSSION.

It was earlier considered (Davies and Sutherland, *loc. cit.*), that the extinction coefficient, k, might vary both with temperature and with monomer concentration, c_m; the results obtained during this work, however, indicate that, over the limited concentration range studied, k does not vary with c_m for propionic acid or ethyl alcohol.

The results obtained for the hydroxy-acid indicate that the percentage concentration of free $CH_2{\cdot}OH$ groups remains constant in the concentration range studied. The value obtained for the percentage monomer present is, within the accuracy of the method, 100%. The latter theoretical figure would be obtained only if (*a*) none of the alcoholic hydroxyl groups were involved in association, either inter- or intra-molecularly; (*b*) there were no experimental errors; or (*c*) the correct extinction coefficients for the hydroxy-acid absorptions were known. Within the limitations imposed by (*b*) and (*c*), we can regard condition (*a*) as established.

The accuracy of this study can reasonably be taken to surpass that of the earlier work (Davies, *loc. cit.*), and so to correct the previous conclusion that cyclisation of the monomeric molecules occurs. This negative result, however, cannot be generally extended to other solvents and solutes, but it is of importance in view of the earlier infra-red and some recent X-ray studies in solution (Kratky and Worthmann, *Monatsh.*, 1946, **76**, 263).

The value of c_m/c for the OH band of the carboxyl group increases steadily as the concentration decreases. This indicates the breakdown of associated complexes to give simpler units with free carboxyl groups. Over the measured range it is clear that the carboxyl groups are still involved in associative interaction. This is perhaps not surprising, as they are certainly far more liable to be so engaged than the alcoholic hydroxyl groups. Thus it is difficult to draw any precise conclusion as to a possible cyclisation from the carboxyl group data, except in the negative confirmatory sense that it does not serve to establish such a feature.

Accepting the earlier indication that the alcoholic hydroxy-groups are not taking part in any interaction, then the simplest basis for the carboxyl group interactions would be a monomer $\rightleftharpoons$ dimer equilibrium in which they alone are participating. Quantitatively, however, this assumption is not substantiated by the " constant " $k_{eq.} = 2c\alpha^2/(1 - \alpha)$, estimated as 0·041, 0·026, 0·011, for solutions 10^3c = 1·338, 2·390, and 5·976 respectively. It is evident that the process is more complex than that suggested above.

Further detailed study at lower concentrations and higher temperatures is evidently needed for the elucidation of the molecular interactions of ω-hydroxypalmitic acid in dilute solution. Probably a more fruitful approach would be to use a polar solvent where the degree of association would be less at concentrations comparable with those studied here.

This problem was suggested by Dr. Mansel Davies to whom I am grateful for much useful discussion.

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