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A Lamellar Liquid Crystal as an *in Situ* Surface Balance

I. The Conformation of 5- (and 6-)Carboxy-4-hexyl-2-cyclohexene-1-yl Octanoic Acid and Its Monosoap

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The interfacial conformation of a dicarboxylic acid, 5- (and 6-)carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid, and its monosodium soap was determined from the change of liquid crystal dimensions after introduction of the diacid compounds. The results showed that both functional groups of the monosoap form were present at the interface and that increased water content of the liquid crystal matrix had little effect on the conformation of the monosoap. On the other hand, the results indicated the conformation of the diacid as such to depend on the water content of the matrix. At low water content, the diacid form was in a conformation similar to that found for the monosoap. However, increasing the water content of the matrix resulted in a sharp decrease in the calculated partial molecular areas for the diacid, indicating an extended conformation for the diacid.

INTRODUCTION

The unique properties of difunctional surfactants have recently spurred interest in the synthesis of such compounds. Responding to this need, Westvaco Corporation in 1975 introduced a group of dicarboxylic acids known collectively as DIACID, Westvaco Co. (1). The principal dicarboxylic acid component is 5- (and 6-)carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Fig. 1A) which is formed by a Diels-Alder addition of acrylic acid to a naturally occurring tall oil. From this difunctional acid, a new class of amides, esters, and mono- and disoaps may be produced, all of which are surface active (2).

Soon after introduction of these dicarboxylic acid compounds, it was found that the monosodium salt (Fig. 1B) was an efficient hydrotrope, that is, when present in sufficient concentration, it significantly increased the solubility of poorly water soluble materials in water-surfactant solution. Friberg and Cox (3) demonstrated that the hydrotropic action of the disodium soap was to inhibit the formation

of a lamellar liquid crystalline phase at concentrations below the critical micellization concentration (CMC) of a surfactant when combined with a more hydrophobic amphiphile such as a long chain alcohol. The mechanism of action of the dicarboxylate soap paralleled that of common hydrotropes such as sodium xylene sulfonates. These function by extension of the region of the aqueous micellar phase as earlier demonstrated by Lawrence (4) and others (5). In all cases, disruption of the liquid crystal structure could be attributed to the bulky structure of hydrotropes as compared to normal, straight-chained amphiphiles. Quite simply, the presence of hydrotropes too greatly perturbed the orderly packing necessary for the stability of a liquid crystal. It is obvious, from even superficial observation of molecular models, that the combination of sodium xylene sulfonates and straight-chained amphiphiles of similar molecular weight does not lend itself readily to a regular lamellar packing and hence, the hydrotropic action could be understood intuitively.

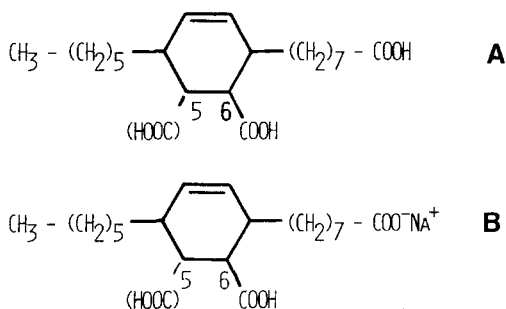


FIG. 1. The structure of the dicarboxylic acid (A) and its monosodium soap (B).

The mechanism of hydrotropic action for dicarboxylic acid compounds is not as directly perceived. In light of the mechanism found for traditional hydrotropes (4, 5), one may offer that the interfacial conformation of the dicarboxylic acid materials gives rise to their hydrotropic action. However, because of the large size and inherent flexibility of these compounds, their interfacial conformation cannot be known immediately. The question arises if the compounds are extended as a typical straight-chained amphiphile would be, with a single active group at the interface, or if both functional groups are at the interface giving rise to a "coiled" conformation for the molecule. The latter case implies that dicarboxylic acid compounds would be unusually bulky amphiphiles, and, as a result, should produce considerable disorder at an interface. If so, the hydrotropic action would follow directly.

In this context, it is interesting to discuss the hydrotropic action of dicarboxylic acid compounds on the basis of the association model of Israelachvili *et al.* (6). The model, which has recently been extended by Ninham and Mitchell (7) to explain the HLB concept, microemulsification, etc., considers the packing constraints imposed on association structures of different symmetries (spherical, cylindrical, planar, etc.). The underlying concept is that the ratio of amphiphile chain volume (v) to chain length (l_c) and cross-sectional area near the head group (a_0) defines a unitless quantity, the packing ratio, or

$$\frac{v}{l_c a_0} = \text{packing ratio.}$$

Importantly, the geometry of a particular structure fixes the values over which the packing ratio may range when the structure exists. For example, it can be shown that normal micelles will be preferred when the packing ratio is less than or equal to $1/3$, assuming no voids are present in the micelles. With such an approach, the predominance of one form of association structure becomes understandable in terms of molecular structure.

Packing ratio arguments may be applied to the extension of the aqueous micellar phase below the CMC when dicarboxylate soap is combined with a normal surfactant and long chain alcohol. If one compares an ionizable surfactant molecule and an alcohol molecule of similar chain length, the alcohol will display a smaller a_0 in terms of the packing ratio. Thus the tendency of the composite packing ratio will be to increase when alcohol is added to an aqueous solution of the surfactant. As the packing ratio increases with added alcohol, new structures corresponding to higher packing ratio values are favored, and one observes that a lamellar liquid crystalline phase and an inverted phase appear in equilibrium with the aqueous phase after addition of alcohol (see Fig. 2B, Ref. 3). However, the effect of added alcohol may be delayed to higher alcohol contents if an opposing influence on the composite packing ratio is present. The presence of a dicarboxylate soap should have the proper effect. For a molecule of this type, the interfacial area will be disproportionately large relative to chain volume since the two functional groups cannot move independently at the interface. As such, addition of the dicarboxylate soap will suppress the packing ratio and nullify the effect of added alcohol. In other words, the aqueous micellar region will be extended to higher alcohol contents because the composite packing ratio remains small through the influence of the disoap.

For a dicarboxylate soap, it is logical to assume that both anionic groups will reside

at the interface and that the dianion will be in a nonlinear conformation. Consequently, a capacity for hydrotropic action is implied naturally by packing ratio arguments. On the other hand, the conformation of the related monosoap or dicarboxylic acid, which are hydrotropically active as well, is not certain as discussed earlier. Thus it is necessary to ascertain their interfacial conformation before suggesting a direct relationship between structure and hydrotropic action. The determination of their conformation is the principal problem which has been addressed here.

Recently, the problem of the conformation of the parent dicarboxylic acid (DIACID, Westvaco Co.) has been studied by Pethica *et al.* (8) who conducted film balance investigations on monolayers supported by an aqueous electrolyte substrate at pH 2. They concluded that both carboxylic acid groups were in contact with the aqueous solution even at the high pressures shortly preceding film rupture. At low pressures, the large area per molecule obtained justified their conclusion that the two acid functions of the dicarboxylic acid were widely separated with the intervening carbon chain closely approaching the solution surface. The air/water surface balance technique provides excellent information about the conformation of amphiphiles at an interface and a great number of outstanding scientific contributions have been obtained by the use of it (9-11). However, the inherent limitations are obvious; the amphiphilic molecules either must be extremely insoluble in water, *per se*, or rendered so by addition of electrolyte to the aqueous subphase.

To circumvent these limitations, we have used a new method to ascertain the conformation of dicarboxylic acid compounds in an environment where the conformation of both water-soluble and water-insoluble species could be directly compared. The method involves incorporating the compounds into a host liquid crystal and determining any changes in liquid crystal dimensions by low-angle X-ray diffraction (12).

Since the changes that occur are presumably

indicative of the physical characteristics of the incorporated material, one can establish the partial molar area (PMA) for the subject material, and then, as is common in film balance determinations, use molecular models to arrive at a conformation consistent with the obtained area.

The method was also a more direct bearing on the problem at hand, the hydrotropic action of the dicarboxylic acid compounds. Since our primary interest was relating the conformation of such compounds to destabilization of lamellar phases, establishing their conformation in a lamellar phase provided the most direct evidence for explaining their hydrotropic action.

EXPERIMENTAL

Commercially obtained compounds. The surfactants used were Aldrich 1-octanesulfonic acid, sodium salt monohydrate 98%, sodium octanoate synthesized from Aldrich Gold Label 99.5+% octanoic acid, and sodium oleate obtained from ICN Pharmaceuticals. (Syntheses are described below.) DIACID was obtained from Westvaco Corporation in commercial grade, corresponding to approximately 80% by weight dicarboxylic acid material. The major constituent of the remaining 20% (by weight) was C-18 fatty acid. From this material, the monosodium soap was produced in a manner similar to sodium octanoate. Octanoic acid as a cosurfactant was the same as that used for synthesis of sodium octanoate. The cosurfactant 1-octanol was Fisher Certified quality. No commercially obtained compounds underwent further purification. All water was doubly distilled.

Synthesis of sodium octanoate and the monosodium soap of the dicarboxylic acid. Sodium octanoate and the monosodium soap of the dicarboxylic acid were synthesized by nonaqueous methods. Octanoic acid or the dicarboxylic acid was first dissolved in dry ethanol. Sodium ethoxide was added in stoichiometric amount and the solution was refluxed for 1 hr. As the monosoap was some-

what soluble in ethanol, acetone was added to the refluxed solution to aid the precipitation. The soaps produced were washed with ethanol (and acetone) and dried over phosphorous pentoxide and under vacuum for several days. Infrared spectra of the monosoap confirmed that the monosoap rather than the disoap was produced by the titration. The spectra showed strong infrared absorption at 1710 and 1550 cm^{-1} indicating the presence of both carboxylic and carboxylate groupings. According to Mino *et al.* (2), the pK_a of the primary acid group of the dicarboxylic acid has the smaller value. Therefore, the structure of the monosoap was taken as shown in Fig. 1B.

Systems investigated. The host liquid crystal used for the monosoap studies was formed from sodium octylsulfonate, octanol, and water (13). The relatively short chain length of the surfactant and cosurfactant was necessary to prevent crystal packing forces from influencing the monosoap conformation. Furthermore, the low pK_a of the sulfonate surfactant lessened the possibility of proton transfer from the acid group of the monosoap to the principal surfactant.

Three systems involving the host matrix were compared to establish the conformation of the monosoap; the host matrix with no added compounds, the host matrix with monosoap, and the host matrix with sodium oleate. The moles of surfactant in the latter systems were taken as moles of sodium octylsulfonate plus moles of monosoap or sodium oleate. Throughout the investigations with monosoap or sodium oleate, the molar ratio of sodium octylsulfonate to monosoap or sodium oleate was maintained at 2:1. Higher monosoap concentrations rendered the host matrix unstable. The three systems were studied at normally 3 to 5 cosurfactant (Cos) to surfactant (Sur) ratios while varying water content.

The conformation of the dicarboxylic acid was studied similarly but in an alternate host matrix since the acid could not be incorporated in the surfactant/alcohol/water matrix with retained stability. The host system was now comprised of sodium octanoate, octanoic

acid, and water. Investigations were made at three Cos/Sur ratios with a 3:1 molar ratio of octanoic acid to dicarboxylic acid being maintained. Furthermore, only two systems were compared to determine the conformation of the dicarboxylic acid. They were the host matrix and the matrix plus dicarboxylic acid.

Determination of phase boundaries. As a prerequisite to the X-ray investigations, the boundaries for the lamellar regions of the systems studied were determined by titration. Samples were prepared by weighing components into 10-ml culture tubes with screw caps. After allowing them to reach equilibrium at 25°C, visual inspection of the samples in a microscope with polarized light provided the single-phase limits of the lamellar regions. The samples for X-ray determinations were prepared identically.

RESULTS

Liquid Crystal Dimensions

For all liquid crystal systems investigated by low-angle X-ray diffraction there was a linear correlation of interlayer spacing, d , (Fig. 2) with the moles of water per functional group (w./f.g.) at a fixed Cos/Sur ratio. The dicarboxylic acid and its monosoap were counted as having two functional groups in the evaluations. The slope of the plots indicated the inverse tendency for water to intercalate the amphiphile layers of the liquid crystal, e.g., a larger slope implied a smaller tendency for

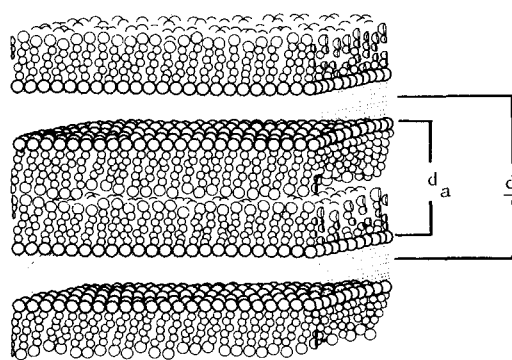


FIG. 2. The dimensions d and d_a in a lamellar liquid crystal.

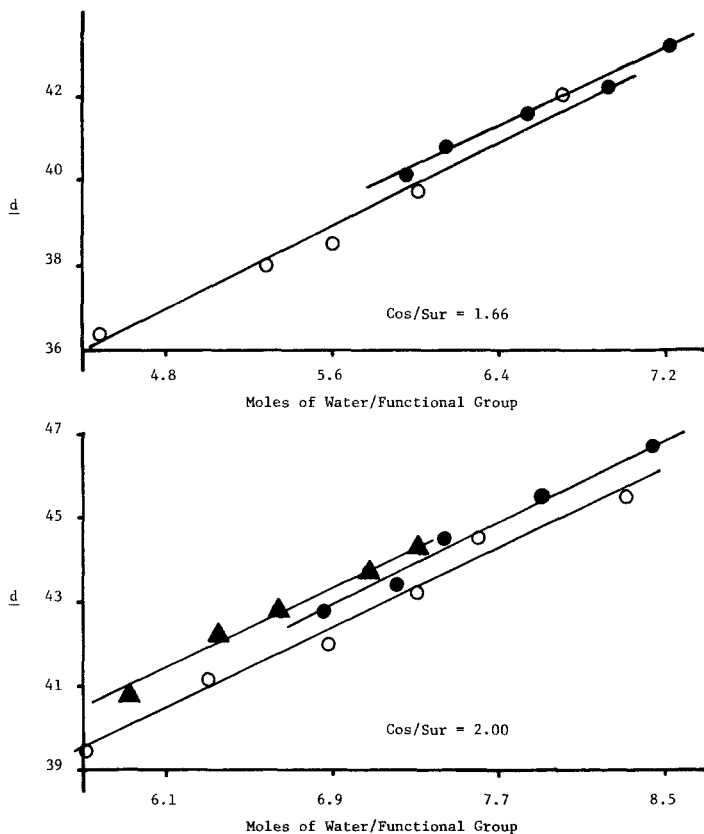


FIG. 3. The interlayer spacing, d , in the lamellar liquid crystal of water, sodium octyl sulfonate and octanol (host, O) and with partial substitution of the sulfonate with sodium oleate (\blacktriangle) or with the monosoap of the dicarboxylic acid (\bullet) for different cosurfactant/surfactant (Cos/Sur) ratios. d is given in Å.

intercalation. While the intercept is usually taken as d_a , the amphiphile layer thickness (Fig. 2), this interpretation seemed unsuitable for our findings. While it is not easily seen in Figs. 3 and 4, each set of curves, e.g., the host matrix at several Cos/Sur ratios, the host plus monosoap at the same ratios, etc., intersected at approximately 4, or in a few cases, 5 mole of w./f.g. which suggested that linear behavior did not begin until these water concentrations were reached. Furthermore, since no system actually existed below 4 mole of w./f.g., extrapolation to a value of d_a was of questionable validity.

The systems used to determine the monosoap conformation were studied at molar ra-

tios of primary octanol to sodium octylsulfonate plus added surfactants (if any) of 1.11:1, 1.25:1, 1.42:1, 1.66:1, and 2.00:1. The X-ray results for these systems are shown graphically as plots of interlayer spacing d versus moles of w./f.g. in Fig. 3. The least-squares slope and intercept for each plot appear in Table I along with a correlation coefficient for each data set.

The two systems used for the study of the dicarboxylic acid conformation were investigated at three molar ratios of octanoic acid plus dicarboxylic acid (if any) to sodium octanoate. The ratios were 0.69:1, 0.82:1, and 0.96:1. The results of plotting d versus moles of w./f.g. are shown in Fig. 4. The least-squares analysis of the data appears in Table I.

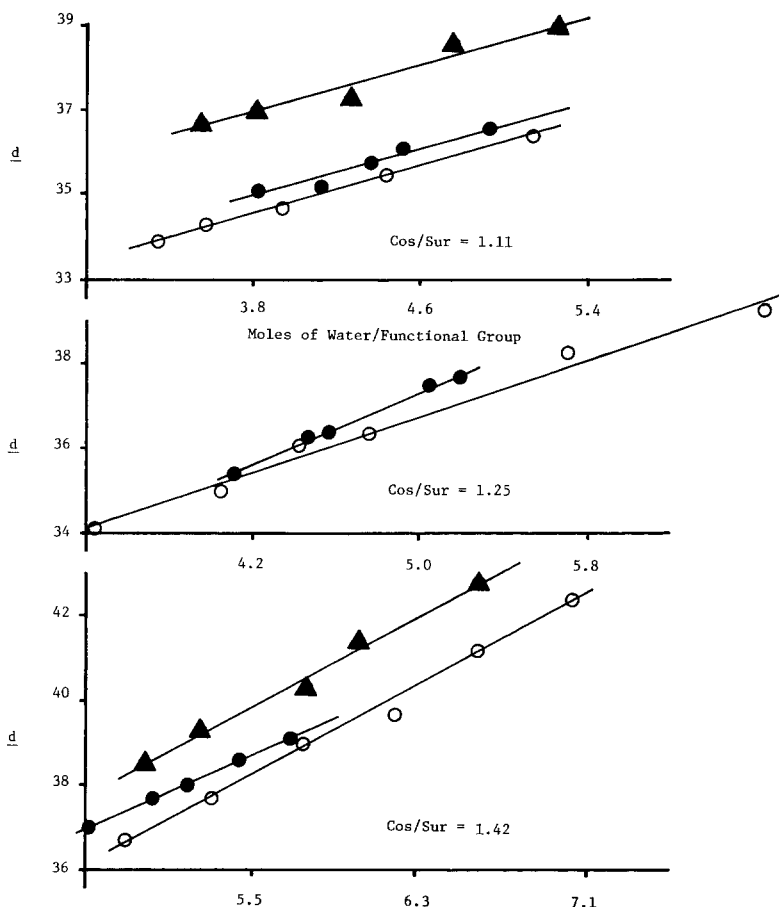


FIG. 3—Continued.

Calculation of the Mean Area per Amphiphile

For lamellar phases the mean area per amphiphile at the interface (S) is given (14) as

$$\bar{S} = 2\bar{V}_a/d_a \quad [1]$$

where \bar{V}_a is the average volume per amphiphile and d_a is the thickness of the amphiphile layer. As explained above, d_a is normally an extrapolated value taken from X-ray data. \bar{V}_a is estimated from the pure component densities and the known molar ratios used for combining components.

Since d_a extrapolated from our data showed a wide variance depending on the Cos/Sur ratio, we have used Eq. [1] in a modified form.

As is easily realized, Eq. [1] can be derived from simple arguments based on the geometry of lamellar phases. Using similar arguments, Eq. [1] may be written as

$$\bar{S} = 2\bar{V}_a^*/d \quad [2]$$

where \bar{V}_a^* equals \bar{V}_a plus $(MW_{H_2O}/1.0 \text{ g/cm}^3 \times \text{moles of water/functional group})$ and d is the measured interlayer spacing. \bar{S} will now be the molecular area of the amphiphilic compound with adhering water molecules. Since \bar{V}_a^* and d are linear functions of the moles of water per functional group at any fixed Cos/Sur ratio, \bar{S} may be calculated as a function of the water content of the matrix. Comparative plots of \bar{S} for the sodium octylsulfonate

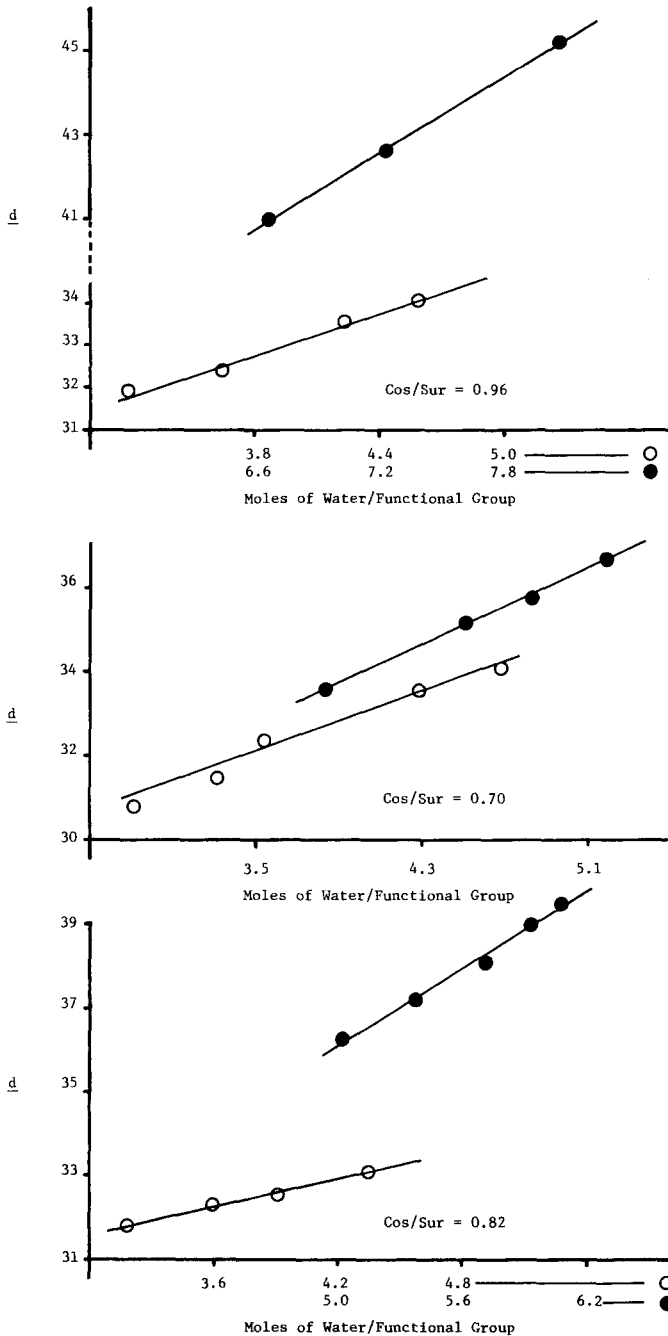


FIG. 4. The interlayer spacing, d , in the lamellar liquid crystal of water, sodium octanoate and octanoic acid (host, O) and with partial substitution of the acid with the dicarboxylic acid (●) for different cosurfactant/surfactant (Cos/Sur) ratios. d is given in Å.

host matrix alone, with monosoap, and with sodium oleate are given in Fig. 5. Shown in Fig. 6 are similar plots for the sodium octa-

noate host matrix with and without the dicarboxylic acid. While most experimental systems did not exist over the entire w./f.g. range

TABLE I
Regression Analysis of Curves in Figs. 3 and 4

System ^a	Cos/Sur	Slope	Intercept	Correlation coefficient
1	1.11	1.39	29.3	0.999
	1.25	1.76	28.1	0.996
	1.42	2.65	23.7	0.997
	1.66	2.50	24.9	0.988
	2.00	2.34	26.2	0.991
2	1.11	1.47	29.4	0.976
	1.25	2.14	26.6	0.998
	1.42	2.16	26.8	0.999
	1.66	2.27	26.7	0.992
	2.00	2.53	25.4	0.993
3	1.11	1.43	31.6	0.993
	1.42	2.67	25.2	0.995
	2.00	2.16	28.5	0.999
4	0.70	1.90	25.4	0.989
	0.84	1.08	28.4	0.993
	0.97	1.65	26.6	0.995
5	0.70	2.28	24.9	0.999
	0.83	3.04	21.0	0.995
	0.96	3.03	20.8	0.999

^a The systems are as follows: (1) sodium octylsulfonate, octanol, and water; (2) sodium octylsulfonate, monosoap, octanol, and water; (3) sodium octylsulfonate, sodium oleate, octanol, and water; (4) sodium octanoate, octanoic acid, and water; (5) sodium octanoate, octanoic acid, diacid, and water.

shown, \bar{S} was projected to follow the trends in the area per amphiphile as water content changed.

DISCUSSION

The discussion will interpret the interlayer spacings for the dicarboxylic acid and its monosoap into molecular conformations of the two molecules at the interface. These sections will be followed by a section reflecting on the importance of the findings for the hydrotropic action of the compounds.

The Monosoap

The curves in Figs. 3 and 5 clearly show that incorporation of the monosoap into a liquid matrix left the interlayer spacing vir-

tually unchanged but significantly increased the mean area per amphiphile (\bar{S}) at the w./f.g. ratios shown. In addition, it is apparent from Fig. 3 that the monosoap did not alter the tendency for water intercalation since for the systems with and without monosoap, the respective slopes of the curves for each Cos/Sur ratio were comparable. One immediately recognizes that the monosoap did not enter the matrix as a linear molecule; if it had done so, there would have been only minor changes in \bar{S} . This is illustrated by the values for sodium oleate, a monofunctional surfactant of similar molecular weight as the monosoap, which produced little change in mean area per amphiphile, but largely increased the interlayer spacing. In only one case did the matrix containing sodium oleate act anomalously when compared to the host matrix. At a Cos/Sur ratio of 1.42:1, the matrix with sodium oleate showed a sharp dependence on water concentration whereas the host matrix did not. However, over the range of existence of the sodium oleate plus host system (4–6.5 mole w./f.g.), the difference in \bar{S} for the two systems was less than $1 \text{ \AA}^2/\text{amphiphile}$. While the precise behavior of the sodium oleate remains unknown, a comparison of its effects and that of the monosoap on liquid crystal dimensions revealed that the monosoap did not act like a monofunctional surfactant of similar molecular weight.

Concerning the calculation of the partial molar area (PMA) for the monosoap it is important to note that the difference ($\Delta\bar{S}$) between two curves at fixed water content and Cos/Sur ratio in Fig. 5 is a combination of an increase in area caused by addition of monosoap and a decrease in area caused by addition of cosurfactant to the host matrix. This is true since monosoap was not added alone but with a corresponding amount of cosurfactant to maintain a certain Cos/Sur ratio. (Presumably, the cosurfactant at low water concentration had a smaller PMA than either the monosoap or the principal surfactant.) One manner of obtaining the PMA of the monosoap was to estimate first the inter-

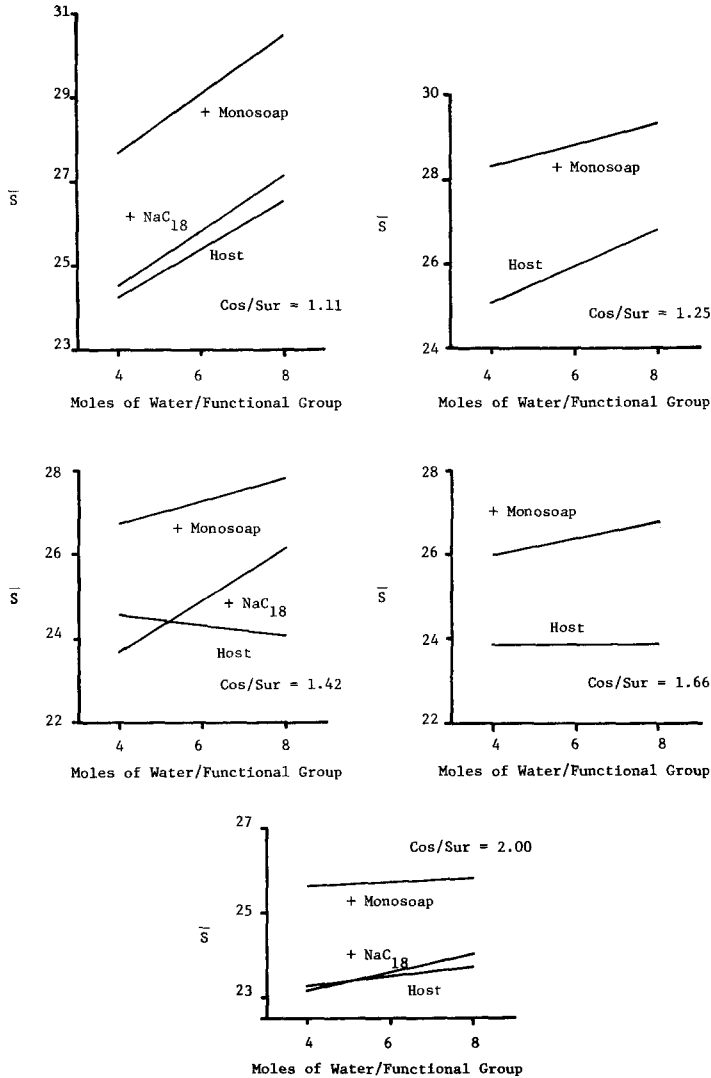


FIG. 5. Molecular areas of the polar groups in the systems in Fig. 3. \bar{S} is given in Å².

facial areas of the SOS and octanol at constant water content. As all systems existed in the vicinity of 5 mole w./f.g., this value seemed an appropriate fixed water content at which to make comparisons. For the Cos/Sur ratios investigated and at 5 mole w./f.g., the value of \bar{S} for the host matrix first increased and then decreased monotonically with increasing Cos/Sur ratio. The latter trend was expected since the liquid crystal was being "diluted" with alcohol. Extrapolating \bar{S} versus X_{Cos} (mole

fraction counted on amphiphiles only) for the highest alcohol contents produced a PMA_{SOS} of 33.2 Å²/molecule at zero mole fraction cosurfactant. At $X_{\text{Cos}} = 1$, the $\text{PMA}_{\text{octanol}}$ appeared as 18.5 Å²/molecule. Assuming PMA values were a function of water content only and using the simple relationship,

$$X_{\text{monosoap}} \cdot \text{PMA}_{\text{monosoap}} + X_{\text{octanol}} \times \text{PMA}_{\text{octanol}} + X_{\text{SOS}} \cdot \text{PMA}_{\text{SOS}} = \bar{S}$$

produced the following $\text{PMA}_{\text{monosoap}}$ values:

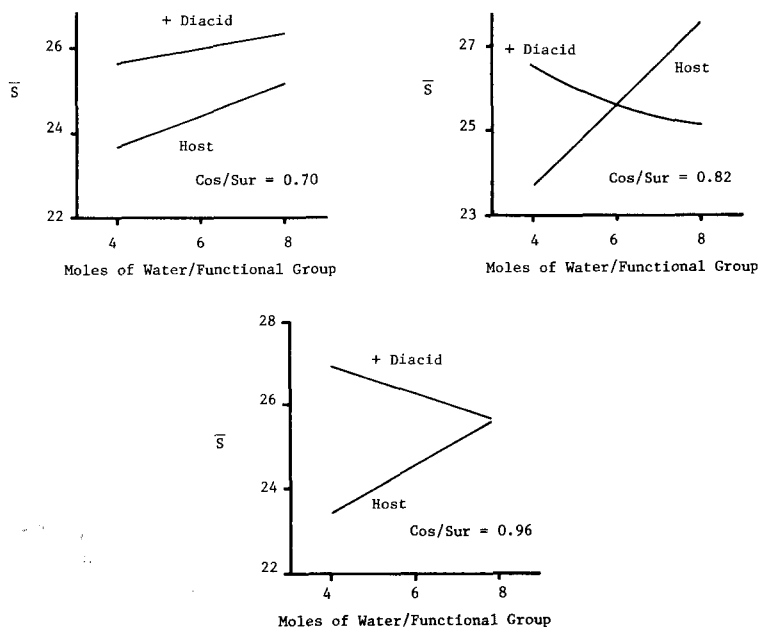


FIG. 6. Molecular areas of the polar groups in the systems in Fig. 4. \bar{S} is given in \AA^2 .

Cos/Sur	$\text{PMA}_{\text{monosoap}} (\text{\AA}^2)$
1.11	51.8
1.25	57.3
1.44	50.8
1.66	51.4
2.00	54.0
	<u>PMA = 53.1</u>

A second method of estimating $\text{PMA}_{\text{monosoap}}$ gave essentially the same result. An illustration follows. At a 1.66:1 Cos/Sur ratio, the \bar{S} of the host matrix was $23.9 \text{ \AA}^2/\text{amphiphile}$. If 0.5 mole of monosoap were added to the system, the Cos/Sur (total) ratio became 1.11:1 and the resulting \bar{S} was $28.4 \text{ \AA}^2/\text{amphiphile}$. Since this difference in mean area for the two systems reflected only the effects of incorporating the monosoap, simple calculations could show that the $\text{PMA}_{\text{monosoap}}$ was approximately $52 \text{ \AA}^2/\text{molecule}$. It should be noted that this was 48% larger than the $35 \text{ \AA}^2/\text{molecule}$ reported for monocarboxylate soaps at similar water contents (13). Using the PMA obtained for the monosoap, a study of molecular models predicted a conformation for

the molecule as shown in Fig. 7. In essence, both functional groups lie at the interface. Molecular orbital calculations have shown that this arrangement is particularly stable if the free acid group engages in hydrogen bonding with one carboxylate oxygen and the carbonyl oxygen of the free acid forms a ligand to the sodium ion (15).

The Dicarboxylic Acid

In some cases, the behavior of the dicarboxylic acid was markedly different from that of the monosoap. From Fig. 6 it is clear that at the higher Cos/Sur ratios the dicarboxylic acid displayed large PMA values only at low water concentrations of the matrix. Only at the lowest Cos/Sur ratio (0.70) did the dicarboxylic acid behave similarly to the monosoap, that is, the trend in \bar{S} was to gradually increase with increasing water content.

Estimating the PMA of the dicarboxylic acid was best accomplished by comparing (again at 5 mole of w./f.g.) the change in area for adding the dicarboxylic acid to the host matrix. For the matrix containing no dicarboxylic acid

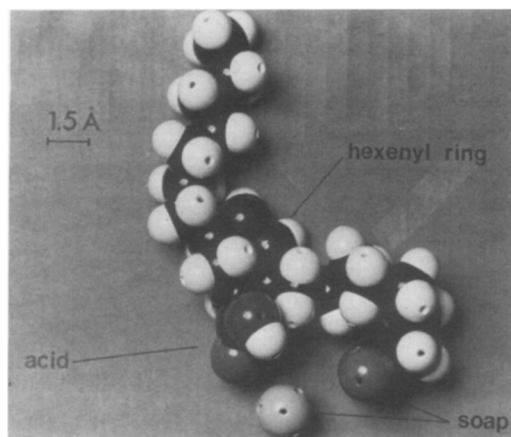


FIG. 7. The interfacial conformation of the monosoap of the dicarboxylic acid.

and at a Cos/Sur ratio of 0.70:1, the \bar{S} value was $24.1 \text{ \AA}^2/\text{amphiphile}$. Adding 0.23 mole of the acid increased the Cos(total)/Sur ratio to 0.93:1 and the determined \bar{S} was about $26.5 \text{ \AA}^2/\text{amphiphile}$. Calculation gave the PMA of the dicarboxylic acid to be approximately $44 \text{ \AA}^2/\text{molecule}$, a smaller value than that found for the monosoap at 5 mole of w./f.g. For a PMA of this value, molecular models showed that the dicarboxylic acid must assume a conformation resembling that shown in Fig. 8 with one acid group at the interface and the second acid group slightly removed from the interface. However, the strong negative dependence of \bar{S} for the matrix plus dicarboxylic acid indicated that the molecule likely become more extended as water content increased. In all probability, the acid group of the ring (Fig. 1A) moved further from the interface, in a sense "uncoiling" the diacidic molecule. Such a change in conformation would explain the relatively large slopes found for d versus moles of w./f.g. for the matrix containing the dicarboxylic acid at Cos/Sur ratios of 0.82:1 and 0.96:1. As water content increases, the part of the water located between the layers contributes to an increase in the interlayer spacing. The increase of interlayer distance with increased water content for the above-mentioned Cos/Sur ratios is greater than for the case with all the added water

located between the layers. It appears reasonable to assume the addition of water to lead to a more extended conformation for the dicarboxylic acid.

Hydrotropic Action of the Dicarboxylic Acid and Its Monosoap

The results conform with the hydrotropic action of the monosoap. The "coiled" conformation according to Fig. 7 occupies a larger area in the liquid crystalline matrix and visual observation indicates the form of this molecule does not readily lend itself to the ordered packing in a lamellar liquid crystal. This conclusion is also supported by the fact that the presence of the hydrotrope leads to a significant shrinkage of the liquid crystalline region.

With the additional evidence earlier presented (3) it may be concluded that the monosoap of the dicarboxylic acid functions as a hydrotrope by perturbing the order in a liquid crystalline phase.

On the other hand, the acid form of the molecule does not show hydrotropic action to a comparable degree. In accordance with this fact, the present results indicate the dicarboxylic acid as such does not interact with the ordered lamellar phase. In the presence of a straight chain carboxylic acid it could be introduced into the structure, but the propensity

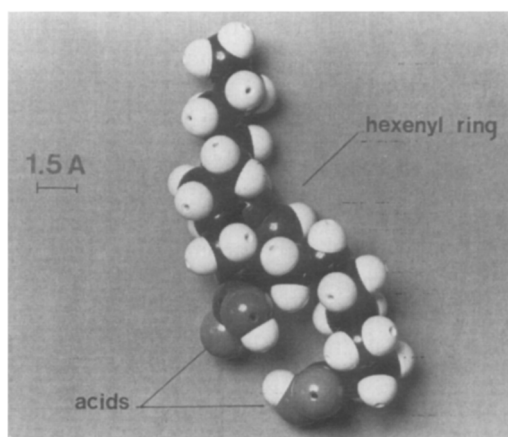


FIG. 8. The interfacial conformation of the dicarboxylic acid in acid form.

of its conformation toward a more elongated structure with increased water content reveals a feature that would alleviate its hydrotropic action.

The reason for the acid form being soluble in the soap/carboxylic acid amphiphile combination but not in a sulfonate/alcohol pair at corresponding pH value is an interesting structural problem to be clarified. It was not considered an appropriate part of the present investigation. Conjectural structures involving hydrogen bonded pairs of the dicarboxylic acid with an elongated form are a possibility, but a closer examination of the implication will be deferred until further experimental evidence is at hand.

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