Characteristic Features of Hydroxystearic Acid Monolayers at the Air/Water Interface

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The effect of high NaCl concentrations in the aqueous subphase on the structure and phase properties of selected *n*-hydroxystearic acid monolayers is studied. The surface pressure−area (π−A) isotherms, the BAM (Brewster angle microscopy) images of the condensed phase domains, and the lattice structures obtained by GIXD (grazing incidence X-ray diffraction) of 2-, 9-, 11-, and 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase are determined. Large differences exist between the monolayer characteristics of stearic acid OH-substituted near the COOH-group (2-position) when both groups act as a monopolar entity and those OH-substituted in the mid-position of the alkyl chain (9-, 11-, 12-position) when the molecule has bipolar character. The π−A isotherms of the bipolar hydroxystearic acid monolayers have an extended flat plateau region only slightly dependent on temperature. In the case of 2-hydroxystearic acid monolayers, first at $T > 30$ °C an inclined small "plateau" region, which is strongly temperature dependent, indicates the fluid/condensed phase coexistence. Analogous differences between the hydroxystearic acid OH-substituted near the COOH group and those OH-substituted in mid-position of the alkyl chain are also demonstrated by the temperature dependence of the phase transition pressure and the entropy changes for the main phase transition. The comparison of the selected *n*-hydroxystearic acid monolayers spread, on one hand, on 1 M NaCl aqueous pH 3 subphase and, on the other hand, on pH 3 water shows that, in general, the characteristics of the π−A isotherms and the structure features obtained on the two different subphases are similar. However, specific differences in the domain morphology and lattice structure are observed and are obviously related to the tendency of high NaCl concentrations to give rise to tighter molecule packing and a reduced polar tilt of the alkyl chain. In the special case of 9-hydroxystearic acid monolayer at 5 °C, the phase transition observed at spreading on pH 3 water in the π−A isotherm at ∼18 mN/m between two condensed phases with a NNN−NN transition disappears at spreading on 1 M NaCl aqueous pH 3 subphase and only a low-tilted phase toward NN and untilted phase occur.

Introduction

Over decades, there have been a long-term interest in the monolayer properties of lipids having second polar groups substituted at the lipophilic alkyl chain because of their significance in biological systems.[1−7] For example, hydroxyl groups of membrane lipids can modify membrane characteristics in a unique way. The hydroxyl group is the simplest hydrophilic group with the smallest cross-section area.[8] Hydroxy fatty acids are good candidates for such model amphiphiles in which one OH group as a second polar group with a small cross-section area is substituted in different positions of the alkyl chain. In their previous papers, Cadenhead et al. provided some important initial information on selected hydroxy fatty acids.[9−11] They found large differences in the surface pressure−area isotherms between hexadecanoic acids OH-substituted in the 2- or 3-position and those where the OH-substitution is in mid-position of the alkyl chain and concluded that, in the first case, the hydroxyl and carboxyl polar groups act as one combined polar group whereas beyond the fifth or sixth carbon position the molecules showed bipolar behavior in the expanded state. More detailed information on the effect of OH substitution in

the 2-position was obtained by a combination of Brewster angle microscopy (BAM) and grazing incidence X-ray diffraction (GIXD) studies.[12,13] The headgroup, enlarged by a neighboring OH group in the 2-position, gives rise to a loss of ordering of the monolayer structure which has been attributed to a misfit of the alkyl chains. Recent fluorescence microscopy and BAM studies of 12-hydroxystearic acid and 9-hydroxypalmitic acid monolayers provided the first information on the domain morphology of the condensed monolayer phase for fatty acids OH-substituted in the mid-position of the alkyl chain.[14,15] The results suggest that ordered condensed phases are formed when the alkyl chain is OH-substituted in the mid-position.

The presence of a second polar group enhances the polarity of the fatty acid and hence the solubility of the spread material in the aqueous subphase. To avoid the desorption of the monolayer material into the subphase during the measurements of the monolayer characteristics, the experiments of some papers were performed with high electrolyte concentrations (NaCl) in the subphase.[9,10] Therefore it is of interest whether or not, or in which way, the high NaCl concentration affects the main characteristics of hydroxy fatty acid monolayers. The present work focuses on the comparison of the surface pressure−area (π−A) isotherms, the BAM images of the condensed phase domains, and the lattice structure of selected hydroxystearic acid monolayers. In the case of the hydroxystearic acids, the alkyl chain length is large enough that, in the absence of NaCl,

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dissolution into the subphase can be ignored. Correspondingly, these isomeric hydroxystearic acids seem to be well suited to study whether or not, and in which way, high NaCl concentrations in the subphase can affect the monolayer features of these amphiphiles.

Experimental Section

2-, 9-, and 11-Hydroxystearic acids were obtained from Nu-Check Prep Inc., Elysian, and recrystallized several times from heptane prior to use. 12-Hydroxystearic acid purchased from Sigma in a nominal 99.9% purity was used without further purification.

The monolayer materials were dissolved in a 9:1 (*v:v*) mixture of *n*-heptane (for spectroscopy, Merck) and ethanol (p.a., Merck) and spread onto ultrapure pH 3 water or a 1 M aqueous NaCl subphase adjusted with HCl to pH 3. Ultrapure deionized water with a conductivity of 0.055 μS/cm produced by "Purelab Plus" (Seral, Germany) was used.

The experimental setup for the measurements of the surface pressure ($\pi-A$) isotherms and the BAM studies consisted of a self-made computer-interfaced film balance coupled with a Brewster angle microscope (BAM 1+, NFT, Göttingen, Germany). The surface pressure was measured with the Wilhelmy method. Using a roughened glass plate, the accuracy of the surface pressure was reproducible to ±0.1 mN m^{-1} and the area per molecule to $\pm5 \times 10^{-3}$ nm^2. The lateral resolution of the BAM1+ was approximately 4 μm. The image distortion due to observation at the Brewster angle was corrected by utilizing image-processing software. More detailed information on the BAM method is given elsewhere.[16,17]

The GIXD experiments were performed on the undulator beamline BW1 at HASYLAB, DESY, Hamburg, Germany, using the liquid-surface diffractometer. For the GIXD experiments, the film trough is located in a sealed and He-filled container to reduce the background in the X-ray scattering experiments. A monochromatic synchrotron beam strikes the helium/water interface at the grazing incidence angle $\alpha_i = 0.85\alpha_c$, where $\alpha_c \sim 0.14°$ is the critical angle for total reflection. A linear position-sensitive detector (PSD) (OED-100-M, Braun, Garching, Germany) was used to monitor the diffracted intensity as a function of the vertical scattering angle α_f. A Soller collimator in front of the PSD provides the resolution for the horizontal scattering angle $2\theta_{xy}$ which was approximately 0.01 Å^{-1}. The scattering vector $Q = k_f - k_i$ consists of an in-plane component $Q_{xy} \approx (4\pi/\lambda)\sin\theta_{xy}$ and an out-of-plane component $Q_z \approx (2\pi/\lambda)\sin\alpha_f$, where λ is the X-ray wavelength. The diffracted intensities were corrected for polarization, effective area, and the Lorentz factor.

The lattice parameters are obtained from the peak positions.[18] The lattice spacing d_{hk}, the polar tilt angle t of the long molecule axis, and the tilt azimuth ψ_{xy} are calculated from the positions of the Q_{xy} and Q_z maxima according to $d_{hk} = 2\pi/Q_{xy}^{hk}$ and $Q_z^{hk} = Q_{xy}^{hk}\cos\psi_{hk}\tan t$, where h,k denotes the order of reflection. The lattice parameters *a, b,* and γ are obtained from the lattice spacing d_{hk}, and from these the unit cell area A_{xy} which is defined by $A_{xy} = ab \sin\gamma$. The cross-section per alkyl chain A_0 is related to the unit cell area A_{xy} (area per molecule parallel to the interface) and the tilt angle t according to $A_0 = A_{xy} \cos t$.

Results and Discussion

At first, we consider the temperature dependence of the $\pi-A$ isotherms of four *n*-hydroxystearic acid monolayers ($n = 2, 9, 11, 12$) spread on 1 M NaCl solution at a subphase pH 3 (Figures 1–4). At this pH of the aqueous subphase, all the hydroxy fatty
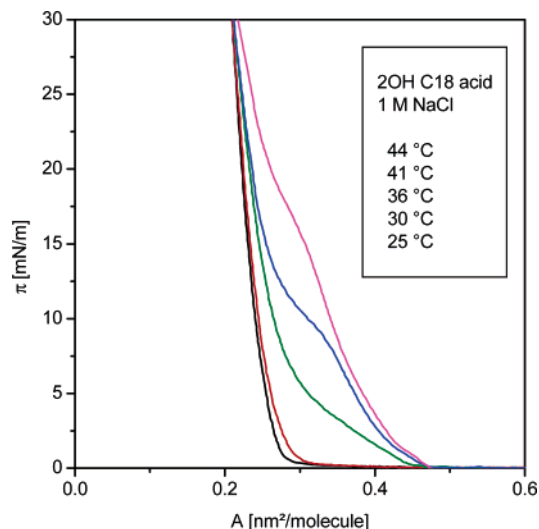

Figure 1. Surface pressure–area isotherms of 2-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase at different temperatures.

acid monolayers are almost completely undissociated. Generally, we see large differences in the $\pi-A$ isotherms between stearic acids OH-substituted near the carboxyl group ($n = 2$) and those where the OH-substitution is in mid-position of the alkyl chain ($n = 9, 11, 12$).

Figure 1 shows the isotherms for 2-hydroxystearic acid measured between 25 and 44 °C. The isotherms have no plateau over a wide temperature range ($T \leq 30$ °C). That means that in this temperature range, a two-phase coexistence exists already at near zero pressure and the isotherms do not give any indication of a transition from the fluid (liquid-expanded, gaseous) to the condensed phase. In this region, the surface pressure increases abruptly on compression to $A < 30$ Å^2/molecule. At T > 30 °C, the pressure increase begins already at $A \sim 48$ Å^2/molecule and a strongly inclined small "plateau" region indicates a fluid/condensed phase coexistence.

Generally the monolayer characteristics of the stearic acids OH-substituted in mid-position of the alkyl chain are completely different. The experimental $\pi-A$ isotherms of the monolayers of *n*-hydroxystearic acid ($n = 9, 11, 12$) spread on a 1 M NaCl aqueous subsolution of pH 3 and measured at various temperatures are shown in Figures 2–4. The $\pi-A$ isotherms have the fluid/condensed main phase transition at $\Pi > 0$ for all measured temperatures in the accessible region. With increasing temperature the surface pressure of the plateau also increases. A kink point at $A = A_c$ indicates the onset of the first-order phase transition. It is followed by an extended plateau region the pressure of which increases as the temperature increases. At $A > A_c$ the monolayer exist in the fluid state. Specific features of these isotherms are the large and nearly horizontal extension of the two-phase coexistence region and a comparably small change of the plateau pressure with temperature.

A comparison of the three selected *n*-hydroxystearic acids ($n = 9, 11, 12$) also reveals clear differences in the $\pi-A$ isotherms (see Figures 2–4). The extension of the plateau region increases from 9- to 12-hydroxystearic acid whereas the plateau pressure decreases for a given temperature. Usually, the presence of high NaCl concentrations does not greatly affect the $\pi-A$ isotherms. In the selected cases of OH-substitution in mid-position (9, 11, 12), the presence of 1 M NaCl increases the plateau pressure and shows slight shifts to smaller areas/molecule at the onset of the pressure increase. We observed this by a comparison with isotherms obtained for an aqueous
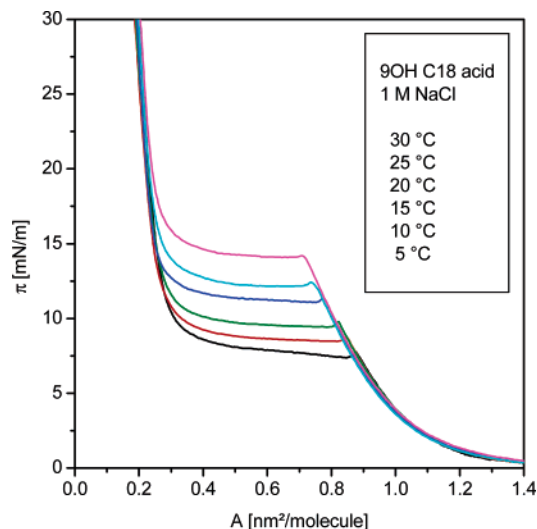
Figure 2. Surface pressure−area isotherms of 9-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase at different temperatures.
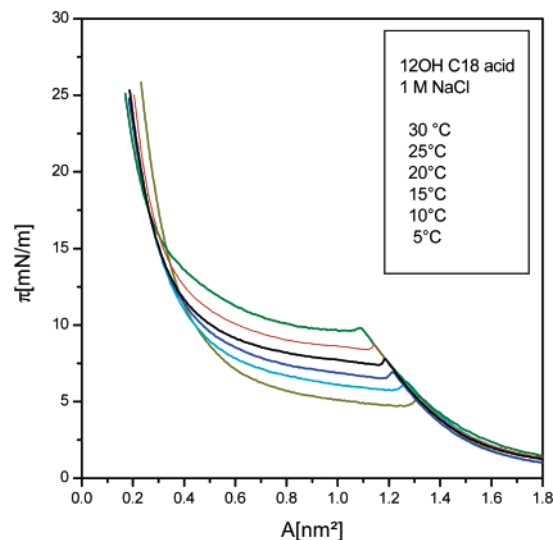

Figure 4. Surface pressure−area isotherms of 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase at different temperatures.
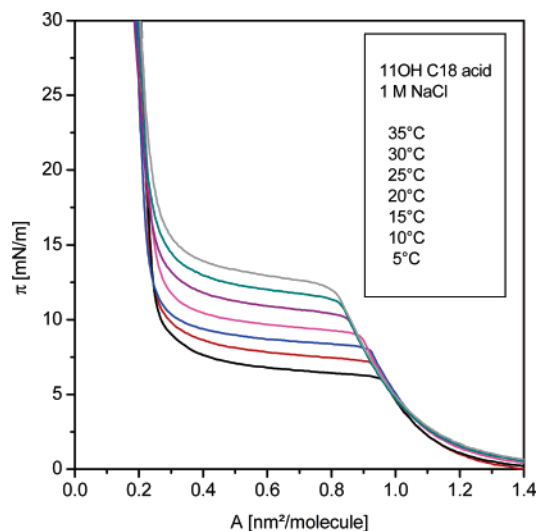

Figure 3. Surface pressure−area isotherms of 11-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase at different temperatures.

pH 3 subphase in the absence of NaCl. Figure 5a and 5b show two examples with an even more significant effect of high NaCl subphase concentrations. In the case of 2-hydroxystearic acid, the presence of 1 M NaCl in the subphase shifts the $\pi−A$ isotherm to considerably lower area values as shown for 30 °C in Figure 5a. A comparison of the $\pi−A$ isotherms of 9-hydroxystearic acid monolayers at low temperatures (5 °C) indicates that differences in the phase behavior are induced by high NaCl subphase concentrations (Figure 5b). In the absence of NaCl in the subphase, a break in the steep pressure rise of the condensed phase suggests a phase transition. This is missing in the presence of high NaCl concentrations in the subphase. As will be shown later, more detailed information about these differences in phase behavior are given by our GIXD results. The detailed thermodynamic analysis of the OH-substituted stearic acid monolayers is performed elsewhere.[19]

Large differences exist in the temperature dependence of the phase transition pressure π_t at A_c (Figure 6) of stearic acids OH-substituted near the COOH headgroup (in the 2-position) and those OH-substituted in mid-position of the alkyl chain (in the 9-, 11-, 12-position) spread on 1 M NaCl aqueous pH 3
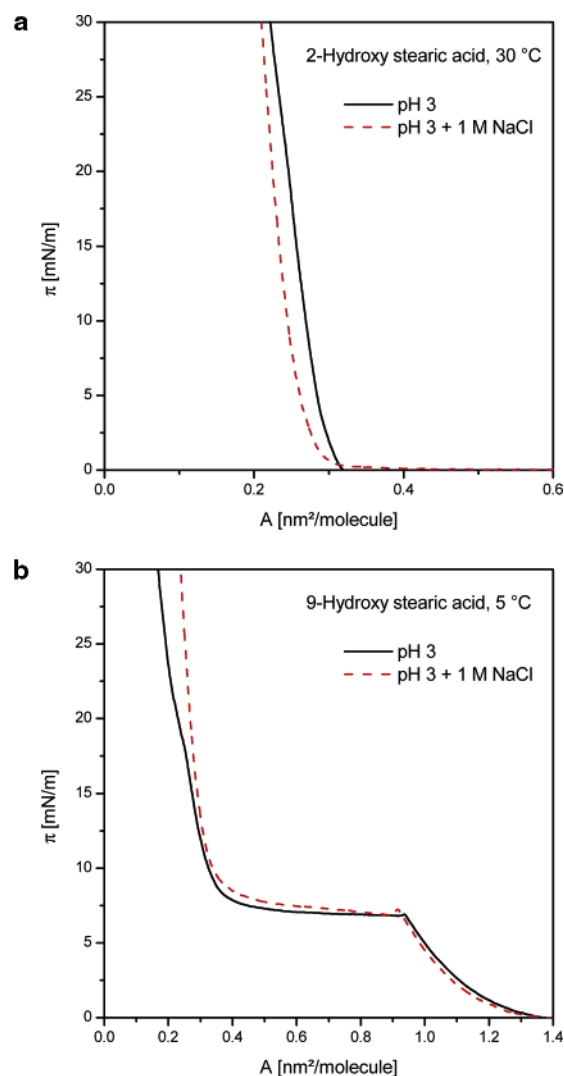

Figure 5. Comparison of surface pressure−area isotherms of *n*-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase and on pH 3 water under selected conditions: (a) 2-hydroxystearic acid at 30 °C, b) 9-hydroxystearic acid at 5 °C.

subphase. Linear π_t (*T*) relations are obtained for all OH-substituted stearic acids studied. However, in comparison with
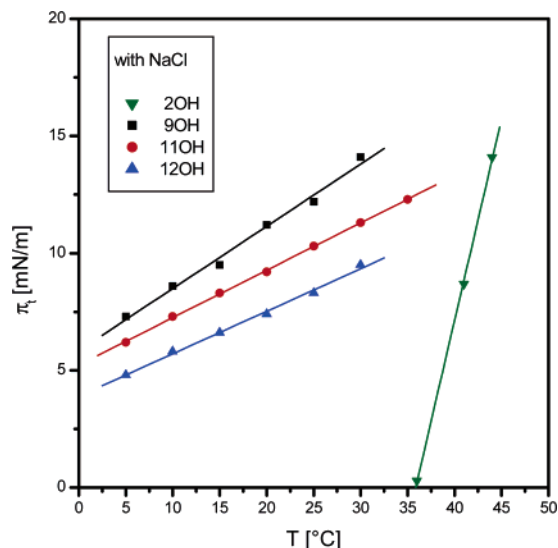
Figure 6. Temperature dependence of the main phase transition pressure (p_t) of 2-, 9-, 11-, and 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase.

usual amphiphiles with one alkyl chain (with $d\pi_t/dT \sim 1$ mN/m per 1 K) the $d\pi_t/dT$ slopes are very different. The $d\pi_t/dT$ value of the 2OH-substituted stearic acid monolayer is notably high with 1.72 mN/m per 1 K). A comparison with the $d\pi_t/dT$ value of 1.44 mN/m per K for the lower homologue 2-hydroxyhexdecanonoic acid shows that in addition the $d\pi_t/dT$ slope increases considerably as the alkyl chain length increases. On the other hand, the $d\pi_t/dT$ slopes of the three 9-, 11-, and 12-hydroxystearic acids are very small (0.27 mN/m per K for 9-hydroxystearic acid, 0.20 mN/m per K for 11-hydroxystearic acid, and 0.18 mN/m per K for 12-hydroxystearic acid) and the values decrease slightly from 9-OH- to 12-OH-substitution.

The temperature dependence of the entropy change ΔS for the phase transition can be determined by using the two-dimensional Clapeyron equation calculating the enthalpy ΔH of the phase transition

$$\Delta H = (A_c - A_e)T \frac{d\pi_t}{dT}$$

which is related with ΔS by the expression $\Delta H/T$.

The exothermic nature of the main phase transition on compression and an increase in the ordering of the system of amphiphilic monolayers give rise to negative ΔH and ΔS values. Figure 7 demonstrates large differences in the temperature dependence of ΔH and ΔS between the stearic acids OH-substituted near the COOH headgroup (in the 2-position) and those OH-substituted in mid-position of the alkyl chain (in the 12-position) spread on 1 M NaCl aqueous pH 3 subphase. It is easy to understand that, in both cases, the absolute $-\Delta S$ values increase as the temperature decreases since the ordering of the condensed phase increases with the decrease of temperature. However, for a further discussion of the thermodynamic data, the structure features of the corresponding monolayers must be considered. The BAM and GIXD studies discussed later, reveal a higher ordering of the condensed phases of hydroxystearic acids, when the OH substitution takes place in the mid-position, whereas with the OH group in the 2-position this will result in a loss of ordering of the monolayer structure.[12,13] On the other hand, the calculated absolute $-\Delta S$ values are lower for hydroxstearic acids OH-substituted in mid-position than for 2-hydroxystearic acid. In the case of 2-hydroxystearic acid
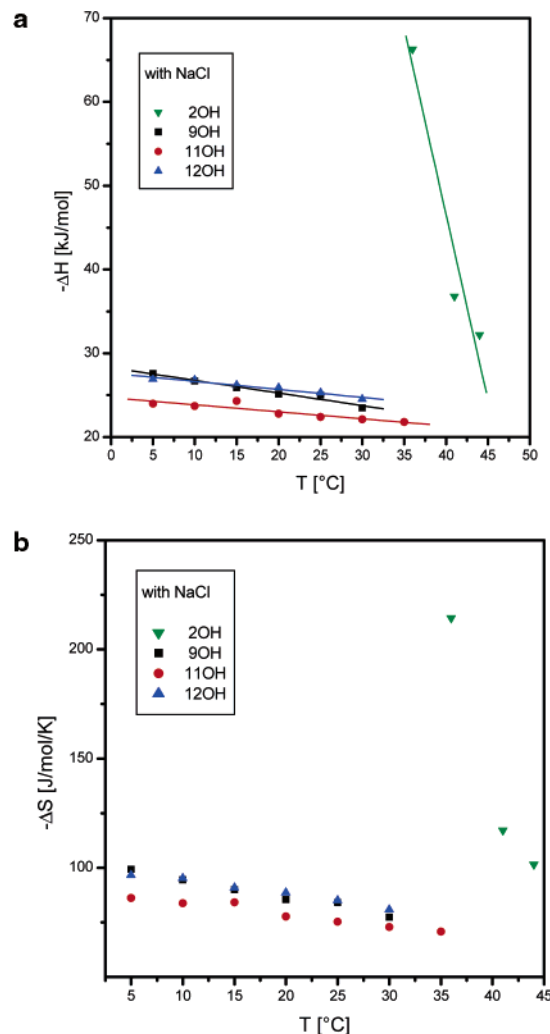

Figure 7. Temperature dependence of the change of enthalpy (a) and entropy (b) for the main phase transition of 2-, 9-, 11-, and 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase.

monolayers the absolute $-\Delta S$ values change drastically with temperature and attain comparably high absolute values. According to the GIXD and BAM results, it can be concluded that for OH-substitution near the COOH group, i.e., in the 2-position, both groups act as a monopolar entity. The enlargement of the headgroup gives rise to a misfit of the alkyl chain packing and a loss of ordering. Correspondingly, the thermal movement of the alkyl chains is strongly dependent on temperature (see Figure 7). In the case of 12-hydroxystearic acid (just as 9- and 11-hydroxystearic acid) the $-\Delta S$ change and its absolute values are comparably small. Thus, differences in the condensed phase ordering cannot be the sole reason for the thermodynamic characteristics. It is probable that, because of the bipolar character of the stearic acids OH-substituted in the mid-chain position, both polar groups contact the water interface and the molecules are oriented horizontally at the interface over a large area range. The lower absolute $-\Delta S$ values are understandable if, before the main phase transition, the fluid monolayer phase is subjected to a structure improvement conceivable in form of reorientation or even dimerization.

BAM studies provide information on the morphological features of the condensed phase domains formed in the two-phase coexistence region. In the case of 2-hydroxystearic acid, however, the $\pi-A$ isotherms (Figure 1) reveal that a strongly inclined small "plateau" region with a transition from the fluid

Figure 8. Representative condensed phase domains of 9-hydroxystearic acid monolayers at different temperatures spread on 1 M NaCl aqueous pH 3 subphase. Image size: $750 \times 750 \ \mu$m.
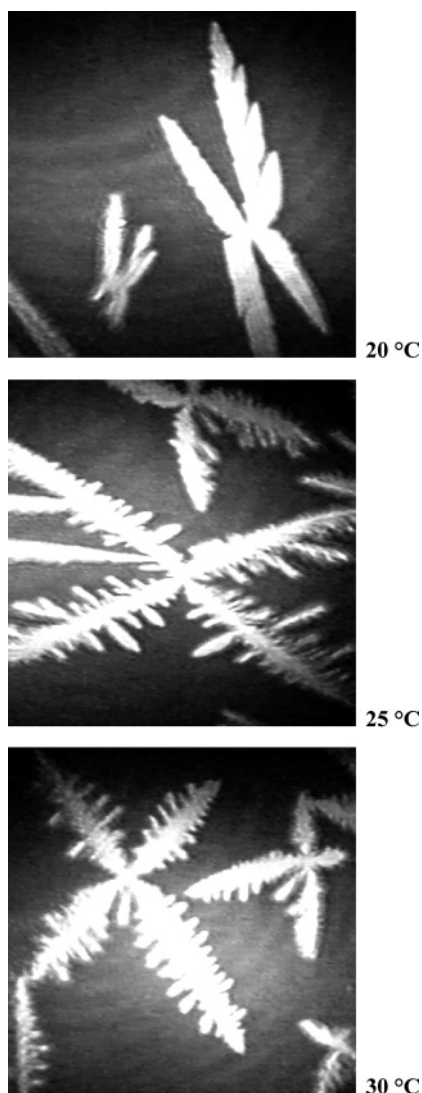

Figure 9. Representative condensed phase domains of 11-hydroxystearic acid monolayers at different temperatures spread on 1 M NaCl aqueous pH 3 subphase. Image size: 750×750 mm.

to a condensed phase is formed only at $T > 30$ °C. It is difficult to perform BAM experiments at such high temperatures. On the other hand, regular domain textures cannot be formed upon simple monolayer compression under the conditions at $T \leq 30$ °C where the isotherms indicate zero pressure for a fluid/condensed phase coexistence.[17,20] Depending on the experimental and spreading conditions, a rather irregularly shaped condensed phase is formed that does not allow any clear conclusion about its two-dimensional ordering.

In contrast to 2-hydroxystearic acid, the $\pi-A$ isotherms of all stearic acids OH-substituted in mid-position of the alkyl chain show an extended flat plateau region in the accessible temperature range so that within the fluid/condensed phase coexistence good conditions exist for the development of condensed phase domains under slow monolayer compression. The presentation of representative domains of the 9-, 11-, and 12OH-substituted stearic acid monolayers clearly show essential differences in the shapes, but they are always homogeneously reflecting, indicating that they have no inner texture (Figures 8−10).

In the case of 9-hydroxystearic acid, four-arm structures are formed which evolve many small sidearms with further growth (Figure 8). Details of the arm growth from a center are dependent on temperature. At 20 °C, two small acute angles

and two large obtuse angles between the four main arms are formed in opposing directions. At 25 °C, the angles approach each other, and at 30 °C, they are approximately equal each being about 90°.

Figure 9 shows characteristic domains of 11-hydroxystearic acid monolayers formed by growth in the fluid/condensed phase coexistence region at different temperatures. The needlelike crystalline character has a tendency, essentially independent of temperature, to split up at the ends.

Finally, typical domains of 12-hydroxystearic acid monolayers are presented in Figure 10 for 15, 20, and 25 °C and demonstrate that, in all cases, the shape is specifically determined by the position of OH-substitution. Here, several thin arms grow from a center which are curved at the lower temperatures (15 and 20 °C) and more or less straight at higher temperatures (25 °C) but always exhibit a tendency to undergo branching.

It is interesting to compare the characteristic domain shapes of monolayers spread on 1 M NaCl aqueous pH 3 subphase with those obtained on pure pH 3 water. Figure 11 shows a characteristic example for each *n*-hydroxystearic acid OH-substituted in mid-position at a selected temperature: on the left-hand side, the examples spread on pH 3 water, and on the right-hand side, the samples were spread on 1 M NaCl aqueous pH 3 water (top: 9-hydroxystearic acid, middle: 11-hydroxystearic acid, bottom: 12-hydroxystearic acid). Generally, the domain shapes obtained on both subphases are similar, but some
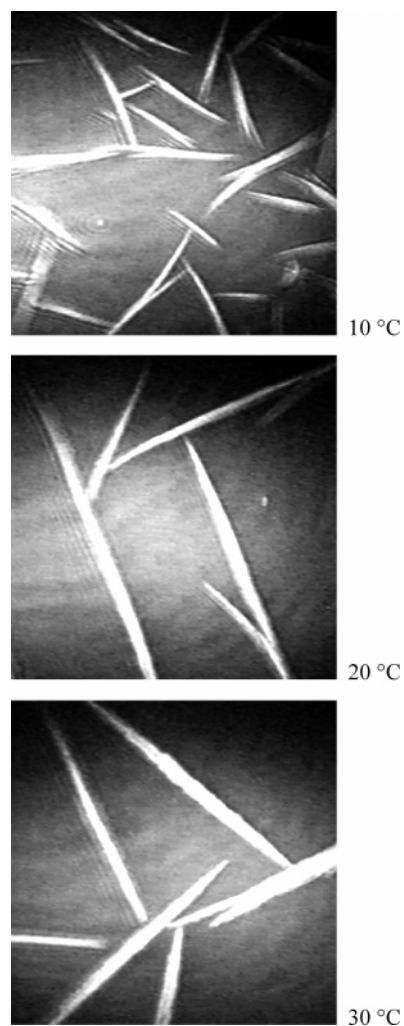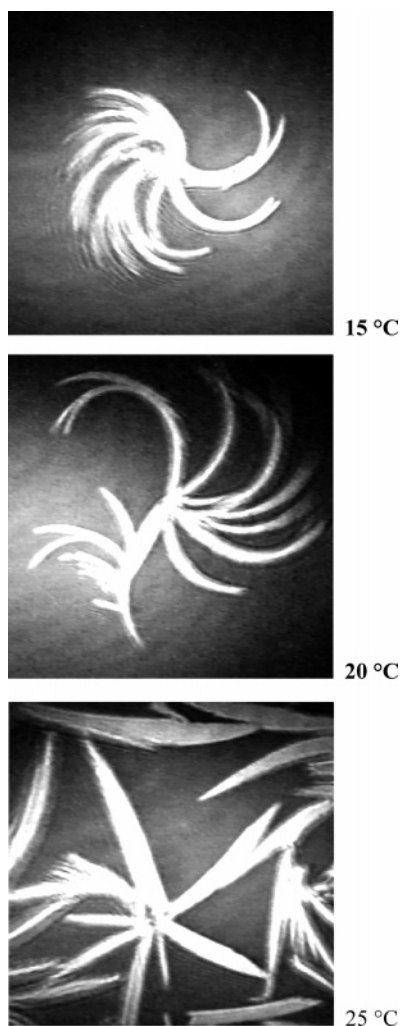
Figure 10. Representative condensed phase domains of 12-hydroxy-stearic acid monolayers at different temperatures spread on 1 M NaCl aqueous pH 3 subphase. Image size: 750 × 750 mm.

characteristic differences are clearly seen. Despite the differences in the domain shape between the isomeric hydroxystearic acids, the domains which are formed from monolayers spread on 1 M NaCl aqueous pH 3 subphase look more filigree and crystalline. This is apparent in the case of 9-hydroxystearic acid in a more regular growth of the four main arms, in the case of 11-hydroxystearic acid in the needlelike shape compared to the lancet-like shapes obtained on pH 3 water, and in the case of 12-hydroxystearic acid in the straighter shape and the preservation of growth from a center.

GIXD experiments were performed to study whether and which lattice structures are formed by *n*-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 solution and in which way the high NaCl subphase concentration affects the lattice structure of the monolayers. The contour plots of the corrected diffraction intensities as a function of the in-plane (Q_{xy}) and out-of-plane (Q_z) components of the scattering vectors of the monolayer of 9-, 11-, and 12-hydroxystearic acids are presented in Figures 12−14. The structure data calculated for different surface pressures of the three amphiphiles spread on 1 M NaCl aqueous pH 3 solution and on pH 3 water (for comparison) are listed in Table 1, wherein *a*, *b*, and *γ* are the unit cell parameters, A_{xy} is the in-plane molecule area, Ψ_a is the angle between azimuthal tilt direction and *a*-axis, *t* is the polar tilt angle, and A_0 is the cross-section area of the alkyl chain.
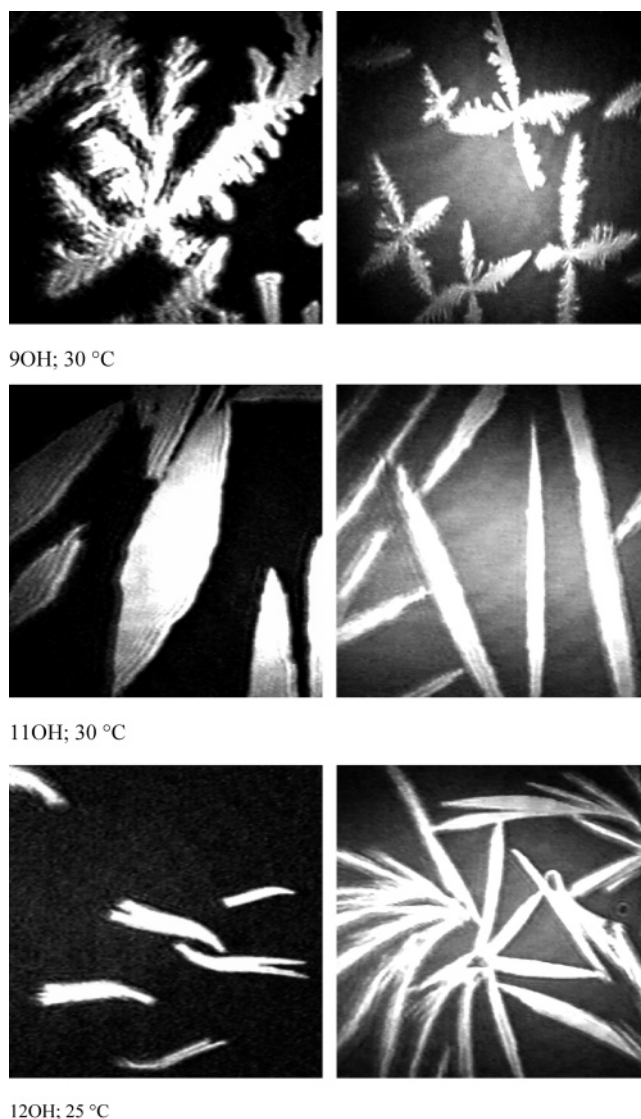

Figure 11. Comparison of characteristic condensed phase domains of 9-hydroxystearic acid monolayers (above), 11-hydroxystearic acid monolayers (middle), and 12-hydroxystearic acid monolayers (below): (a) on the left-hand side, spread on pH 3 water (b) on the right-hand side, spread on 1 M NaCl aqueous pH 3 subphase.

The patterns of the contour plots indicate different lattice types for the three isomeric *n*-hydroxystearic acids. The contour plot of 9-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 solution at relatively low surface pressure ($\pi =$ 6.4 mN/m) shows two reflexes with maxima at $Q_z = 0$ and $Q_z > 0$ characteristic of a centered rectangular lattice and alkyl chains are tilted toward their nearest neighbor (NN) direction (Figure 12). Already at $\pi \geq 10$ mN/m, the alkyl chains are normally erected, indicating that the polar tilt t is zero. The structure data obtained from GIXD measurements at 5 °C and 10 °C are nearly identical (see Table 1). Similar to the $\pi{-}A$ isotherms, the 2D lattice structure is only very slightly dependent on temperature.

In the case of 11-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 solution, the contour plots also show two reflexes, but here with both maxima at $Q_z > 0$ (Figure 13). Consequently, the alkyl chains are tilted toward next nearest neighbors (NNN) over the entire surface pressure range. Although the polar tilt angle t decreases as the surface pressure increases, the alkyl chains remain slightly tilted ($t = 2.5$ deg) at high surface pressure ($\pi = 30$ mN/m).

TABLE 1: Lattice Structure Data of 9-Hydroxyoctadecanoic Acid, 11-Hydroxyoctadecanoic Acid, and 12-Hydroxyoctadecanoic Acid Monolayers[a]

conditions	π, mN/m	a, Å	b, Å	γ, deg	A_{xy}, Å^2	t, deg	td	A_0, Å^2
				9-Hydroxyoctadecanoic Acid				
pH 3, 5 °C	10	4.79	4.89	120.7	20.7	12.6	NNN	20.2
	20	4.63	4.82	122.6	19.6	4.8	NN	19.5
	25	4.62	4.81	122.6	19.5	0		19.5
pH 3, 1 M NaCl, 5 °C	10	4.74	4.87	121.8	20.2	6.9	NN	20.0
	20	4.66	4.83	122.4	19.7	0		19.7
	25	4.62	4.81	122.6	19.5	0		19.5
	30	4.61	4.81	122.7	19.4	0		19.4
pH 3, 1 M NaCl, 10 °C	15	4.64	4.82	122.4	19.6	4.8		19.5
	20	4.63	4.81	122.4	19.5	0		19.5
				11-Hydroxyoctadecanoic Acid				
pH 3, 5 °C	10	4.95	4.99	120.5	21.4	21.5	NNN	19.9
	20	4.69	4.85	122.1	19.9	9.3	NNN	19.7
pH 3, 1 M NaCl, 5 °C	10	4.87	5.00	120.9	20.9	16.4	NNN	20.1
	20	4.81	4.96	121.1	20.4	8.7	NNN	20.2
	30	4.76	4.94	121.2	20.1	2.5	NNN	20.1

conditions	π, mN/m	a, Å	b, Å	γ, deg	A_{xy}, Å^2	t, deg	Ψ_a	A_0, Å^2
				12-Hydroxyoctadecanoic Acid				
pH 3, 5 °C	6	4.61	4.99	112.3	21.3	20.3	28	20.0
	10	4.60	4.99	112.3	21.2	19.5	25	20.0
	20	4.40	5.01	114.0	20.2	5.5	30	20.0
pH 3, 1 M NaCl, 5 °C	10	4.56	5.00	112.7	21.0	17.6	24	20.0
	20	4.40	5.03	114.5	20.1	9.7	27	19.9

[a] π, surface pressure; a, b, g, lattice constants; A_{xy}, molecular area; t, polar tilt angle; A_0, cross-section area of alkyl chain; td, tilt direction; y_a, angle between azimuthal tilt direction and a-axis.
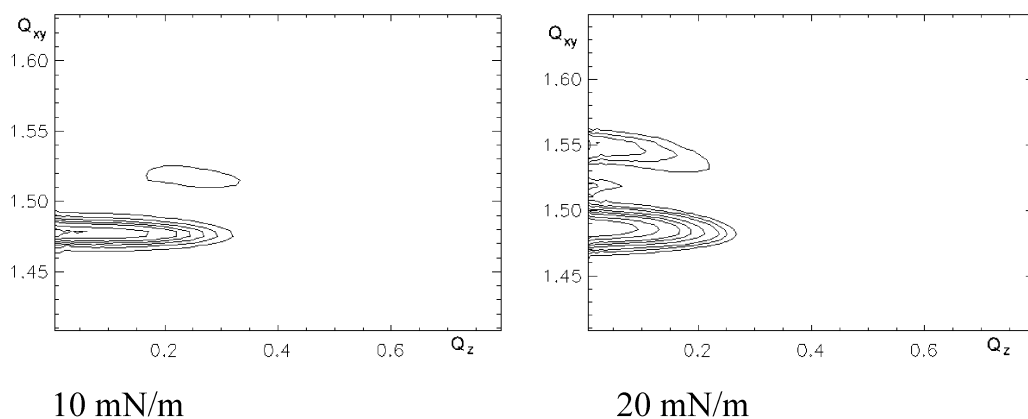

Figure 12. Contour plots of the corrected diffraction intensities as a function of the in-plane (Q_{xy}) and out-of-plane (Q_z) components of the scattering vectors of 9-hydroxystearic acid monolayer spread on 1 M NaCl aqueous pH 3 subphase at 5 °C; $\pi = 10$ mN/m, (left), $\pi = 20$ mN/m (right).

Figure 13. Contour plots of the corrected diffraction intensities as a function of the in-plane (Q_{xy}) and out-of-plane (Q_z) components of the scattering vectors of 11-hydroxstearic acid monolayer spread on 1 M NaCl aqueous pH 3 subphase at 5 °C; $\pi = 10$ mN/m, (left), $\pi = 20$ mN/m (right).
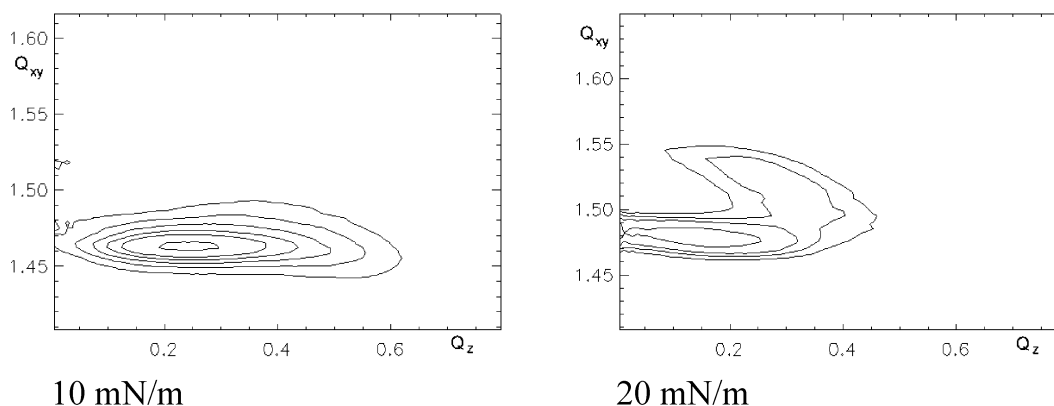
The three reflexes ($Q_z > 0$) of the contour plots obtained for 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 solution (Figure 14) indicate an oblique lattice of the alkyl chains in the accessible surface pressure range. A comparison of the GIXD results therefore clearly show that the lattice structures of the condensed monolayer phases of the bipolar
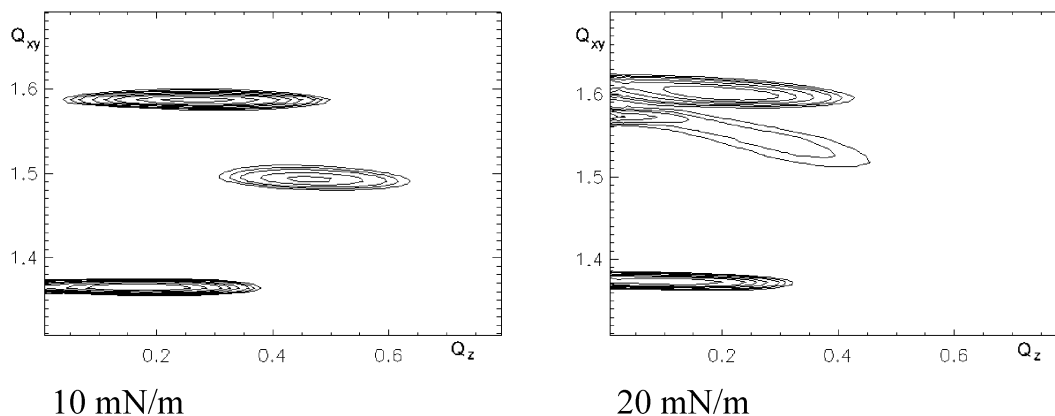
10 mN/m   20 mN/m

Figure 14. Contour plots of the corrected diffraction intensities as a function of the in-plane (Q_{xy}) and out-of-plane (Q_z) components of the scattering vectors of 12-hydroxyostearic acid monolayer spread on 1 M NaCl aqueous pH 3 subphase at 5 °C; $\pi = 10$ mN/m, (left), $\pi = 20$ mN/m (right).

n-hydroxystearic acids are highly sensitive to the position of OH-substitution of the alkyl chain.

A comparison with GIXD results obtained for the same *n*-hydroxystearic acid monolayers but spread on pH3 water[21,22] provides information whether or not, and in which way, the two-dimensional lattice structure is affected by high concentrations of a simple electrolyte (1 M NaCl) in the aqueous subphase. In the case of 11- and 12-hydroxystearic acid monolayers, the same lattice type is formed for both subphases. The high concentration of a simple electrolyte in the aqueous subphase merely gives rise to a tighter molecular packing, as demonstrated by the lattice data listed in Table 1. At the same surface pressure, the polar tilt of the alkyl chains is reduced by the effect of the high NaCl concentration with consequences on the in-plane molecule area A_{xy} and the unit cell parameters *a*, *b*, and *γ*.

The tendency that a high NaCl concentration gives rise to tighter molecule packing and reduced polar tilt of the alkyl chain also exists in 9-hydroxystearic acid monolayers. However, in this case it is associated with a change in the lattice structure. The monolayers spread on pH 3 water at 5 °C indicate a phase transition between two condensed phases between 10 and 20 mN/m. According to the position of the two reflexes of the contour plots, the molecular tilt in the lower surface pressure region at $\pi=10$ mN/m (both reflexes with $Q_z > 0$) are in the NNN (next nearest neighbor) direction, whereas at higher surface pressures ($\pi=20$ mN/m) the molecules are tilted toward the NN (nearest neighbor) direction ($Q_z = 0$ and $Q_z > 0$). In the presence of the high electrolyte concentration in the aqueous subphase, the reduced polar tilt of the alkyl chain prevents the formation of the NNN rectangular lattice, as observed at lower surface pressures ($\pi \leq 10$ mN/m). These GIXD results on the effect of high NaCl concentration on the phase behavior of 9-hydroxystearic acid monolayers provide detailed information on the corresponding lattice types and support the conclusions suggested on the basis of the $\pi-A$ isotherms.

Conclusions

Selected *n*-hydroxystearic acids are well suited to study whether and in which way high NaCl concentrations in the subphase affect the monolayer features of these amphiphiles. Therefore, the main characteristic features of 2-, 9-,11-, and 12-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase have been determined by studying the phase behavior, morphological texture, and lattice structure. Large differences have been found between the monolayer characteristics of stearic acid OH-substituted near the COOH-group (2-

position) when both groups act as a monopolar entity and those OH-substituted in mid-position of the alkyl chain (9-, 11-, 12-position) when the molecule has bipolar character. The extended flat plateau regions of the $\pi-A$ isotherms of the bipolar 9-, 11-, and 12-hydroxystearic acid monolayers are only slightly dependent on temperature indicating a fluid/condensed main phase transition at $\pi > 0$ for all measured temperatures in the accessible region. In the case of 2-hydroxystearic acid monolayers, beginning at $T > 30$ °C**,** an inclined small "plateau" region which is strongly temperature dependent shows a fluid/condensed phase coexistence. Corresponding differences exist in the linear temperature dependencies of the phase transition pressure (π_t). Compared with the usual nonsubstituted amphiphiles, the $d\pi_t/dT$ slope is much smaller for the hydroxystearic acids OH-substituted in mid-position, and it is larger for 2-hydroxystearic acid**.** Analogous differences have been calculated for the entropy changes ΔS of the main phase transition. The ΔS values have been discussed on the basis of the structural features and their dependence on the OH-position on the alkyl chain. The morphology of the condensed phase domains formed in the fluid/condensed coexistence region is specific for the position of OH substitution of the alkyl chain, as are the lattice structures of the condensed monolayer phase. An analysis of the irregular structures of 2-hydroxystearic acid monolayers was not performed. 9-Hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase form centered rectangular lattices with chain tilt toward the NN direction and are untilted to higher pressures, 11-hydroxystearic acid monolayers form centered rectangular lattices with chain tilt toward the NNN direction and 12-hydroxystearic acid monolayers have an oblique lattice over the entire pressure range.

The comparison of the selected *n*-hydroxystearic acid monolayers spread on 1 M NaCl aqueous pH 3 subphase with those spread on pH 3 water shows that differences in the main characteristics of the $\pi-A$ isotherms and the structure features exist only in detail and are obviously related to the tendency that high NaCl concentration induces a tighter molecular packing and, consequently, a reduced polar tilt of the alkyl chain. This has consequences in the special case of 9-hydroxystearic acid monolayer**s** spread on pH 3 water at 5 °C for the phase transition between two condensed phases which occurs between a rectangular lattice with chain tilt toward NNN and that with chain tilt toward NN and is indicated in the $\pi-A$ isotherm at ~18 mN/m. This phase transition disappears if the monolayer is spread on a 1 M NaCl aqueous pH 3 subphase and only a slightly tilted phase toward NN occurs at lower pressures followed by an untilted phase at higher pressures.

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