Effect of the Hydroxyl Group Position on the Phase Behavior of Hydroxyoctadecanoic Acid Monolayers at the Air/Water Interface

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Surface pressure–area per molecule (Π–A) isotherms and lattice structures of *n*-hydroxyoctadecanoic acid monolayers with $n = 2, 9, 11,$ and 12 are experimentally studied to obtain information on the effect of the hydroxyl group position on the phase behavior and properties of the monolayers. Striking differences exist between the monolayers of 2-hydroxyoctadecanoic acid and hydroxyoctadecanoic acids with $n = 9$–12. Theoretical calculations of the Π–A isotherms are performed to explain the strong effect of the position of the OH-substitution on the thermodynamic properties of the monolayers. The calculations provide reasonable agreement between the theoretical predictions and the experimental Π–A isotherms are obtained as well as between the parameters calculated from the theoretical model and those obtained from the GIXD measurements. The combination with the experimental GIXD data allows conclusions on the orientation of the molecules in the different monolayer states and their changes at the main phase transition. For 2-hydroxyoctadecanoic acid monolayers, a disordered packing is found in all monolayer states, whereas for (9–12)-hydroxyoctade-canoic acid monolayers, well-ordered 2D lattice structures stabilized by hydrogen bonding between the OH-groups are formed. The data analysis indicates that at OH-substitution in the 2-position the neighboring polar group acts as a monopolar entity. At OH-substitution in the (9–12)-position both polar groups lead to bipolar behavior. At the main phase transition, the weaker polar OH-group is forced out of the water interface and well-ordered 2D lattice structures stabilized by hydrogen bonding between the OH-groups are formed. 9-Hydroxyoctadecanoic acid monolayers show an interesting second phase transition at $\Pi = 18$ mN/m between two condensed phases which can be satisfactorily described by the theoretical model which assumes two-dimensional compressibility of the condensed monolayer.

Introduction

In recent years, phase behavior, morphological texture, and lattice structure of amphiphilic monolayers of various homologous series have been effectively studied.[1,2] Correspondingly, new information has been obtained on the effect of the chemical headgroup structure on the monolayer features and their systematic change in dependence on the alkyl chain length.

New studies on the effect of alkyl chain branching or substitution of a second polar group are comparatively rare. Monolayers of hydroxy fatty acids are ideal candidates as bipolar model amphiphiles for studying the effect of an attached secondary polar group. The hydroxyl group is the simplest hydrophilic group with the smallest cross-section area. Therefore it has been of interest to study the effect of the hydroxyl position in the alkyl chain on the features of the monolayers. More than 50 years ago, Bergström et al.[3] synthesized all seventeen isomeric hydroxyoctadecanoic acids but they did not publish their surface properties. Later, Cadenhead et al. drew attention to hydroxy fatty acids and their esters as model systems to characterize bipolar monolayers.[4–6] Recent fluorescence microscopy and Brewster angle microscopy studies of selected OH-substituted fatty acids provided the first information on the domain morphology of the condensed monolayer phase.[7–10]

The present work focuses on the thermodynamic peculiarities of the OH-substituted monolayers. When the hydroxyl group is positioned beyond the fifth or sixth carbon position the surface pressure–area per molecule (Π–A) isotherms show a large area/molecule change for the main phase transition which is much larger than that for typical amphiphiles nonsubstituted in the alkyl chain. In contrast, OH substitution in the 2-position gives rise to a loss of ordering. The absence of long-range tilt orientational order observed in these systems is obviously correlated to a disordered packing of alkyl chains.[9] The objective of this work is to provide first theoretical information on the effect of the OH-substitution of the alkyl chain in different positions. As the basis for the theoretical analysis, Π–A isotherms of 2-, 9-, 11-, and 12-hydroxyoctadecanoic acid monolayers are experimentally studied at selected temperatures. Theoretical models which are based on the generalized Volmer's equation and the mass action law[11–15] are used to describe the differences in the Π–A isotherms and the two-dimensional phase transition of these OH-substituted octadecanoic acid monolayers. The theoretical results are supported by data of grazing incidence X-ray diffraction (GIXD) measurements.

Experimental Section

The surface pressure–area (Π–A) isotherms were measured at different temperatures using a computer-interfaced film balance. The trough was equipped with a Wilhelmy balance for surface pressure determination and a temperature control system. Using a roughened glass plate the surface pressures

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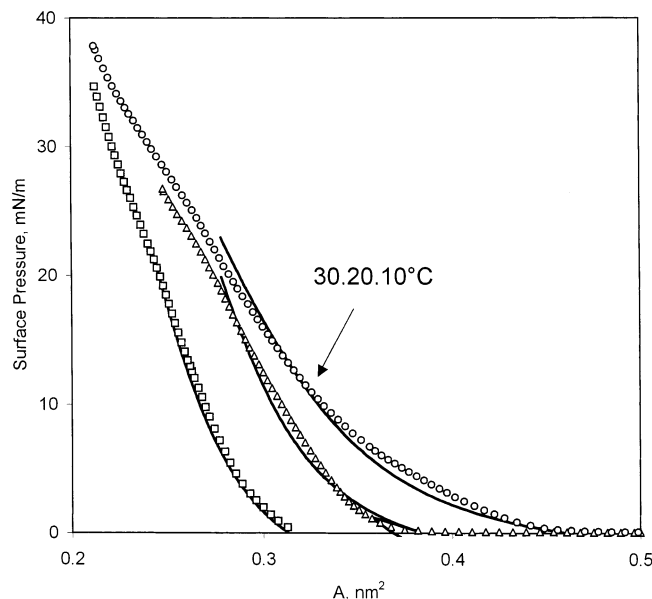† Max Planck Institute of Colloids and Interfaces.
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Figure 1. Experimental and theoretical $\Pi-A$ isotherms of the 2-hydroxyoctadecanoic acid monolayer at different temperatures on pH 3 subphase (dotted lines; the numbers at the lines indicate the temperature in °C). Solid lines, the values calculated from the theoretical model on the basis of eqs 1−5.

measured were reproducible to ± 0.1 mN m^{-1} and the areas per molecule to ± 0.005 nm^2. The temperature of the experimental system was controlled to within ± 0.1 °C. The film balance was sheltered in a cabinet to avoid excessive disturbances by convection and contamination by impurities.

The 2-, 9-, 11-, and 12-hydroxyoctadecanoic acids purchased from Nu-Check Prep Inc., Elysian, Minnesota, were dissolved in a 9:1 hexane−ethanol mixture. After evaporating the spreading solvent the molecules remaining at the air−water interface were continuously compressed at rates of 0.1 nm^2 molecule^{-1} min^{-1}. Ultrapure deionized water with the conductivity of 0.055 μS/cm produced by "Purelab Plus" was adjusted with HCl to pH 3 and used as subphase.

The GIXD data used are part of a comprehensive study of the texture and structure features of OH-substituted octadecanoic acids which will be published elsewhere. The GIXD experiments were performed using the liquid-surface diffractometer on the undulator beamline BW1 at HASYLAB, DESY, Hamburg, Germany. The measuring procedure and data treatment was performed analogously to that described in ref 17.

Results and Discussion

The experimental $\Pi-A$ isotherms of the monolayers of n-hydroxyoctadecanoic acid ($n = 2, 9, 11, 12$) measured at various temperatures and pH 3 for the subphase are shown in Figures 1−4. It is seen that the behavior of the isotherms of 2-hydroxyoctadecanoic acid monolayers is essentially different from those obtained for $n = 9-12$. For $n = 2$, the isotherms do not exhibit any fluid (gaseous or liquid-expanded) monolayer state. Similar to the nonsubstituted octadecanoic acid, the two-phase coexistence region exists already at zero pressure (no plateau in the $\Pi-A$ isotherm). This can be also concluded from the $\Pi-A$ isotherms of the homologous 2-hydroxypalmitic acid monolayers.[9,10] Grazing incidence X-ray diffraction (GIXD) studies of this monolayer reveal diffraction patterns that indicate a disordered packing of alkyl chains. These GIXD data result from a distortion of the alkyl chain packing and could be explained by the superposition of lattices with varying tilt
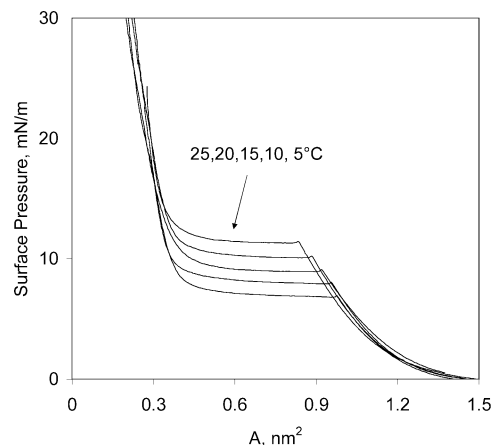

Figure 2. Experimental $\Pi-A$ isotherms of the 9-hydroxyoctadecanoic acid monolayer at different temperatures on pH 3 subphase.
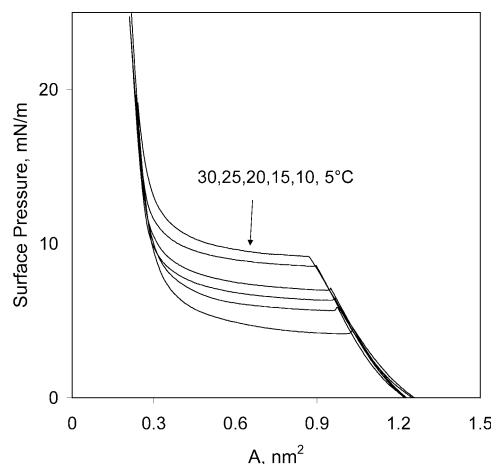

Figure 3. Experimental $\Pi-A$ isotherms of the 11-hydroxyoctadecanoic acid monolayer at different temperatures on pH 3 subphase.
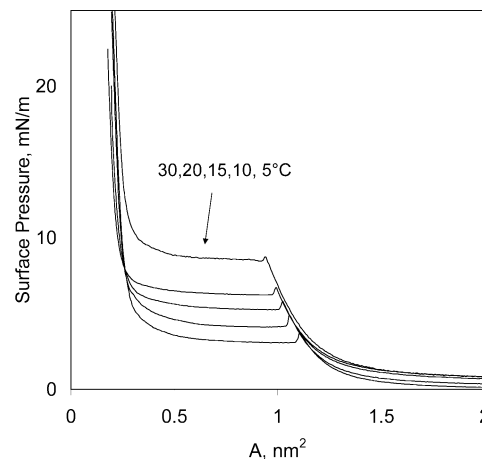

Figure 4. Experimental $\Pi-A$ isotherms of the 12-hydroxyoctadecanoic acid monolayer at different temperatures on pH 3 subphase.

azimuth of alkyl chains. A simple geometric comparison between the headgroup and alkyl chain lattices shows that the chain packing needs to be distorted to allow an adaptation of alkyl chains to headgroups which are too large perpendicular to the chain tilt direction because the −COOH headgroup and the neighbored OH-group in the 2-position act as a monopolar entity. The alkyl chains are not able to adapt their packing to the lattice of this monopolar entity. The disordered packing is obviously related to the low long-range tilt orientational order, as also observed with other amphiphiles substituted in the
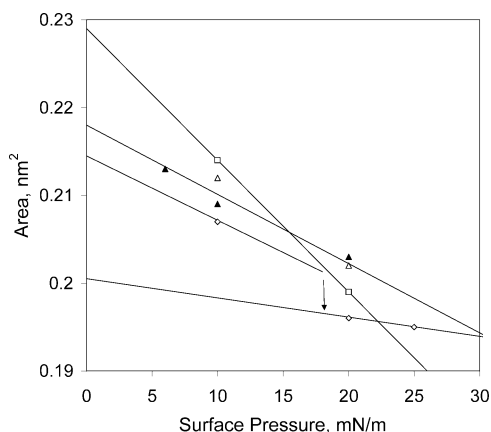
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Figure 5. Dependence of the molecule area of *n*-hydroxyoctadecanoic acid monolayers in the condensed monolayer state on the surface pressure obtained from GIXD data: ◇, *n* = 9 at 5 °C; □, *n* = 11 at 5 °C; △, *n* = 12 at 5 °C; ▲, *n* = 9 at 10 °C. See detailed discussion in the text.

Figure 6. Experimental (dotted line) and theoretical (model on the basis of eqs 1−5, solid line) Π−*A* isotherms of the 9-hydroxyoctadecanoic acid monolayer at different temperatures. Curve A was calculated for the fluid monolayer from eq 1 with ω = 0.29 nm^2 and 25 °C.

Figure 7. Experimental (dotted line) and theoretical (model on the basis of eqs 1−5, solid line) Π−*A* isotherms of the 11-hydroxyocta-decanoic acid monolayer at different temperatures.

2-position by a second polar group. Consequently, the mono-layers of these amphiphiles do not form well-shaped condensed phase domains with inner texture.

In the case of (9, 11, or 12) OH-substituted octadecanoic acids, the monolayer characteristics are completely different. It can be seen from Figures 2−4 that for all measured temperatures in the accessible region the Π−*A* isotherms have the main phase transition between the fluid and condensed phase at Π > 0 and follow the general rule that with increasing temperature the surface pressure of the plateau also increases with a kink point at the beginning of the first-order phase transition at *A* = *A*$_c$. Consequently, at *A* > *A*$_c$ the monolayer exists in the fluid (gaseous, LE) state. The large extension of the two-phase coexistence region is noteworthy.

The GIXD data of these monolayers indicate the formation of condensed phase with ordered lattice structures. Figure 5 illustrates the dependence of the horizontal projection area of *n*-hydroxyoctadecanoic acid molecule in the condensed state on the surface pressure. These data, similar to those reported earlier for other amphiphilic molecules,[16−20] indicate two-dimensional compressibility of the condensed monolayers. It is interesting to note that for the 9-hydroxyoctadecanoic acid at Π = 18 mN/m, a second condensed phase was found (shown by an arrow in the Figure); this fact is discussed below.

To understand this drastic difference in the behavior of the 2OH- and (9−12) OH-substituted octadecanoic acids, it is instructive to compare the experimental Π−*A* isotherms with the theoretical predictions. At pH 3 of the subphase, all hydroxyoctadecanoic acids are nondissociated in the monolayer, and therefore the equation of state for monolayers in the fluid (G or LE) state is represented by Volmer's equation:[13, 14]

$$\Pi = \frac{kT}{A - \omega} - \Pi_{\text{coh}} \qquad (1)$$

In the phase coexistence region (*A* < *A*$_c$) the generalized Volmer's equation leads to[13,14]

$$\Pi = \frac{kT\alpha\beta}{A - \omega[1 + \epsilon(\alpha\beta - 1)]} - \Pi_{\text{coh}} \qquad (2)$$

In these equations, Π is the surface pressure, *k* is the Boltzmann constant, *T* is temperature, ω is the partial molecular area for monomers (or the limiting area of molecule in the gaseous state), *A* is the area per molecule, *A*$_c$ is the molecular area which
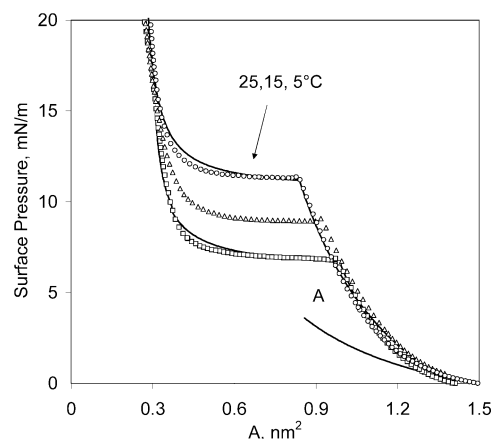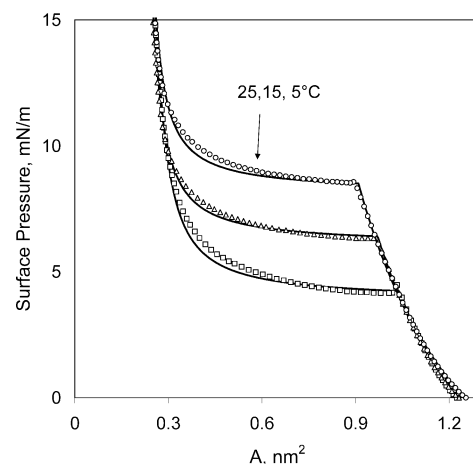
corresponds to the onset of the phase transition (i.e., at Π = Π$_c$), and Π$_{\text{coh}}$ is the cohesion pressure, which accounts for the intermolecular interaction. The parameter α expresses the dependence of the aggregation constant on the surface pressure:

$$\alpha = \frac{A}{A_c}\exp\left[-\epsilon\frac{\Pi - \Pi_c}{kT}\omega\right] \qquad (3)$$

and β is the fraction of the monolayer free from aggregates:

$$\beta = 1 + \omega(1 - \epsilon)(\alpha - 1)/A \qquad (4)$$

where $\epsilon = 1 - \omega_{\text{cl}}/\omega$, and ω_{cl} is the area per monomer in a cluster.

The area per molecule in the cluster can be different from the limiting area per molecule in the gaseous state. This fact is accounted for by the parameter $\epsilon = \epsilon_0 + \eta\Pi$:[20]

$$\omega_{\text{cl}} = \omega(1 - \epsilon) = \omega(1 - \epsilon_0 - \eta\Pi) \qquad (5)$$

where ϵ_0 is the relative jump of the area per molecule, and η is a relative two-dimensional compressibility of the condensed monolayer.

The theoretical and experimental surface pressure isotherms of *n*-hydroxyoctadecanoic acids are compared in Figures 1 and Figures 6−8 for selected temperature values. The parameters of eqs 1−5 are listed in Tables 1−4. Note that a rather
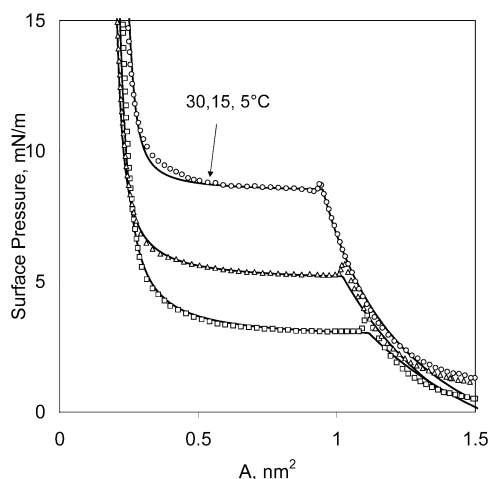
Figure 8. Experimental (dotted line) and theoretical (model on the basis of eqs 1−5, solid line) Π−A isotherms of the 12-hydroxyocta-decanoic acid monolayer at different temperatures.

TABLE 1: Characteristics of the 2-Hydroxyoctadecanoic Acid Monolayer

temperature, °C	10	20	30
ω, nm^2	0.27	0.30	0.31
A_c, nm^2	0.87	0.87	0.87
η, m/mN	0.0045	0.0045	0.0045
ϵ_0	0	0	0
ω_{cl0}, nm^2	0.27(0.23)^a	0.30(0.26)	0.31(0.27)
Π_{coh}	9.7	8.7	8.5

^{a} In parentheses in this and other tables shown is the ω_{cl} value at Π = 30 mN/m.

TABLE 2: Characteristics of the 9-Hydroxyoctadecanoic Acid Monolayer

temperature, °C	5	5(II)^a	15	25
ω, nm^2	0.67	0.67	0.65	0.60
A_c, nm^2	0.99	0.85	0.93	0.85
η, m/mN	0.0015	0.0005	0.0015	0.0015
ϵ_0	0.56	0.64	0.55	0.57
ω_{cl0}, nm^2	0.29(0.26)	0.24(0.22)	0.29(0.26)	0.29(0.26)
Π_{coh}	5.6	5.6	5.0	4.9

^{a} In this column shown are the parameters of second phase transition.

TABLE 3: Characteristics of the 11-Hydroxyoctadecanoic Acid Monolayer

temperature, °C	5	15	25
ω, nm^2	0.71	0.68	0.64
A_c, nm^2	1.04	0.97	0.91
η, m/mN	0.002	0.002	0.002
ϵ_0	0.62	0.62	0.6
ω_{cl0}, nm^2	0.26(0.22)	0.26(0.22)	0.25(0.21)
Π_{coh}	7.6	7.2	6.4

TABLE 4: Characteristics of the 12-Hydroxyoctadecanoic Acid Monolayer

temperature, °C	5	15	30
ω, nm^2	0.59	0.62	0.62
A_c, nm^2	1.12	1.03	0.95
η, m/mN	0.002	0.0015	0.002
ϵ_0	0.60	0.64	0.6
ω_{cl0}, nm^2	0.23(0.195)	0.22(0.192)	0.24(0.203)
Π_{coh}	4.1	4.2	4.3

satisfactory agreement between the theoretical and experimental isotherms is seen to exist for all the OH-substituted acids. Comparing the parameters listed in Table 1 with those shown in Tables 2−4 one notes an essential difference between these parameters for the different OH-substituted acids. For the 2-hydroxyoctadecanoic acid the value $\epsilon_0 = 0$, and therefore,

according to eq 5, the ω value is equal to the ω_{cl0}, where ω_{cl0} is the value of ω_{cl} at Π = 0. This suggests a similar orientation of the 2-hydroxyoctadecanoic acid molecule in the fluid (gaseous) monolayer as in the aggregated monolayer. These thermodynamic conclusions are in reasonable agreement with the structure information obtained by BAM and GIXD that also in the condensed state the 2-hydroxyoctadecanoic acid molecule are rather disordered in the monolayer.

For the monolayers of the (9−12)-hydroxyoctadecanoic acids the parameter values are much higher than those of the 2-hydroxyoctadecanoic acid: $\epsilon_0 = 0.55-0.65$, and $\omega = 0.6-0.7$ nm^2 where ω is the limiting area of the molecule in the gaseous state. After the onset of phase transition, however, the molar area ω_{c10} of these (9−12)-hydroxyoctadecanoic acids becomes significantly lower ($\omega_{c10} = 0.22-0.29$ nm^2). These ω values are quite realistic for the (9−12)-hydroxyoctadecanoic acids. That can be demonstrated by using the ω_{c10} value of the condensed phase after the phase transition (i.e., $\omega = 0.29$ nm^2) for the fluid (LE and gaseous) monolayer in eq 1, i.e., assuming $\epsilon_0 = 0$. For this case, curve A in Figure 6 shows considerable differences to the experiment whereas with the calculated parameter values reasonable agreement with the experimental exists. The large difference of the ω-values before and after the phase transition point indicate corresponding differences in the orientation of the molecules. In the fluid state, both polar groups interact with the water molecules and according to the high ω-values, the molecules lie approximately flat at the water surface. At OH-substitution in 9−12 position of the alkyl chain the molecules show bipolar behavior. At phase transition, i.e., at compression to A_c (the area per molecule which corresponds the onset of the phase transition) the molecules undergo a conformational change. In the aggregated state, the weaker polar OH-group is forced out of the water. Obviously, well-ordered 2D lattice structures stabilized by hydrogen bonding between the OH-groups[21] are formed in the condensed state in which the molecules are perpendicularly aligned.

Compare next the experimental ω_{cl0} values obtained by GIXD (the intersection point of the corresponding straight line in Figure 5) with the ordinate axis and the two-dimensional (2D) compressibility of condensed monolayers (the slopes of the straight lines in Figure 5) with the model values shown in Tables 2−4. It follows from Figure 5 that the absolute values of the 2D-compressibility are 0.0008 nm^2/(mN/m) for $n = 12$ and $n = 9$ (for the last only at Π < 18 mN/m), and 0.0015 nm^2/(mN/m) for $n = 11$. As in this case of $n = 9$ at Π < 18 mN/m there is only one experimental point, the slope was assumed to be equal to that for $n = 12$. These values, recalculated into the relative two-dimensional compressibility, cf. eq 5, become 0.0013−0.0014 m/mN and 0.002−0.0025 m/mN, respectively, which fairly well coincide with the theoretical estimates made using eqs 1−5 of the model and listed in the tables. The ω_{c10} values given by the GIXD data (see Figure 5) for (9−12)-hydroxyoctadecanoic acid monolayers are 0.218 nm^2 for $n = 12$, 0.215 nm^2 for $n = 9$ (at Π < 18 mN/m), and 0.229 nm^2 for $n = 11$. At the same time, the calculations using the theoretical model yield values of the area per molecule in the clusters of the condensed phase by 10−25% higher than those given above. The ω_{cl}-values at Π = 30 mN/m calculated from eq 5 are listed in the parentheses of Table 1. One possible cause of the disagreement between the GIXD and model data is the approximate nature of the theory,[13,14,20] which neglects the influence of clusters (as kinetic entities) on the surface pressure. In fact, it is completely correct only at the initial stage of the two-dimensional condensation and for very large clusters.
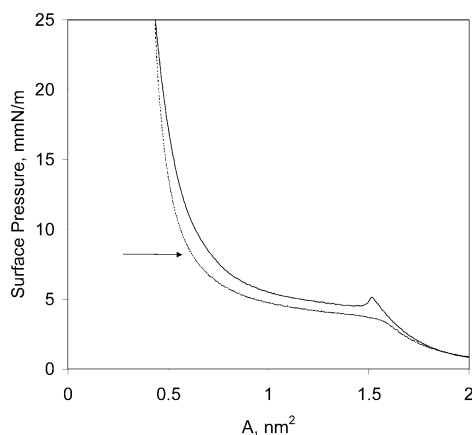
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Figure 9. Experimental $\Pi-A$ isotherm of the 12-hydroxyoctadecanoic acid monolayer at 5 °C (subphase pH 3, 1 M NaCl) for compression (solid line) and decompression (dotted line).
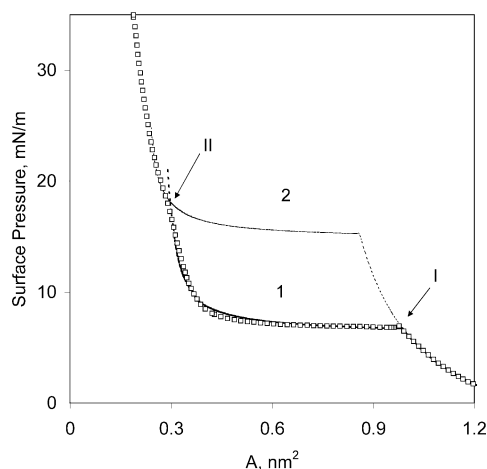

Figure 10. Experimental (dotted line) and theoretical $\Pi-A$ isotherm of the 9-hydroxyoctadecanoic acid monolayer at 5 °C. Solid lines calculated from the theoretical model on the basis of eqs 1–5 for the main phase transition (curve 1) and the phase transition between two condensed phases (curve 2). See detailed discussion in the text.

Another possible cause for certain differences can arise from the surface pressure experiments. In this study, the compression isotherms of *n*-hydroxyoctadecanoic acids monolayers are analyzed. However, even at a very low compression rate it is conceivable that equilibrium between monomers and aggregates is not yet completely reached, and thus, an excess of monomers in the monolayer can result in an increase of surface pressure. As an example, the compression and decompression isotherms of a 12-hydroxyoctadecanoic acid monolayer on 1 M NaCl aqueous subphase at pH 3 and 5 °C are shown in Figure 9. It is seen that the difference of the area per molecule amounts to about 15–20% in the region where the surface pressure increases strongly in the compression and decompression isotherms. This is the amount by which the ω_{c10} values, calculated with eqs 1–5 of the model for the decompression isotherm, are lower than those corresponding to the compression isotherm shown in Figure 9. Assuming that the equilibrium isotherm is located between the compression and decompression isotherms, the error for the determination of the ω_{c10} values for the *n*-hydroxyoctadecanoic acid monolayers is lower than the difference of 10–25% referred to above, and amounts to, say 5–15%, which is a quite acceptable error for the approximate theory.

In Figure 10, only one isotherm for the 9-hydroxyoctadecanoic acid (that for 5 °C) of those shown in Figure 2 is

presented. In addition to the main phase transition (indicated by arrow I), another (structural) phase transition is seen to exist, indicated by arrow II. According to a recent GIXD experiment, a rectangular lattice is formed on both sides of the phase transition, but in the lower surface pressure region at $\Pi = 10$ mN/m the molecular tilt is in NNN (next nearest neighbor) direction, whereas at higher surface pressures ($\Pi = 20$ mN/m) the molecules are tilted toward NN (nearest neighbor) direction. This change of the lattice structure, which takes place at ~18 mN/m, indicates a phase transition of two condensed phases. It is related with a decrease of the ω_{c10} value by 0.015 nm² and is accompanied by an approximately 3-fold decrease of the compressibility in the condensed state, cf. Figure 5. Both phase transitions of the experimental $\Pi-A$ isotherm can be well described by the theoretical model. Figure 10 shows the theoretical isotherms for the two states of the condensed monolayer. The model parameters for the second phase transition are listed in Table 2 along with the parameters of the main phase transition. It is seen that the variations of ω_{c10} and η values for the second phase transition, as compared with the values characteristic for the main phase transition, agree well with the GIXD experiment, i.e., the proportion in which these two parameters decrease is correct. According to the theory,[20,22] the behavior of the system is described by the lowest branch. In Figure 10 therefore, line 1 corresponds to the states of the system in the range between the first and second phase transition, whereas at compression-to-area values after the second phase transition, the system is described by curve 2. It is seen that the experimental data with two phase transitions in the $\Pi-A$ isotherm can well be described by these two theoretical curves.

Conclusions

The thermodynamic behavior and the structure features of hydroxyoctadecanoic acid monolayers are largely affected by the position of the hydroxyl group in the alkyl chain. In the case of OH-substitution in the 2-position, the COOH-headgroup and the neighbored OH-group act as monopolar entity. When the OH-group is positioned in the middle of the alkyl chain, the monolayer properties are determined by the bipolar character of the amphiphile. Experimental studies ($\Pi-A$ isotherms and GIXD measurements) of *n*-hydroxyoctadecanoic acid monolayers with $n = 2, 9, 11$, and 12 were performed. The $\Pi-A$ isotherms of the 2-hydroxyoctadecanoic acid monolayers are essentially different from those obtained for hydroxyoctadecanoic acid with $n = 9–12$. For $n = 2$, the two-phase coexistence region exists already at zero pressure (no plateau in the $\Pi-A$ isotherm) in the accessible temperature region, so the isotherms do not have a fluid monolayer state. Contrary to that, the (9, 11, or 12) OH-substituted octadecanoic acid monolayers show for all measured temperatures the main phase transition (plateau region) between the fluid and condensed phase at $\Pi > 0$ with a striking large extension of the two-phase coexistence region in the $\Pi-A$ isotherms. Theoretical calculations of the $\Pi-A$ isotherms are helpful to explain the strong effect of the position of the OH-substitution on the thermodynamic properties of the monolayers. For the (2, 9, 11, 12)-hydroxyoctadecanoic acid monolayers studied, reasonable agreement between the theoretical predictions and the experimental $\Pi-A$ isotherms can be obtained. In combination with the GIXD experimental data it is possible to draw conclusions on the orientation of the molecules in the different monolayer states and their changes at the main phase transition. The parameters calculated from the theoretical model were found to be quite similar to those measured using the GIXD technique. In the

case of the neighbored OH-group in the 2-position, the OH-group acts as monopolar entity with the COOH-headgroup and a disordered packing results in all monolayer states as the alkyl chains are not able to adapt their packing to the lattice of this monopolar entity.

In the case of the (9−12)-hydroxyoctadecanoic acid monolayers, the analysis of the parameter values and their drastic change at the main phase transition point indicate a bipolar behavior. In the fluid state, both polar groups interact with the water molecules. In the aggregated state after the phase transition, the weaker polar OH-group is forced out of the water interface and well-ordered 2D lattice structures stabilized by hydrogen bonding between the OH-groups are formed.

The $\Pi-A$ isotherms and the GIXD data of the 9-hydroxyoctadecanoic acid monolayers reveal an interesting second phase transition at $\Pi = 18$ mN/m. Here, a phase transition of the rectangular lattice occurs from the molecular tilt in NNN direction in the lower surface pressure region to the molecular tilt in NN direction above the transition point. This phase transition can be satisfactorily described by the theoretical model which assumes two-dimensional compressibility of the condensed monolayer.

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