Intramolecular Effects on the Fundamental Hydroxyl Stretching Vibration in Derivatives of Fats and Related Compounds[1]

C. ROLAND EDDY, JOHN S. SHOWELL, and TATIANA E. ZELL, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

The intramolecular environment of the hydroxyl group in several compounds related to fats has been investigated by infrared measurements of the fundamental stretching vibration, using a lithium fluoride double monochromator and sufficiently low concentrations (.001–.05 M) in carbon tetrachloride to avoid intermolecular effects. In saturated alcohols and saturated hydroxyl derivatives of esters, the OH stretching frequency is found to depend on the number of hydrogen and carbon atoms which form the immediate environment of the OH group. Since this varies with rotational isomerism about the C-O single bond, the infrared hydroxyl band is composite, made up of components whose strengths give information about the relative amount of each rotational isomer present.

In unsaturated alcohols and unsaturated hydroxy-esters, rotational isomers permitting hydrogen bonding to π-electrons are stabilized according to the accessibility of the unsaturated link to the hydroxyl group, thus altering the proportions of the rotational isomers.

Introduction

SEVERAL PAPERS in recent years (1,2,3,4,5,6,7) have demonstrated the usefulness of infrared spectroscopy in studying the environment of the hydroxyl group in complex molecules. It was the purpose of this investigation to apply these techniques to hydroxyl derivatives of fats, in order to determine some of the fundamental properties of fatty compounds and to attempt to answer some of the still unanswered questions in the chemistry and physical properties of fats. As an aid in interpreting the results, several other similar compounds were also examined. This paper reports the qualitative conclusions that can be drawn from the infrared spectra. To supplement the qualitative interpretations, quantitative work is in progress analyzing the detailed shapes and areas of these curves by means of a digital computer. Results of this analysis will be reported in a later publication.

Experimental

Infrared spectra were obtained with a Beckman IR-3 spectrophotometer using two lithium fluoride prisms in a double monochromator. A mechanical slit width of 0.10 mm was used in the 3500–3750 cm^{-1} region, which corresponds to a spectral resolution of 2 cm^{-1} as estimated by comparison with the separation of the chlorine isotopic doublets of hydrogen chloride gas in the 2600–3100 cm^{-1} region when using the same mechanical slit width. Resolution was not as narrow for the differential spectra and varied with wavelength, since this instrument programs the slit width to give constant energy to compensate for absorption by the solution used for reference. Reproducibility of the absorption maxima of sharp symmetrical bands was within $\pm$ 1 cm^{-1}, and absolute accuracy of the band positions was within $\pm$ 2 cm^{-1} as checked by calibration with water vapor and ammonia. Accuracy of some of the broader bands was further limited by uncertainty in locating the position of maximum absorption.

Samples were run as solutions in carbon tetrachloride at 30C, in 10 mm and 25 mm cells of fused quartz, the same cell being used for both blank and sample to avoid inequalities in quartz window absorptions in the hydroxyl stretching region. Concentrations ranged from 0.001–0.05 molar, in order to avoid intermolecular hydrogen bonding. Samples were dissolved and cells filled in a gloved box continuously flushed with dry nitrogen. The carbon tetrachloride was of spectroscopic quality obtained from Matheson, Coleman, and Bell, was dried by bubbling dry nitrogen through it, was maintained dry by a small amount of Type 4A molecular sieve in the bottom of the bottle, and was kept in the gloved box until used. Infrared spectra of the solvent confirmed the fact that this drying process was effective. Since the quartz cells were merely stoppered and not vacuum tight, the cell compartment was continuously flushed with dry nitrogen, the rest of the instrument being under vacuum.

Preparation of Compounds

The following compounds, the highest purity obtainable commercially, were dried and distilled before use: Methanol, ethanol, 1-propanol, 1-hexanol, 1-heptanol, 1-tetradecanol, 2-propanol, 2-butanol, 2-octanol, 3-heptanol, allyl alcohol, crotyl alcohol, cinnamyl alcohol, geraniol, benzyl alcohol, nopol, 1-phenylethanol, 2-(2′,4′,6′-trimethylphenyl)-ethanol, 2-phenylcyclohexanol, cyclohex-3-en-1-ol, 3-butyn-1-ol, 3-butyn-2-ol, chloroethanol, and t-butanol.

The samples of diundecyl carbinol, diheptadecyl carbinol, cholesterol, and diosgenin were recrystallized to constant melting point.

A number of acyclic and cyclic homoallylic alcohols were analytical grade samples kindly supplied by Dr. Richard T. Arnold (8,9). They were 1-cyclohexenyloctan-2-ol, *trans*-2-(1′-*cis*-octenyl)-cyclopentanol, *trans*-2-(1′-*cis*-heptenyl)-cyclohexanol, *trans*-2-(1′-*cis*-hexenyl)-cycloheptanol, *trans*-2-(1′-octynyl)-cyclopentanol, *trans*-2-(1′-heptynyl)-cyclohexanol, *trans*-2-(1′-hexynyl)-cycloheptanol, 3-ethyldodec-5-en-3-ol, and 6-phenyl-3-ethylhex-5-en-3-ol.

1-Octadecanol. A highly purified sample of methyl stearate (99+ purity) was reduced by lithium aluminum hydride. The resulting 1-octadecanol was recrystallized from methanol three times to a compound melting at 58.0–58.5C.

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[2] Eastern Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

2-Octadecanol. A sample of commercial 1-octadecene was purified by the procedure of Showell, et al. (10) to remove the internal isomers. The highly purified 1-octadecene was epoxidized in ether with monoperphthalic acid at room temperature. The crude reaction mixture was chromatographed on Florisil using hexane. The unreacted olefin eluted immediately, followed by the desired 1,2-epoxyoctadecane, leaving ring opening products on the column. The epoxide was recrystallized from methanol-water (6–1) to obtain a white solid (mp 32.5–33.0C). Theory: C, 80.52; H, 13.52; specific oxirane 6.00. Expr., C, 80.14; H, 13.57; specific oxirane 6.03.

The highly purified 1,2-epoxyoctadecane (1.0 gm) was reduced at room temperature in dry tetrahydrofuran (15 ml) containing lithium aluminum hydride (0.2 gm) by stirring under nitrogen overnight. The excess hydride was destroyed by adding ethyl acetate and pouring the entire reaction mixture into 6 N HCl (50 ml). The resulting solid precipitate was extracted with benzene to obtain a white solid (1.0 gm) residue on evaporation. The solid was recrystallized several times from methanol to yield a shiny, white solid (mp 50.5–51.5C).

9-Octadecanol. A highly purified sample of *cis*-9,10-epoxyoctadecanol (3.0 gm, 0.011 mole), prepared by procedure of Gelb, et al. (11) was reduced by lithium aluminum hydride (0.5 gm, 0.011 mole) in refluxing dry tetrahydrofuran (30 ml) for 6 hr. The excess hydride was decomposed with hydrochloric acid (6 N, 50 ml); the mixture was then poured into water (300 ml) and was extracted with benzene (100 ml). The benzene layer was washed first with hydrochloric acid (6 N) then water until neutral, and dried over Na_2SO_4. The solvent was removed and the residue recrystallized several times from methanol to give white solid 9-octadecanol (mp 58.5C sharp).

Miscellaneous Long-Chain Alcohols. The following alcohols were high purity samples that were chromatographed and then recrystallized to obtain the infrared sample: methyl 10-hydroxystearate, methyl 12-hydroxystearate, methyl ricinoleate, methyl ricinelaidate, *cis-* and *trans*-9,10-epoxyoctadecanol-1.

Results and Discussion

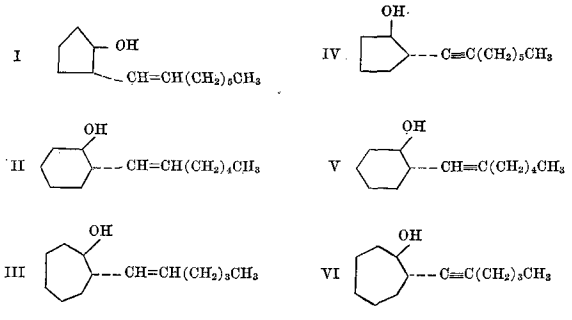
Table 1 lists the compounds included in this study. Where peaks are actually resolved, wavenumbers of their maxima are given. Shoulders are merely designated as being at lower or higher frequency than the principal maximum of the curve.

Saturated Alcohols. Figure 1 shows three 18-carbon saturated monohydric alcohols, along with methanol and tertiary butyl alcohol for comparison. The curves for the C_{18} alcohols are obviously composite, made up of overlapping peaks of width comparable to those of methanol and t-butanol. All of the primary alcohols in Table I, except methanol, have curve shapes similar to Curve A of Figure 1, maximum at slightly lower frequency than methanol, peak wider than that of methanol, without a definite shoulder, its composite nature merely indicated by asymmetry with the weaker component at lower frequency. The secondary alcohols have maxima at substantially lower frequency than methanol and can be divided into two groups, those which have one methyl group attached to the alcoholic carbon and those which have two chains longer than methyl. The methyl carbinols have curves similar to Curve B of Figure 1, a distinct shoulder on the low-frequency side of the main peak.

TABLE I
Infrared Absorption Bands of Monomeric Hydroxyl Group

Compound [a]	Main maxima (cm^{-1})	Weaker maxima (cm^{-1})	Shoulders [b]
Saturated primary alcohols			
Methanol	3644	.....	.....
Ethanol	3634	.....	L
1-Propanol	3639	.....	L
1-Hexanol	3638	.....	L
1-Heptanol	3639	.....	L
1-Tetradecanol	3640	.....	L
1-Octadecanol	3638	.....	L
Saturated methyl carbinols			
2-Propanol	3626	.....	L
2-Butanol	3628	.....	L
2-Octanol	3628	.....	L
2-Octadecanol [c]	3627	.....	L
Saturated secondary alcohols other than methyl carbinols			
3-Heptanol [d]	3631	.....	L
9-Octadecanol [d]	3629	.....	L
Di-undecyl carbinol [d]	3630	.....	L
Di-heptadecyl carbinol [d]	3630	.....	L
Methyl 10-hydroxystearate	3631	.....	L
Methyl 12-hydroxystearate	3631	ca. 3550	L
Allylic alcohols			
Allyl alcohol	3620	.....	H
Crotyl alcohol	3620	.....	H
Cinnamyl alcohol	3619	3538	H
Geraniol	3624	3562	H
Benzyl alcohol	3618	.....	H
Homoallylic alcohols			
Methyl ricinoleate	3627, 3589	3605	.....
Methyl ricinelaidate	3627, 3583	.....	L
3-Ethyldodec-5-en-3-ol	3619	3577	L
6-Phenyl-3-ethylhex-5-en-3-ol	3618	3582	.....
Nopol	3634	3591	.....
Phenylethanol	3635, 3606	.....	L
β(2,4,6-trimethylphenyl)-ethanol	3633	3606	.....
1-Cyclohexenyloctan-2-ol	3571, 3623	3604	.....
2-Phenylcyclohexanol	3599	.....	H
Cholesterol	3623	.....	L
Diosgenin	3623	.....	L
Cyclohex-3-en-1-ol	3623	.....	L
trans-2-(1′-*cis*-octenyl)-cyclopentanol (I) [e]	3622	.....	L
trans-2-(1′-*cis*-heptenyl)-cyclohexanol (II)	3585	.....	H
trans-2-(1′-*cis*-hexenyl)-cycloheptanol (III)	3621, 3576	.....	.....
Acetylenic alcohols			
3-Butyn-1-ol	3600, 3636	.....	.....
3-Butyn-2-ol	3618	.....	L
trans-2-(1′-octynyl)-cyclopentanol (IV)	3623	.....	L
trans-2-(1′-heptynyl)-cyclohexanol (V)	3583	3624	.....
trans-2-(1′-hexynyl)-cycloheptanol (VI)	3623	3571	.....
Miscellaneous compounds			
2-Chloroethanol	3600	3633	.....
Tertiary butanol	3616	.....	.....
cis-9,10-Epoxyoctadecanol-1	3638	.....	L
trans-9,10-Epoxyoctadecanol-1	3632	.....	L

[a] Solutions in CCl_4, 0.003–0.006 molar except where noted.
[b] L = shoulder at lower frequency than main maximum.
H = shoulder at higher frequency than main maximum.
[c] 0.03 molar.
[d] 0.01 molar.
[e]



The secondary alcohols with both chains longer than methyl have a shoulder that is much more pronounced than that of the methyl carbinols and a maximum at slightly higher frequency than the methyl carbinols. These two types of secondary alcohol can be easily distinguished by the shapes of their curves.

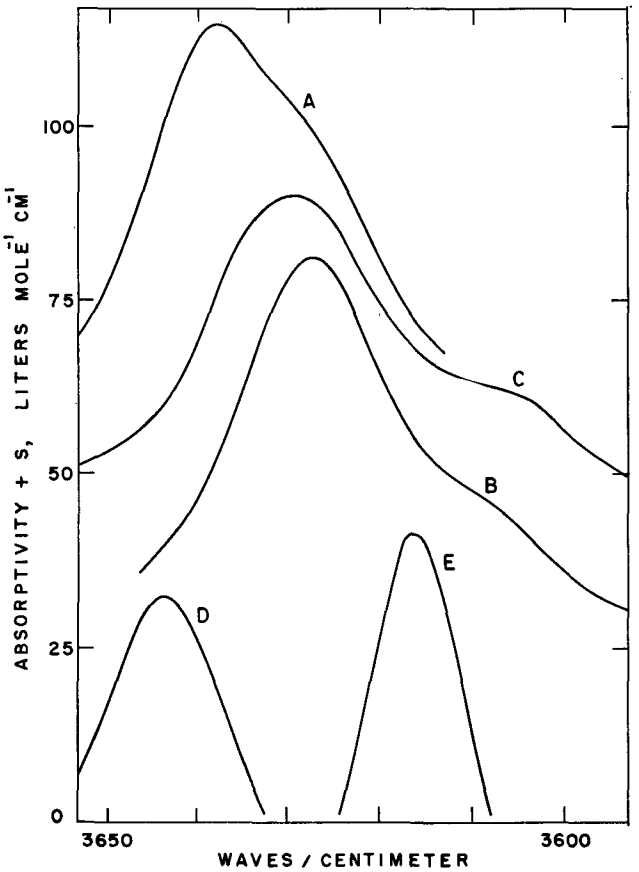


FIG. 1. Infrared hydroxyl bands of monomeric saturated alcohols in CCl_4. Curves displaced vertically for clarity. Subtract scale constant, S, from each curve to get absorptivity. (A) 1-Octadecanol, S = 55. (B) 2-Octadecanol, S = 25. (C) 9-Octadecanol, S = 45. (D) Methanol, S = −30. (E) Tertiary butyl alcohol, S = −30.

The component peaks that make up the composite curves of the saturated alcohols can be correlated with rotational isomers having different interactions between the hydroxyl groups and other parts of the molecule (1,7,12,13). In methanol, the OH is in an environment consisting of three identical hydrogen atoms, so that all three rotational isomers are identical and a single, narrow peak is obtained. In primary alcohols, the nearest neighbors of the OH are two hydrogens and one carbon, as in Figure 2A. One rotational isomer would have the alcoholic hydrogen between two hydrogens (*trans* or *anti* to the carbon atom) in the same type of environment as in methanol, while the other two rotational isomers (*gauche* to the carbon atom) would place the alcoholic hydrogen between a hydrogen atom and a carbon atom. This would be expected to lead to one peak at nearly the same frequency as methanol and another peak at a different frequency, as is observed in Figure 1A. The relative strengths of the two component peaks should reflect the populations of the different rotational isomers, which should in turn depend on the depth of the minima in the curve of potential energy versus angle of rotation about the C–O bond. Since the stronger component of the primary alcohol curves is the peak nearest to the methanol frequency, this suggests that the *anti* rotomer has the lower potential minimum and is more highly populated.

In secondary alcohols, the alcoholic hydrogen can find itself either between two carbons (resembling t-butanol) or between one carbon and one hydrogen (resembling the *gauche* rotomer of primary alcohols),

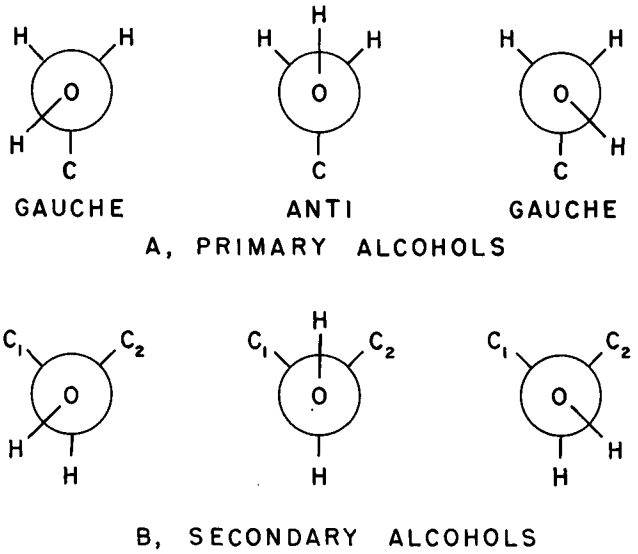


FIG. 2. Rotational isomers of (A) primary, and (B) secondary alcohols, at angles of potential minima with respect to rotation about the C–O single bond.

as in Figure 2B. This should lead to one component peak near the frequency of t-butanol and one peak near the low-frequency component of primary alcohols, as is observed in Figure 1B and the other methyl carbinols listed. The relative strengths of the components suggest that the lower potential minimum in secondary alcohols corresponds to the rotomer having the alcoholic hydrogen between a carbon atom and a hydrogen atom. Thus, as would be expected, increasing the steric interference between the alcoholic hydrogen and its nearest neighbors leads to a higher energy at the potential minimum and a lower population of the corresponding rotomer. Flynn, Werner, and Graham (6) have also noted the composite peaks of some of these alcohols, although our interpretation is different from theirs.

The more prominent shoulder of secondary alcohols having both chains longer than methyl (Fig. 1C) indicates a component peak having a lower frequency than t-butanol and a higher population than in the methyl carbinols. This means that, when both C_1 and C_2 of Figure 2B are chains longer than methyl, atoms beyond the nearest neighbors influence the energies of the rotomers. In this case, atoms beyond the nearest neighbors appear to exert a small attraction on the alcoholic hydrogen and to lower slightly the potential minimum of the less favored rotomer. Branched secondary alcohols would not necessarily follow the simple generalizations noted with these linear secondary alcohols, because the opportunities for interaction are more complex (7,14).

Unsaturated Alcohols. The allylic alcohols listed in Table I show two component peaks, but, unlike the saturated primary alcohols, the component farthest from methanol shows higher population. Fox and Martin (15) have suggested that benzyl alcohol contains two rotomers, one resembling aliphatic primary alcohols, and one permitting interaction between the OH and the benzene ring. The interaction is strong enough to make the latter rotomer the more highly populated one. Allyl alcohol has also been investigated, with similar results (4).

The homoallylic alcohols listed in Table I show an entirely different behavior from the allylic alcohols. Figure 3 shows the hydroxyl bands of two compounds of this type obtained from fats, methyl ricinoleate

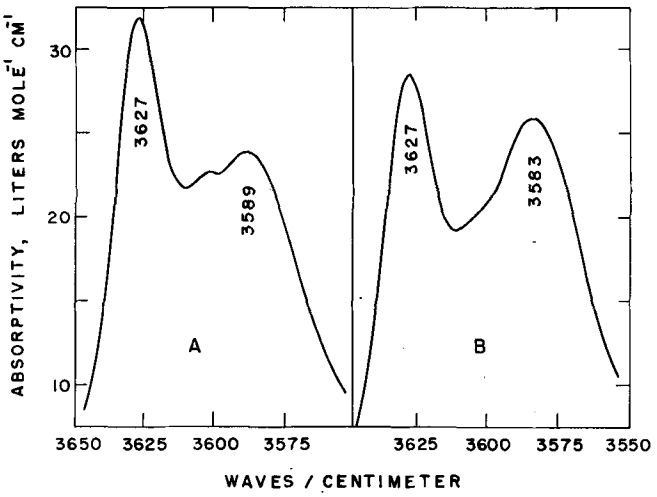


FIG. 3. Monomeric hydroxyl bands of (A) methyl ricinoleate, (B) methyl ricinelaidate, both in CCl_4.

and methyl ricinelaidate. The much greater shift in frequency can be attributed to intramolecular hydrogen bonding between the hydroxyl and the π-electrons of the double bond (4,5,16,17,18). Of the homoallylic alcohols of Table I, the eight compounds which do not contain steric interference with internal hydrogen bonding have frequency shifts in the range 36–52 cm^{-1}.

We have calculated by means of a digital computer (using a program to be described elsewhere) the relative positions in space of the atoms of a homoallylic alcohol for 108 different rotational isomers about the three single bonds between the double bond and hydroxyl. When standard values are used for bond lengths and angles, only twelve of these isomers have the hydroxyl group pointing at some part of the double-bond system. These twelve isomers have the oxygen atom between 2.80 and 3.20 Å from the center of the double bond, which is within the range of the weaker hydrogen bonds shown in the curves of Pimentel and McClellan (19) for bond distance versus frequency shift. Our $\Delta\nu$ values of 36 to 52 cm^{-1} would correspond to a point on the asymptotic part of their curves. On the other hand, computed locations of the atoms of an allylic alcohol show that none of its rotational isomers has the hydroxyl group pointing at the double bond. The question of whether the allylic type of interaction should be called hydrogen bonding we shall leave to a later publication on the quantitative treatment of these curves. The peaks of cinnamyl alcohol at 3538 cm^{-1} and geraniol at 3562 cm^{-1} are very weak and may be due to internal hydrogen bonding to their unsaturated groups beyond the allylic position.

In the homoallylic alcohols, if all 108 rotational isomers were equally probable, only one ninth of the molecules could be in the hydrogen-bonded state at any one time. However, the strengths of the peaks in Figure 3 show that a substantial fraction of the molecules is bonded. Thus the strength of the hydrogen bond must be sufficient to favor the twelve rotomers that permit internal bonding but not strong enough to keep the majority of the molecules in the bonded state. The third peak which appears between the two strong peaks on Figure 3, A and B, will be discussed in a later publication.

The fraction of the molecules in the hydrogen-bonded state is markedly affected by the angles in nearby parts of the molecule. Through the kindness of Richard T. Arnold (then of the Alfred P. Sloan Foundation) we have investigated homoallylic alcohols in which the OH and the double bond are attached to a ring, *trans* to each other. Compounds I, II, and III in Table I show the effect of ring size. A *trans* substituted 5-membered ring prevents the hydroxyl group from reaching the double bond. *Trans* orientation of the two groups on larger rings does not geometrically prohibit interaction. A 6-membered ring produces some rotational isomers in which the hydroxyl is so close to the double bond that hydrogen bonding stabilizes these rotomers almost to the exclusion of the other rotomers. A 7-membered ring behaves like an open chain, giving a percentage of bonded molecules qualitatively similar to that of the compounds of Figure 3. When both hydroxyl and double bond are immobilized in an unfavorable position by rings, no internal hydrogen bond is possible as shown by diosgenin, cholesterol, and cyclohex-3-en-1-ol in Table I. Schleyer et al. (4,5,20) have also shown the effect of other ring systems on internal hydrogen bonding of the homoallylic type.

Table I includes three acetylenic ring compounds obtained from Richard T. Arnold showing the same effect of bond angles on intramolecular hydrogen bonding. The angles of the *trans* 5-membered ring prevent the hydroxyl from reaching the triple bond. The 6-membered ring favors internal hydrogen bonding so that most, but not all, of the molecules are in the bonded state. The 7-membered ring behaves like an open chain, although the intensities of the peaks show that a smaller fraction of the molecules is in the bonded state than in 3-butyn-1-ol. Schleyer, et al. (4) have also investigated acetylenic alcohols.

Mid-Chain Hydroxyl Esters. Table I includes methyl 10-hydroxystearate and methyl 12-hydroxystearate among the secondary alcohols having two chains longer than methyl. The hydroxy acids from which these esters are derived have physical properties markedly different from one another, which have been attributed by O'Connor, et al. (21) to differences in hydrogen bonding in the solid state. They have also suggested that, in chloroform solution, the esters as well as the acids form intramolecular hydrogen bonds between the hydroxyl group and the distant ester (or acid) group.

In carbon tetrachloride at 0.001–0.1 molar, the main hydroxyl stretching band of these hydroxyesters is found to be indistinguishable in appearance from that of 9-octadecanol, with the same shape as Figure 1C. Methyl 10-hydroxystearate shows no visible evidence of hydrogen bonding; methyl 12-hydroxystearate shows a trace of a broad absorption around 3550 cm^{-1}. Molecular models reveal that a 12-hydroxyl group can approach the ester group more easily than a 10-hydroxyl group, due to methylene

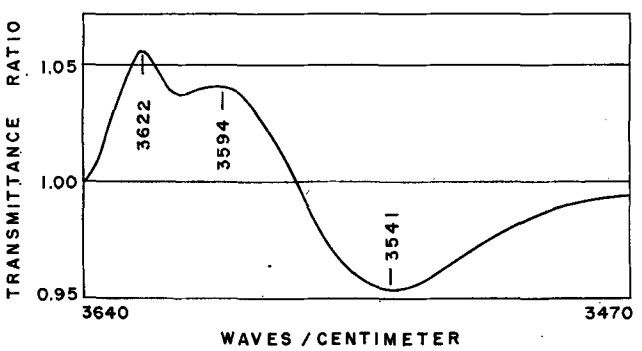


FIG. 4. Differential spectrum of methyl 12-hydroxystearate versus methyl 10-hydroxystearate, both at 0.01 molar in CCl_4.

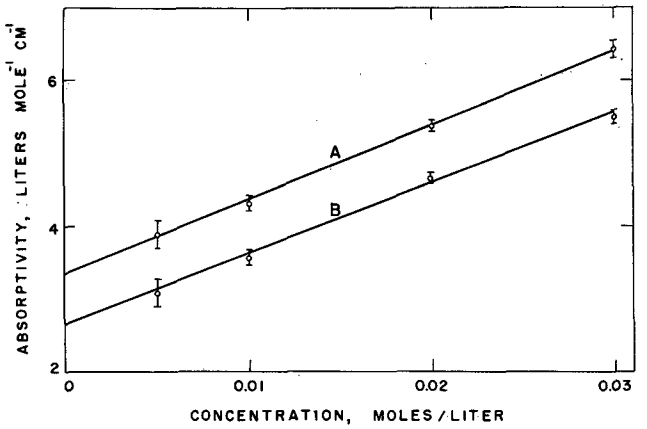


FIG. 5. Absorptivity at 3541 cm^{-1} versus concentration in CCl_4. (A) Methyl 12-hydroxystearate. (B) Methyl 10-hydroxystearate.

interactions similar to the medium-ring effect in cyclic compounds.

The IR-3 spectrophotometer is a single-beam instrument using a tape recorder to provide a reference spectrum. Since this permits the same light path and same absorption cell to be used for both blank and sample, the instrument, as modified in this laboratory, was capable of very sensitive differential spectrophotometry (22). Figure 4 shows a differential spectrum of methyl 12-hydroxystearate versus methyl 10-hydroxystearate, both at 0.01 molar in CCl_4. To check whether the 3541 cm^{-1} band could be due to intermolecular hydrogen bonding, measurements were made at several concentrations between 0.005 and 0.3 M. In interpreting spectra of substances capable of dimerization, it must be remembered that, in any mass-law equilibrium, there does not exist a concentration below which the proportion of dimer is exactly zero. The only reason that spectra can be observed that appear to be independent of concentration is that the concentration is taken sufficiently low that the effect of dimer is less than the experimental noise. It can be easily shown that the over-all absorptivity of an equilibrium mixture of monomer and dimer becomes a linear function of over-all concentration at low concentrations, with a slope that is not zero. Measurements which are made at concentrations where the slope is constant can then be extrapolated down through the experimental noise to obtain an intercept at zero concentration, as is common practice with electrochemistry, viscosity, light scattering, etc. Individual points were read from the curves of methyl 10- and 12-hydroxystearate in the range 3500–3600 cm^{-1} and were found to have absorptivities linear with concentration between 0.005 and 0.03 M. The absorptivities were therefore extrapolated by least squares to zero concentration at each wavenumber. Figure 5 illustrates the procedure for one wavenumber. The curve of absorptivity difference versus wavenumber at zero concentration shows a maximum at 3541 cm^{-1} similar to Figure 4, indicating that this peak must not be intermolecular.

Figure 4 could be interpreted to mean that a small fraction of the methyl 12-hydroxystearate is intramolecularly hydrogen bonded with an absorption band at 3541 cm^{-1}, at the expense of rotomers whose absorption bands would normally be at 3622 and 3594 cm^{-1}. However, the sensitivity of the differential method could also mean that we are merely seeing a trace of an impurity not detected by other methods. The most that can be done with the differential data is to place an upper limit of 1.5% on the fraction of the methyl 12-hydroxystearate molecules that could be in the intramolecularly hydrogen-bonded state in carbon tetrachloride. It does not appear that intramolecular factors could be responsible for the difference in chemical or physical properties of 10- and 12-hydroxyl derivatives of fats.

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Further Studies of Detergency Correlation

A. M. MANKOWICH, Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland

Abstract

The significance of the relationships of the linearity constants of a previously reported detergency-micellar solubilization function (1) to surfactant HLB (hydrophile-lipophile balance), boundary tensions, and soil dipole moment was extended, first, by demonstrating their existence in systems of four homologous surfactants with one soil or four classes of soil with one surfactant, and second, by showing in every case that they are probably physical rather than random because they contain fewer constants than the number of points (four) used in their derivation.

A study of a series of surfactant-soil systems consisting of a family of polyoxyethylated nonyl phenols and a family of saturated fatty acid soils (12–18 carbon) revealed linearity of the R-log (M/CMC) and surfactant HLB-log (M/CMC) functions for values of R (ethylene oxide mole ratio) between 15–50 and 20–100, respectively (M = surfactant concentration giving ca 100% removal of 16 and 18 carbon fatty acids, and CMC = critical micelle concentration). The validity of the semi-logarithmic functions was