

Volumetric Properties of the Components in the Lamellar Phase of the System Water/Sodium N-Octanoate/N-Decanol/N-Octane at 298 K

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The density and X-ray Bragg spacing were determined for a large number of samples in the ternary (and quaternary) lamellar liquid crystalline phase of water/sodium n-octanoate/n-decanol (/n-octane) at 298 K. The features observed are discussed in terms of changes in the hydrocarbon bilayer of the lamellae, the area available for the carboxylate and the hydroxyl groups and the partial molar volumes of the components. The water-rich part was characterized by a one-dimensional swelling of the aqueous layer leaving the amphiphilic layer to a large extent unaffected. The one-dimensional swelling is made possible by the high charge density at the interface and a partial dissociation of counterions. Since the surfactant had a tendency to partly dissolve into the aqueous layer, the rôle of the water-insoluble decanol was to maintain a sufficient lateral cohesion of the amphiphile bilayer. The properties of the water-poor part were dominated by the primary hydration of the polar groups. However, it is suggested that the interaction between the amphiphilic chains contributed significantly to the local phase structure. The addition of 4 % by wt. octane caused the part of the lamellar phase salient-rich in both water and decanol to separate. The main effect of octane when solubilized in the hydrocarbon bilayer was to produce a significant disturbance in the packing efficiency of the amphiphile chains.

In dealing with model systems of amphiphiles (lipids, surfactants, cosurfactants) it is essential to have a knowledge of the phase equilibria and phase structures occurring at different composition ranges of the system. Detailed phase diagrams have been determined for several amphiphile systems and it has been shown that the number of different phases may be quite large.^{1–3} The three-component system chosen for this study, sodium n-octanoate/n-decanol/water, is widely accepted as a reference system for the surfactant-cosurfactant interaction giving rise to the different phases indicated in Fig. 1.

In the present study, which is the third part of investigations of the volumetric properties of the liquid crystalline phases in a number of model

systems,^{4,5} we focused our interest on the behaviour of the lamellar phase denoted D in Fig. 1. These investigations may be considered as a complement to the very thorough structural analysis made by Fontell et al. of the liquid crystalline phases present in this system at 293 K.⁶ Previously, we have reported a similar volumetric analysis of the lamellar phase of the system sodium n-octanoate/n-pentanol/water.^{7,8} The detailed molecular arrangement of the D phase is essentially of a sandwich type (inset, Fig. 1) consisting of successive aqueous sheets and amphiphile bilayers. It was therefore of interest to try to separately influence the properties of the layers. In this study, we first diluted the aqueous layer with water. Secondly, we changed the charge density of the polar interface by adding water-insoluble cosurfactant (decanol). Finally, we solubilized some liquid octane into the lamel-

Dedicated to Professor Per Ekwall on his 90th birthday.

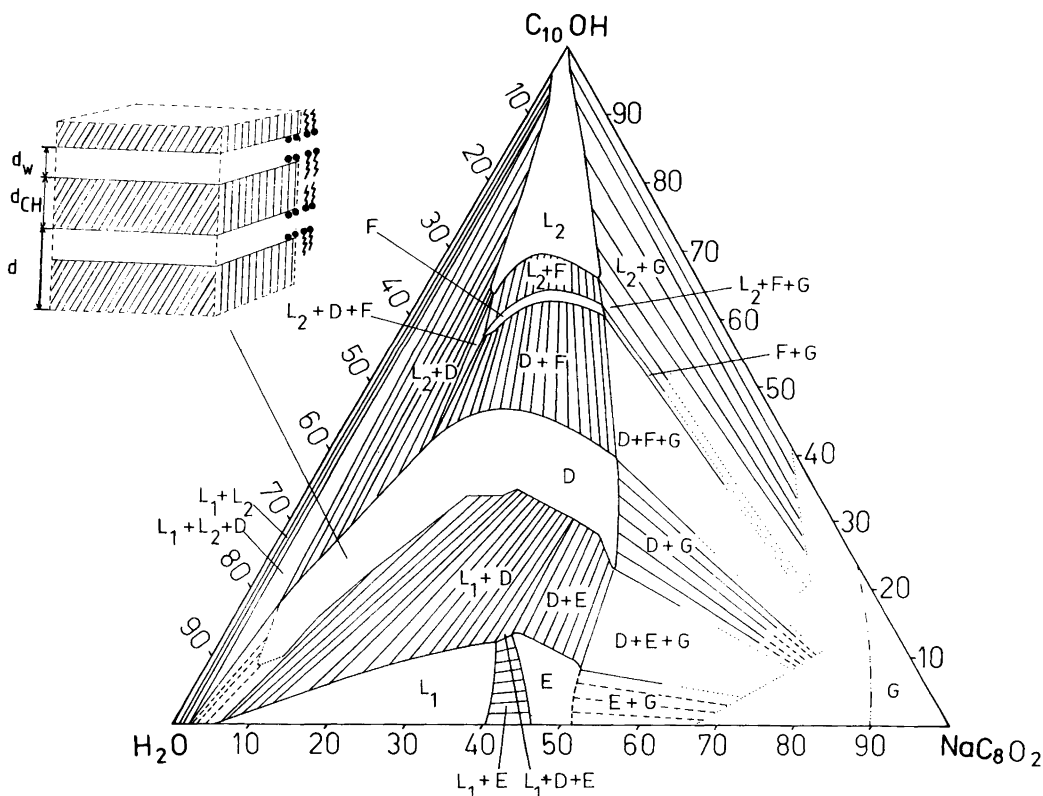


Fig. 1. The phase diagram of the system water/sodium n-octanoate/n-decanol. The composition range of the thermodynamically stable aqueous (L_1), hexagonal (E), lamellar (D), inverted hexagonal (F), and the decanolic (L_2) phases at 293 K are given in weight percent. The bilayer structure of the liquid crystalline lamellar phase as well as the subdivision into a water interface and a hydrocarbon sheet are also indicated.

lar phase in order to influence the chain packing of the amphiphiles.

Experimental

Chemicals. N-Decanol ($C_{10}OH$) (Fluka AG, *puriss.*) and n-Octane (C_8) (Ega-Chemie, *zur analyse*, 99%) were used without further purification. Sodium n-octanoate (NaC_8O_2) was prepared from octanoic acid (Fluka AG, *puriss.*) by neutralization with sodium hydroxide (Merck AG, 1N Titrisol). The salt was then washed several times in ethanol in order to remove residual acid. The molar mass was checked by titration with perchloric acid in glacial acetic acid using crystal violet as an indicator. The molar mass obtained differed less than 0.5% from the theoretical

value. The water was doubly distilled and ion exchanged immediately before use.

Instrumentation. The X-ray diffraction measurements were performed at 298 K using a Rigaku-Denki Low-Angle camera attached to a Philips X-ray diffraction generator connected with an AEG-Telefunken F50/31 X-ray tube. The $Cu K_{\alpha}$ line scattering was monitored with a Wallac SCDA-15 (NaI(Tl) crystal) scintillation detector connected to a Wallac Decem Series AS-12 pulse height analyser and a Wallac SC-32 scaler unit. The densities were measured at 298.15 K using an Anton-Paar DMA 60 densitometer equipped with an external measuring cell DMA 601. The density determinations involved measurements of the period ($1/f$) of oscillations, τ , of a vibrating U-shaped sample tube filled with the solution be-

Table 1. the coefficients and the F values obtained by linear regression of the polynomials given below the table to the molar volume of the ternary and quaternary lamellar liquid crystalline samples of the system water/sodium n-octanoate/n-decanol (/n-octane). For details of the program consult Ref. 11.

Syst.	Obs.	B_0	B_1/F_1	B_2/F_2	B_3/F_3	B_4/F_4	B_5/F_5	B_6/F_6	B_7/F_7	B_8/F_8	B_9/F_9
ter	79	17.981	— —	— —	— —	— —	— —	— —	172.64 16000	— —	— —
quat	116	-254.65	-82.594 4.26	828.58 66.9	-467.61 27.1	2737.7 6.72	-37772 18.6	62498 18.4	10270 29.0	-57469 23.2	87525 22.0

$B_i/F_i = B_i$ should be read from the upper line, F_i should be read from the lower line.

"ter" refers to the system water (1) – sodium octanoate (2) – decanol (3) and the mathematical model used to describe the system was $V_m = B_0 + B_7x_3 + B_{10}x_1x_2 + B_{14}x_1^2x_2^2$

"quat" refers to the system water (1) – sodium octanoate (2) – decanol (3) – octane (4) and the mathematical model used to describe the system was $V_m = B_0 + B_1x_2 + B_2x_2^2 + B_3x_3^2 + B_4x_3 + B_5x_3^2 + B_6x_3^3 + B_7x_4 + B_7x_4 + B_8x_4^2 + B_9x_4^3 + B_{10}x_2x_3 + B_{11}x_2x_4 + B_{12}x_3x_4 + B_{13}x_2x_3x_4 + B_{14}x_2^2x_3^2 + B_{15}x_2^2x_4^2 + B_{16}x_3^2x_4^2 + B_{17}x_2^2x_3^2x_4^2$

B_{10}/F_{10}	B_{11}/F_{11}	B_{12}/F_{12}	B_{13}/F_{13}	B_{14}/F_{14}	B_{15}/F_{15}	B_{16}/F_{16}	B_{17}/F_{17}	F_{tot}	FKRIT	$F^2(\%)$	DF	S_R
130.26 664	— —	— —	— —	561.85 186	— —	— —	— —	133000	3.97	99.98	75	0.1374
-2504.7 6.12	-9962.5 29.5	54732 17.4	-63300 18.4	36252 19.8	48885 22.8	-270194 15.0	378701 10.3	15300	3.95	99.96	98	0.2095

ing investigated. Assuming that the mass performs undamped oscillations with the elastic and the dynamic forces being in equilibrium, the density, ρ , is given by,

$$\rho = A (\tau^2 - B) \quad (1)$$

where A and B are constants determined by calibration of the densitometer against water and dry air for which the densities are known at 298.15 K and 101.3 kPa.

The Bragg spacings are accurate within about 1 %. The estimated accuracy of the densities of the liquid crystalline samples is 4 digits.

Calculation procedures. The densities measured may be recalculated to the molar volume of the samples, V_m , and the partial molar volume of the components, $V(i)$, using the equality

$$V_m = \rho^{-1} \sum x(i)M(i) = V/\sum n(i) = \sum x(i)V(i), \quad (2)$$

where $n(i)$ denotes the amount, $x(i)$ the mole fraction and $M(i)$ the molar mass of component i , respectively.

When investigating the options available for the presentation of the volumetric properties of the present system, the apparent molar volume proved to be of little value since all four components contribute significantly to the overall volumetric state.⁹ Hence, the partial molar volume was engaged to represent the property of the components.

The calculation procedure consisted first of a least square fit¹⁰ of the molar volume of the system, (eq. (2)) to linear and cross-products of the mole fractions.¹¹ The equations chosen are given in Table 1 along with the coefficients and the statistical figures. As shown, the molar volume of the three-component samples were described by a four-parameter equation. This model was found to be superior to the other models tested. Using the significant terms, the model was then

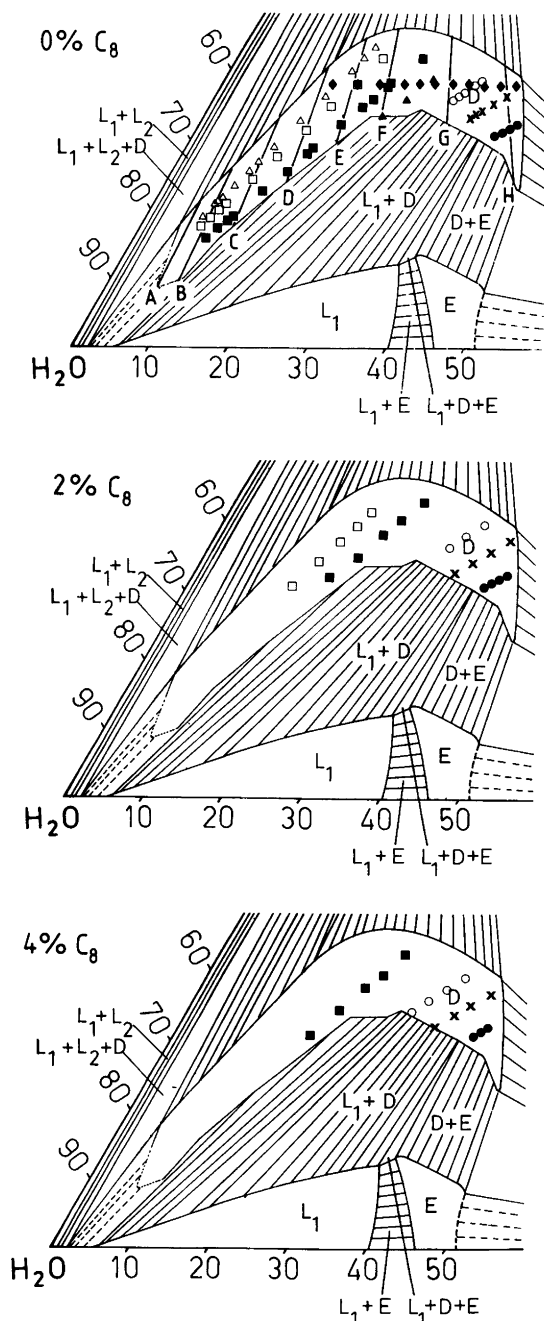


Fig. 2. The composition of the samples in the lamellar phase at constant levels of 0, 2 and 4% by weight of octane present perpendicular projected on the octane-free phase diagram. The samples are grouped in series defined in the figure. The sample series A-H are defined in Fig. 8.

	$n(\text{C}_{10}\text{OH}) / n(\text{NaC}_8\text{O}_2)$
$\triangle = 2$	2.840
$\square = 3$	2.450
$\blacksquare = 4$	1.950
$\blacktriangle = 5$	1.575
$\circ = 6$	1.280
$\times = 7$	1.050
$\bullet = 8$	0.860
$\blacklozenge = 1$	($w(\text{C}_{10}\text{OH}) = 38\%$)

expanded to account for three of the mole fractions of the four-component system. The molar volumes calculated with the complex model developed agreed within 0.25% with the molar volumes of the four-term model. Consequently, both models are to be considered accurate in describing the volumetric state of the present system. Moreover, all the simpler models tested failed to give statistically significant fits.

In the second step, the calculation of the partial molar volumes involved a partial derivation of the V_m function with respect to the mole fractions of the components. For a four-component system, the mole fraction of component 1 may be substituted ($x_1 = 1 - x_2 - x_3 - x_4$) to give the following general matrix of 4×4 linear equations¹¹

$$\begin{bmatrix} V_1 \\ V_2 \\ V_3 \\ V_4 \end{bmatrix} = \begin{bmatrix} V_m & -x_2 & -x_3 & -x_4 \\ V_m & 1-x_2 & -x_3 & -x_4 \\ V_m & -x_2 & 1-x_3 & -x_4 \\ V_m & -x_2 & -x_3 & 1-x_4 \end{bmatrix} \begin{bmatrix} 1 \\ \left\{ \frac{\partial V_m}{\partial x_2} \right\} \\ \left\{ \frac{\partial V_m}{\partial x_3} \right\} \\ \left\{ \frac{\partial V_m}{\partial x_4} \right\} \end{bmatrix}, \quad (3)$$

where 1=H₂O, 2=NaC₈O₂, 3=C₁₀OH and 4=C₈. The partial molar volumes of the three component samples calculated with the three-component model¹² and the four-component model¹⁰ (given in Table 1) from this set of linear equations agreed generally within 11%. This accuracy is typical for partial molar properties of complex systems.

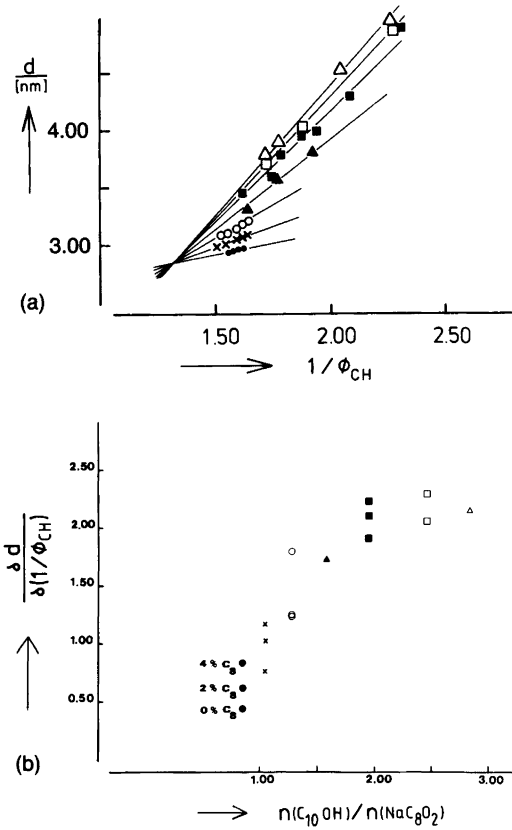


Fig. 3. The dependence of the Bragg spacing on the inverted volume fraction of the hydrocarbon chains, eq. (5), for octane-free samples (a) at 298 K, and the dependence of the slope on the mole ratio of decanol to sodium octanoate for constant levels of 0, 2 and 4 % by weight octane (b). The symbols correspond to those defined in Fig. 2. For convenience, a few samples rich in water are omitted from the figure.

The volume of the samples can also be used, together with the Bragg spacings, to formally divide the lamellar phase into an aqueous domain and an amphiphilic bilayer (Fig. 1). Since we did not know the density of sodium octanoate in the liquidized state in the lamellae we could not calculate the volume fraction of the whole amphiphilic layer as such. Instead we considered the hydrated polar head groups and the hydration water bound to the counterions as a part of the aqueous domain. Assuming that the hydrocarbon chains have the density of liquid hydrocarbon

and that the chains of the different amphiphilic compounds and octane mix ideally we can express the molar volumes of the hydrocarbon chains of the hydrocarbon layer as follows

$$V_{CH}^{\bullet}(NaC_8O_2) = (M(NaC_8O_2) - M(NaCO_2))/\rho^{\bullet}(C_7) \quad \text{and} \quad (4a)$$

$$V_{CH}^{\bullet}(C_{10}OH) = (M(C_{10}OH) - M(OH))/\rho^{\bullet}(C_{10}) \quad (4b)$$

where the density of pure heptane ($\rho^{\bullet}(C_7) = 0.67941 \text{ g cm}^{-3}$) and pure decane ($\rho^{\bullet}(C_{10}) = 0.72636 \text{ g cm}^{-3}$)¹³ represent the density of the hydrocarbon chains of the octanoate and decanol, respectively. $M(NaCO_2)$ and $M(OH)$ are the molar masses of the sodium carboxylate and the hydroxyl groups, respectively. The volume fraction of the hydrocarbon part of the amphiphilic layer then takes the form

$$\Phi_{CH} = \frac{\sum n(k)V_{CH}^{\bullet}(k)}{V}, \quad (5)$$

where k denotes the amphiphilic components for the three-component system but includes the octane of the four-component system. In the latter case $V_{CH}^{\bullet}(C_8) = V^{\bullet}(C_8) = M(C_8)/\rho^{\bullet}(C_8)$, where $\rho^{\bullet}(C_8) = 0.69853 \text{ g cm}^{-3}$.¹³

Using these volume fractions, we can now subdivide the total repetition distance into the amphiphilic and the water layer, respectively

$$d_{CH} = \Phi_{CH} d, \quad d_w = \Phi_w d = d - d_{CH}. \quad (6)$$

Consequently, a constant slope (corresponding to d_{CH}) when the Bragg spacing is plotted against the inverse volume fraction of the hydrocarbon layer indicates a one-dimensional swelling of the lamellae.⁶

The area per ionizable group in the lamellae is given by^{5,6}

$$A^{\text{tot}}(NaC_8O_2) = \frac{2V}{n(NaC_8O_2)Ld}, \quad (7)$$

where V denotes the volume of the sample in eq. (2) and L the Avogadro constant. $A^{\text{tot}}(NaC_8O_2)$ thus gives an estimate of the maximum charge

density at the interface. An extrapolation of a plot of $A^{\text{tot}}(\text{NaC}_8\text{O}_2)$ versus Φ_{CH}^{-1} to $\Phi_{\text{CH}}^{-1} = 1.0$ (ie. when $d = d_{\text{CH}}$) gives the area per ionizable group (maximum charge density) in the "dry" lamella, $A^{\text{extr}}(\text{NaC}_8\text{O}_2)$. This area can now be divided into contributions from both surfactants:

$$A^{\text{extr}}(\text{NaC}_8\text{O}_2) = A^\circ(\text{NaC}_8\text{O}_2) + A^\circ(\text{C}_{10}\text{OH}) \frac{n(\text{C}_{10}\text{OH})}{n(\text{NaC}_8\text{O}_2)} \quad (8)$$

If the model developed is reasonable, we should obtain a straight line when $A^{\text{extr}}(\text{NaC}_8\text{O}_2)$ is plotted against $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2)$. As shown in Fig. 6, this is not the case for areas obtained at $\Phi_{\text{CH}}^{-1} = 1.0$. However, if we use $A^{\text{tot}}(\text{NaC}_8\text{O}_2)$ at $\Phi_{\text{CH}}^{-1} = 1.3$ for $A^{\text{extr}}(\text{NaC}_8\text{O}_2)$ (this corresponds to the point of intersection of all the d versus Φ_{CH}^{-1} lines in Fig. 3) a linear relationship is indeed obtained. From the intercept and slope, we obtain the areas occupied by sodium octanoate ($A^\circ(\text{NaC}_8\text{O}_2)$) and by decanol ($A^\circ(\text{NaC}_8\text{O}_2)$) at the mixed interface.

Since octane is fully solubilized in the hydrocarbon interior of the lamellae, there will not be any direct term accounting for it. Instead, the effect of solubilization is embedded in the volume and the Bragg spacing of the liquid crystalline samples, eq. (7).

Experimental results

The composition of the experimental points is shown in Fig. 2. The samples are arranged in series of constant mole ratios of decanol to sodium octanoate (symbols). The lines denoted by letters correspond to the constant mole ratios of water to sodium octanoate given in Fig. 8.

In the (a) part of Fig. 3–5, the Bragg spacing (d), the thickness of the hydrocarbon layer (d_{CH} , eq. (6)) and the "total mean area per ionizable group" ($A^{\text{tot}}(\text{NaC}_8\text{O}_2)$, eq. (7)), are plotted against the inverse volume fraction, eq. (5). The slopes of the linear parts of these plots are shown in the (b) part of each figure. The areas available for each polar group in the mixed interface extracted from the plots of $A^{\text{extr}}(\text{NaC}_8\text{O}_2)$ versus $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2)$ are given in Fig. 6. The molar volumes and the partial molar volumes of

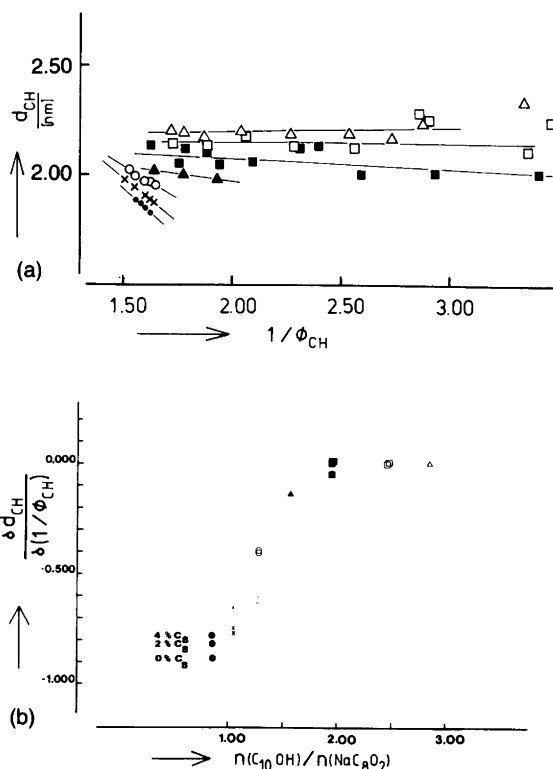


Fig. 4. The dependence of the thickness of the hydrocarbon chain bilayer, eq. (6), on the inverted volume fraction of the hydrocarbon chains, eq. (5), for octane-free samples (a) and the dependence of the slope on the mole ratio of decanol to sodium octanoate for constant levels of 0, 2, and 4% by weight of octane (b), respectively. The symbols correspond to those defined in Fig. 2.

the components have been grouped in order to illustrate the influence of adding water (Fig. 7), decanol (Fig. 8) and octane (Fig. 9) to the system. Fig. 7 then gives the molar volume of the samples, eq. (2), and the partial molar volume of the components, eq. (3), of the system $\text{H}_2\text{O}/\text{NaC}_8\text{O}_2/\text{C}_{10}\text{OH}$ at 298 K plotted against the mole fraction of water (Fig. 7) and decanol (Fig. 8), respectively.

Fig. 9 presents the molar volume of the samples, eq. (2), and the partial molar volumes of the components, eq. (3), of the quaternary system $\text{H}_2\text{O}/\text{NaC}_8\text{O}_2/\text{C}_{10}\text{OH}/\text{C}_8$ at 298 K plotted against the mole fraction of octane.

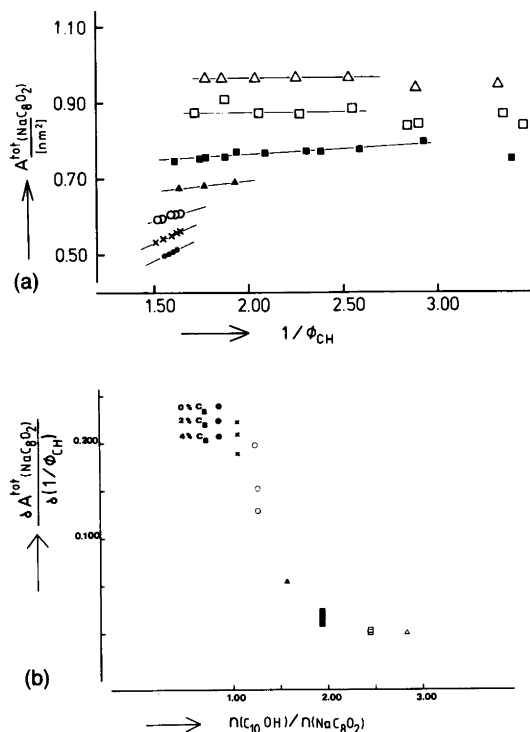


Fig. 5. The dependence of the area available for each charged group, eq. (5), on the inverted volume fraction of the hydrocarbon chains, eq. (7), for octane-free samples (a) and the dependence of the slope on the mole ratio of decanol to sodium octanoate for constant levels of 0, 2 and 4 % by weight octane (b), respectively. The symbols correspond to those defined in Fig. 2.

It is important to realize that the lines located at $x(\text{C}_8) = 0.005-0.010$ in Fig. 9 all represent 2 % octane while the lines at $x(\text{C}_8) = 0.011-0.018$ correspond to 4 % octane, respectively. The lines thus connect quaternary samples which are defined by the same constant mole ratio of decanol to sodium octanoate as the ternary samples in Fig. 7.

Discussion

The lamellar D phase can, according to the model outlined above, be considered to consist of three layers with distinguishable properties. The hy-

drocarbon chains form an anhydrous layer. When octane is added to the system, all the molecules are solubilized in this region. The aqueous domain can be subdivided into two parts. One consists of "free" water which is not firmly bound to the surface, counterions dissociated from the interface and some amphiphilic molecules.⁶⁻⁸ Between this domain and the hydrocarbon layer is an "interface" consisting of the polar head groups of the amphiphiles, the bound counterions plus the hydration water.^{15,16} The ion adsorption can be estimated by solving the Poisson-Boltzmann equation for highly charged surfaces.^{15,16} The number of ions bound to the surface has then been found to be constant for charge densities of one charge per 0.8 nm^2 (cf. Fig. 5) as long as the water layer thickness is larger than 2 nm (cf. Fig. 3, 4).¹⁵ This special property has been denoted ion condensation on charged surfaces.

Depending on the concentration parameters chosen, a border between "water-rich" and "water-poor" regions can be placed at $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2) \approx 1.6-2.0$, at $n(\text{H}_2\text{O})/n(\text{NaC}_8\text{O}_2) \approx 11$ or at $n(\text{H}_2\text{O})/n(\text{C}_{10}\text{OH}) \approx 10$. At all these limits, one may observe macroscopic changes or alternations in the molecular interactions. The limits roughly coincide with the maximum amount of water that can be bound by the polar groups (6 $\text{H}_2\text{O}/\text{Na}^+$, 5 $\text{H}_2\text{O}/\text{COO}^-$ and 3 $\text{H}_2\text{O}/\text{OH}$).¹ The lamellar D phase separates when 4 percent by weight of octane is added to the samples with $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2) > 2.0$ (Fig. 2). This limit roughly corresponds to the lower water-rich phase boundary previously claimed for the lamellar D phase.^{1,6}

The 3-component system: $\text{NaC}_8\text{O}_2/\text{C}_{10}\text{OH}/\text{H}_2\text{O}$

X-ray measurements. Consider first the water-rich salient of the lamellar phase. The thickness of the amphiphile bilayer (Fig. 4) is independent of the Bragg spacing (Fig. 3). This suggests a one-dimensional swelling of the aqueous sheet upon addition of water. For the same phase region (i.e. when $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2) > 2$) we also find a roughly constant mean area per carboxylate group at the interface (Fig. 5). This is assumed in the ion condensation theory¹⁵ and is in accordance with the constant quadrupole-splitting reported for the counterions.¹⁷ It was originally suggested by Ekwall that counterions are partially liberated from the polar surfaces of the meso-

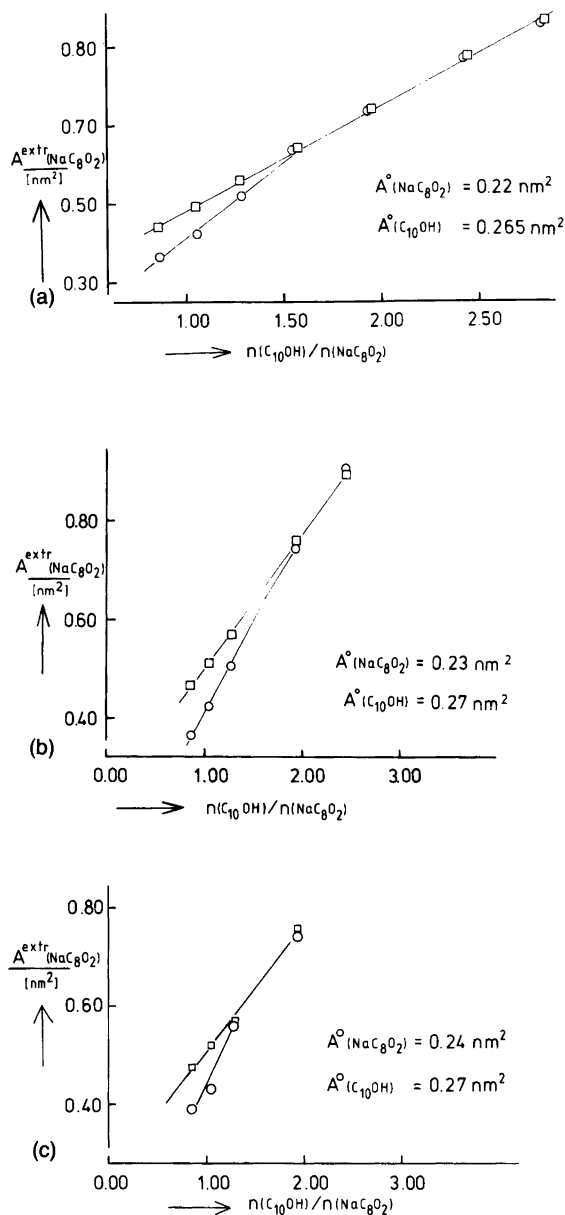


Fig. 6. The extrapolated area for each charged group at $\Phi_{\text{CH}}^{-1} = 1.0$ (circles) and at $\Phi_{\text{CH}}^{-1} = 1.3$ (squares) respectively, plotted against the mole ratio of decanol to sodium octanoate. The area calculated for the carboxylate and the hydroxyl groups are given in the diagrams corresponding to the constant percent by weight level of octane = 0 (a), 2 (b) and 4 (c). The symbols correspond to those defined in Fig. 2.

phase and that the charge distribution created the conditions needed for the stability of the water-rich phase region.¹⁸

The situation changes somewhat when decanol is exchanged for pentanol.^{7,8,19} In this case, the charge density varies also in the water-rich phase region. This has been explained as due to a partial dissolution of some of the surfactant (or pentanol) molecules into the aqueous layer.⁸ The explanation is suggested by comparing the area occupied by the polar groups (Fig. 6). The considerably larger area found for the surfactant (0.33 nm^2) in the pentanol system as compared with the area found for the surfactant in the decanol system (0.22 nm^2) may also be a consequence of a decrease in the alkyl chain order induced by the short chain alcohol.¹⁷

When the number of ionizable groups increases to $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2) < 2$, d_{CH} (Fig. 4) the area per carboxylate group (Fig. 5) then becomes concentration-dependent. Simultaneously, the plots of $A^{\text{extr}}(\text{NaC}_8\text{O}_2)$ versus $n(\text{C}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2)$ become nonlinear (if values for $\Phi_{\text{CH}}^{-1} = 1$ are used). The linear dependency is however restored if the area per carboxylate group is extrapolated to $\Phi_{\text{CH}}^{-1} = 1.3$ which coincides with the intersection of all the d versus Φ_{CH}^{-1} lines (Fig. 3)! It is interesting to note that the compositions of the point of intersection correspond to the water-poor boundary of the lamellar phase. Although we cannot give a thorough explanation for this phenomenon, it seems plausible that the interplay between the hydration forces of the species (all the water is bound) and the interaction between the molecules are of great importance for the state of the system.¹⁸ Using the linearized dependency of the mole ratio of decanol to sodium octanoate, we obtain the area occupied by the polar groups of the amphiphiles reported in Fig. 6. Increasing the amphiphile content (i.e. reducing Φ_{CH}^{-1}) in the water-poor and surfactant rich region leads to an expansion of the amphiphile layer and to a slight reduction of the area per carboxylate group. On the other hand, if the maximum charge density is decreased by adding more decanol at constant mole ratio of water to sodium octanoate, a rapid increase in both the thickness of the amphiphile layer and the area per carboxylate group is observed. Since the latter effect is probably mainly due to the separation of the carboxylate group in the presence of more decanol, this

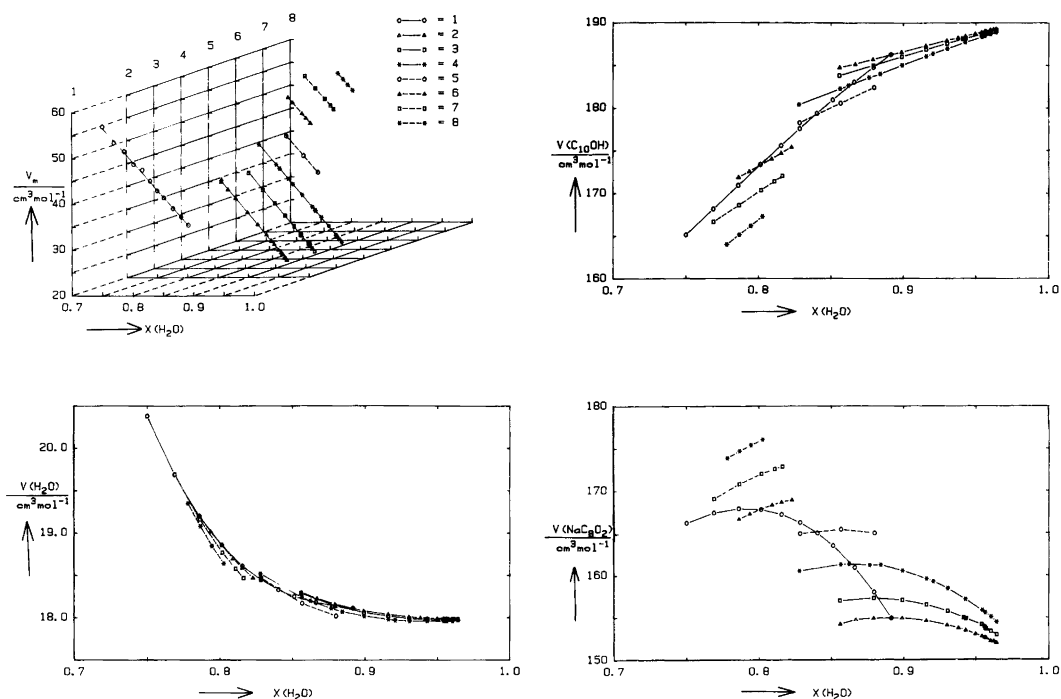


Fig. 7. The molar volume and the partial molar volumes of the components of the system water/sodium octanoate/decanol at 298.15 K plotted against the mole fraction of water. In the V_m versus $X(\text{H}_2\text{O})$ diagram, the coordinate axis has been successively shifted since all the lines are closely superimposed on each other. The numbers correspond to the sample series defined in Fig. 2.

change also points to a more stretched configuration of the hydrocarbon chains. Both observations are in accordance with the increased order parameter reported for octanoate and decanol when the amphiphile and the decanol content, respectively, are increased.¹⁴ The efficient chain packing is in the former case probably made possible by the reduced charge density due to a strong adsorption of the counterions^{17,19} in the absence of sufficient hydration water²⁰ and in the latter case by the separation of the carboxylate groups when the interface is diluted with decanol. Reversing the process, the water added to the lamellar phase allows for a successively larger distance between the sodium and carboxylate ions thus increasing the repulsion (and distance) between the charged groups. The condition for the one-dimensional swelling seems to be that a partial dissociation of the sodium ions produces a sufficiently high charge density of the interface. The rôle played by the water insoluble decanol is

to maintain a large enough lateral cohesion of the amphiphile bilayer.¹⁴

Density measurements. According to recent investigations of alcohols mixed with hydrocarbons, the major change in volume can be ascribed to unspecific van der Waal type of interactions giving a positive contribution to the volume and to specific interactions producing a negative volume change.^{21,22} The correlations of molecular orientations of the methylene segments of the hydrocarbon chains²³ can be assumed to increase upon enhanced chain packing. When large scale disruptions of hydrogen bonds occur in a narrow concentration range, there is, however, a large and positive volume contribution due to increased unspecific molecular motions of the species.²² Mixed in water, the amphiphilic molecules are embedded in a strong water matrix producing a negative change in volume (\sim

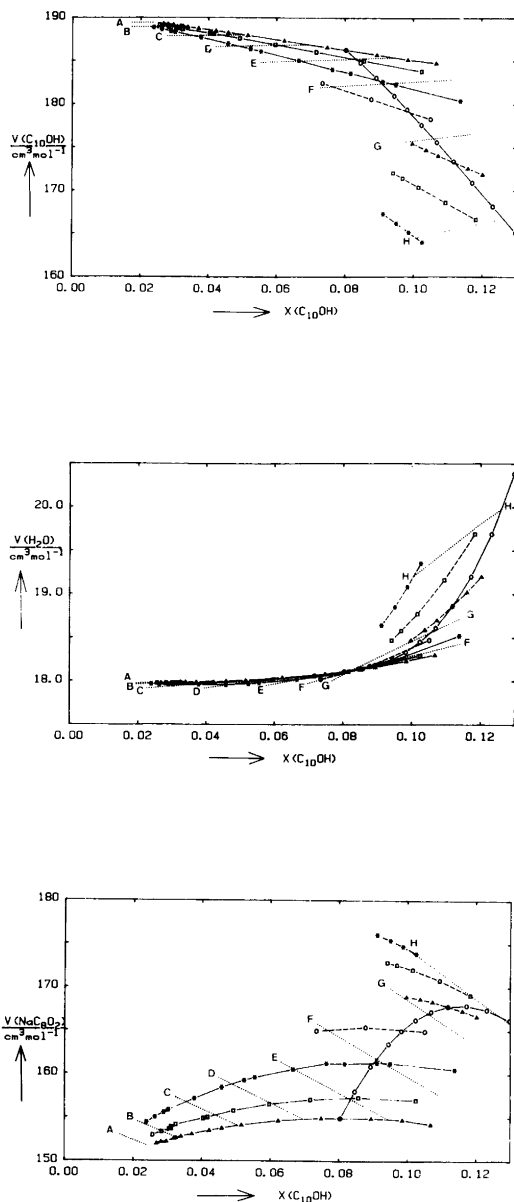


Fig. 8. The partial molar volumes of the components of the system water/sodium octanoate/decanol plotted against the mole fraction of decanol. The symbols connected with full drawn or broken lines correspond to the sample series defined in Fig. 2 and 7. The dotted lines are interpolated from the previous ones for the following constant mole ratios of water to sodium octanoate: A = 113.80, B = 83.00, C = 52.30, D = 37.00, E = 26.20, F = 18.00, G = 10.80, H = 6.68. The lines are also indicated in Fig. 2.

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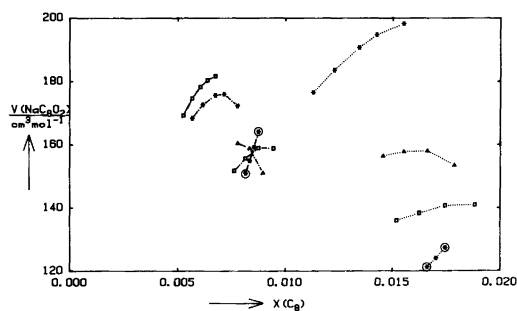
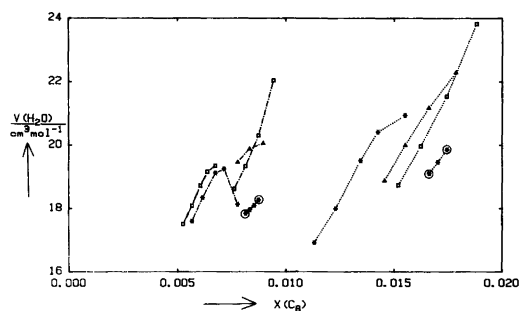
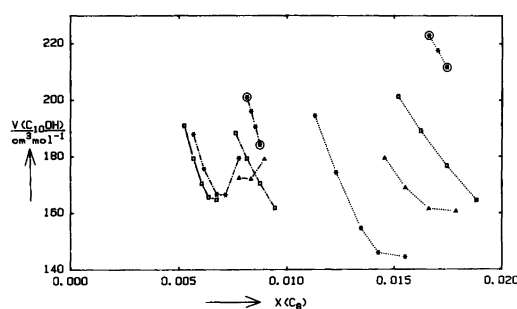
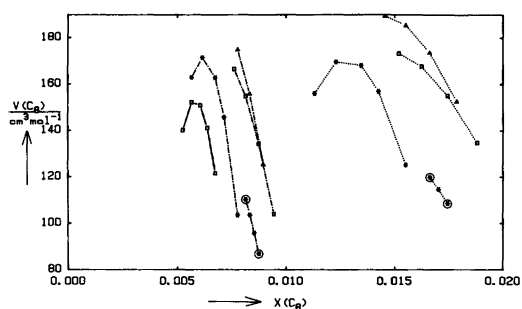
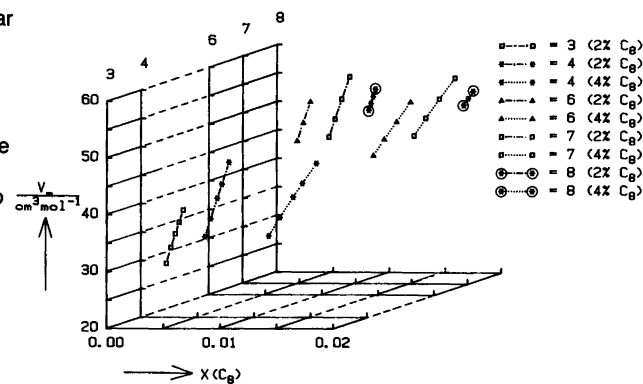
$-10 \text{ cm}^3 \text{ mol}^{-1}$).^{24,25} A negative contribution may also be encountered upon dissociation of ionic species ($\sim -14 \text{ cm}^3 \text{ mol}^{-1}$)²⁶ and, conversely, association of, e.g., counterions provides a positive contribution to the volume. A comparison of the volume change upon association of different anionic, cationic, and neutral surfactants, revealed however, that the contribution of the charge was small.^{27,28} We can thus expect that any change in the packing efficiency of the hydrocarbon chains would affect the volumetric state of the amphiphile components.

On these grounds, it may be interesting first to analyse the information available from the water-poor phase region where large changes in the amphiphile lamella thickness were recorded. When the mole fraction of water decreases, both the partial molar volumes of decanol and octanoate decrease almost linearly (Fig. 7). Increasing the mole fraction of decanol, while maintaining the mole ratio of water to sodium octanoate constant, leads to a volume reduction for sodium octanoate while the opposite is found for decanol (Fig. 8). These observations agree in general with the enhanced chain packing indicated by d_{CH} (Fig. 4)^{14,21-23} and made possible by the reduced charge at the interface. The determinative role played by sodium octanoate is manifested by the fact that many of the experimental properties of the components are superimposed when plotted as a function of the mole fraction of sodium octanoate.^{7,19} The slightly opposite change observed for decanol may be explained by the increased disorder, relatively speaking, of the first methylene groups found at high decanol contents.¹⁴

The exceptional state of water when bound to the ionic groups is demonstrated by the very high partial molar volume of water in the water-poor range. One may thus illustrate the immobilized primary hydration water²⁰ as being bound in a voluminous ice-like arrangement. The dependence of the partial molar volume of water on the mole fraction of decanol becomes important when the mole ratio of water to decanol exceeds approximately 10 (Fig. 8). It is interesting to note that this limit roughly coincides with the lower phase boundary in the water-poor range.

In the water-rich salient, the partial molar volume of water remains in a state approaching the

Fig. 9. The molar volume and the partial molar volume of the components of the system water/sodium octanoate/decanol/octane at 298.15 K plotted against the mole fraction of octane. The volumes of the octane-free samples are omitted from the diagrams. In the V_m versus $X(\text{H}_2\text{O})$ diagram, the coordinate axis has been successively shifted in order to separate the different sample series. To simplify the comparison with the octane-free system (Fig. 7) the symbols are maintained but they are connected with broken-dotted or dotted lines. The sample series are also identified by the same numbers as for the ternary system and are defined in Fig. 2.

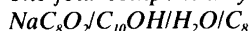


pure liquid. However, the partial molar volume of decanol and octanoate have opposite concentration dependencies. The partial molar volume of sodium octanoate diminishes when the aqueous layer is diluted with water. As discussed above, the change may be produced by a partial dissociation of counterions or surfactant molecules into the aqueous layer,¹⁴ or both. The limiting value obtained by extrapolation to $x(\text{H}_2\text{O})$

= 1.0 is of the order of $148 \text{ cm}^3 \text{ mol}^{-1}$ which is not far from the volume observed for aqueous micellar solutions of sodium octanoate.^{27,28} The corresponding limiting value for the partial molar volume of decanol is close to the molar volume of the pure liquid ($191.5 \text{ cm}^3 \text{ mol}^{-1}$)²⁵ which suggests that the interiors of the lamellae are, indeed, liquid-like and dry in accordance with the observation of a constant d_{CH} and $A^{101}(\text{NaC}_8\text{O}_2)$ value.

The opposite dependencies of the amphiphile components on the mole fraction of water thus support the different role ascribed to them in the previous section.

The four-component system:



The X-ray analysis of the 4-component samples shows the same general dependency on the composition as did the 3-component samples. Consequently, the features are summarized only in the diagrams reporting the slopes of the Bragg spacing (Fig. 3), the thickness of the amphiphile bilayer (Fig. 4) and the mean total area per sodium carboxylate group (Fig. 5). As shown in the figures, the effects produced by octane are small compared with the other components. The smaller slope and total change of d_{CH} and $A^{\text{tot}}(\text{NaC}_8\text{O}_2)$ point to a lower maximum packing efficiency of the chains in the presence of octane in the water-poor range. This conclusion is supported by the larger area obtained for the polar groups (Fig. 6) when the octane fraction increases. In the water-rich salient, the effect of octane is small or insignificant.

The volume changes observed for the hydrocarbon molecules in general also support the view of a slightly reduced interaction intensity between the amphiphile chains. However, in the water-poor phase region, the addition of octane leads to an opposite (negative) change in the partial molar volume of sodium octanoate. The effect is larger the higher the sodium octanoate concentration. Although a negative change could be explained by an increased electrostatic interaction (larger charge separation) the unreasonably low and unsystematic partial molar volumes of NaC_8O_2 found in this range suggest that the effect may be due to an inaccuracy of the mathematical model.

The octane addition also affects the volumetric state of water. Since the effect is small, it seems reasonable and can be explained by the increased electrostatic interaction due to the charge separation. In the water-rich range, the increase in volume of both water and sodium octanoate can be taken as an indication of the octane solubilization leading to an adsorption of the dissolved octanoate molecules in order to accommodate the oc-

tane. The phase separation of the samples poorest in surfactant in the presence of 4 % by weight octane supports this view.

Conclusions

- The combination of X-ray diffraction and volume analysis are capable of giving detailed information about the molecular interactions in the three-component and four-component lamellar phases.
- Depending on the parameters selected, three molar ratios may be chosen to group the gross appearance of the system. Such a limit is, e.g., a water to surfactant mole ratio $\approx 11-14$. The other two "critical" mole ratios, of decanol to sodium octanoate ≈ 1.6 and of water to decanol ≈ 10 , also roughly define the (lower) surfactant-rich phase boundary of the lamellar phase. Another "critical" value found for the former mole ratio ($n(\text{G}_{10}\text{OH})/n(\text{NaC}_8\text{O}_2) \approx 2$) above which a phase separation was found when 4 % by weight octane was solubilized therein roughly coincides with the lower phase boundary of the water-rich salient previously claimed for the lamellar phase.
- In the water-rich salient of the phase, conditions for a composition-independent constant lamella thickness and area of the polar head groups persist in accordance with the basic assumptions made when applying the ion condensation theory to the lamellar liquid crystalline phase. In this concentration range, some of the surfactant seems to dissociate from the lamellae to the aqueous layer.
- As expected, the hydration need of the ionic groups dominates the properties of the water-poor phase region. However, the interactions between the chains in addition to the area available per polar group contribute significantly to the local phase structure.
- Octane is assumed to be solubilized in the bilayer without the constraint of the average perpendicular alignment of the amphiphile chain. As expected, the incorporation is found to cause some disturbance in the hydrocarbon chain interaction which is also reflected as a small increase in the area available for the polar groups. In the water-rich phase region, octane may enforce an adsorption of octanoate molecules from the aqueous domain.

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