Structure Features and Phase Behavior of 1-(12-Hydroxy)stearoyl-rac-glycerol Monolayers

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The effect of the alkyl-chain substitution on ordering and phase behavior of monoglycerol esters is studied by coupling the results of surface pressure—area (π –A) isotherm measurements, Brewster angle microscopy, and grazing incidence X-ray diffraction. In the present work, structure features and phase behavior of 1-(12hydroxy)stearoyl-*rac*-glycerol monolayers are investigated and compared with those of the nonsubstituted 1-stearoyl-*rac*-glycerol and 12-hydroxystearic acid monolayers. The dominating effect of the alkyl-chain substitution by a hydroxyl group in the 12 position on the monolayer properties is demonstrated. Phase behavior, domain morphology, and two-dimensional lattice structure of the two 12OH-substituted amphiphiles are similar to each other but different from those of the usual nonsubstituted amphiphiles. Main characteristics of the 1-(12-hydroxy)stearoyl-*rac*-glycerol monolayers are an extended flat phase-transition (plateau) region of the π –A isotherms related with a small temperature dependence of the main phase-transition points, domains with several arms which reflect homogeneously and grow rather irregularly with different tendencies to form curvatures and oblique lattice structures. The bipolar character of amphiphiles OH substituted in the midposition of the alkyl chain is obviously responsible for the special monolayer characteristics deviating from those of typical amphiphilic monolayers.

Introduction

In the recent decade, it has been established that the unsuspected morphological variety of condensed phase domains depends sensitively on the chemical structure of the amphiphiles, particularly on the chemical structure of the polar headgroups. Correlations have been substantiated between morphological texture, lattice structure, phase behavior of amphiphilic monolayers, and the headgroup structure of the monolayer material.^{1,2} On the other hand, such systematic information does not exist on the effect of alkyl-chain substitution by a second polar group although previous studies particularly Cadenhead et al. draw attention on selected hydroxyfatty acids and esters.³⁻⁵ They found on the basis of surface pressure-area isotherms a remarkable dependence of the two-dimensional phase properties on the position of the OH group in the alkyl chain. Obviously there are large differences in the surface pressure-area isotherms between fatty acids OH-substituted in the 2 position and those where the OH substitution is far from the COOH group. Fluorescence microscopy and Brewster angle microscopy (BAM) studies of selected hydroxyfatty acid monolayers provided first information on the morphology of their condensed phases.^{6,7} The combination of BAM and GIXD (grazing incidence X-ray diffraction) allowed the conclusion that OH substitution in the 2 position gives rise to a loss of ordering which has been attributed to a misfit of the alkyl chain and the headgroup enlarged by the neighboring OH group in the 2 position. Another monolayer study of amphiphiles OH substituted in the 2 position (1,2-hexadecandiol, 2-hydroxypalmitic

acid) has shown that the absence of long-range tilt orientational order observed in these systems is correlated to a disordered packing of alkyl chains.⁸

Completely different behavior is indicated when the OH group is positioned in the alkyl chain farther from the polar headgroup. Then, bipolar behavior of the molecules should be expected in the expanded state and the monolayer should undergo a conformational change at compression. Accordingly, wellshaped condensed phase domains and a defined lattice structure were found after the phase transition in 9-hydroxypalmitic acid monolayers.⁷

Langmuir monolayers of monoglycerolesters are not only good candidates for systematic structure and texture studies but they have also an interesting application potential.^{9–13} Therefore extensive studies on the structure and morphology of these amphiphiles with nonsubstituted alkyl chains have been performed. In 1-monopalmitoyl-*rac*-glycerol (or 1-stearoyl-*rac*glycerol) monolayers, the BAM studies revealed circular or cardioid-shaped domain textures subdivided into defined segments of different uniform brightness. The molecules are tilted along the bisector of each segment, and alkyl chains are tilted toward the nearest neighbors (NN) at room temperature.

The objective of this work is to obtain some knowledge how the monolayer features of nonsubstituted monoglycerol esters are affected by the substitution of 1 OH group in the 12 position of the alkyl chain. Such functionalized monoglycerides and their biotechnological synthesis have been of interest in real application systems.¹⁴ The effect of chain substitution will be demonstrated by comparison of the surface pressure—area per molecule $(\pi - A)$ isotherms, domain morphology, and lattice structure of 1-monostearoyl-glycerol and 1-(12-hydroxy-stearoyl)glycerol. To corroborate the conclusion on the effect of OH substitution

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Figure 1. Surface pressure-area isotherms of 1-(12-hydroxy)monostearoyl-*rac*-glycerol monolayers at different temperatures.

in the 12 position, a comparison is performed with some results of 12-hydroxystearic acid monolayers.

Experimental Section

1-(12-Hydroxy)monostearoyl-*rac*-glycerol was synthesized according to a procedure which provides exclusively monoglycerides using glycerol as polyhydroxy substrate and fatty acids as acyl donors during lipase catalysis.¹⁴ The direct enzymatic monoacylation of glycerol with 12-hydroxystearic acid was performed in *n*-hexane in the presence of phenylboronic acid. A purity of \geq 99% was obtained by crystallization from methanol, liquid chromatography, and thin-layer chromatography.

1-Monostearoyl-*rac*-glycerol (purity < 99%) and 12-hydroxystearic acid (purity > 99%) were purchased from Sigma and used without further purification. Deionized water used for the experiments was made ultrapure by a Millipore desktop system (Millipore, Eschborn, Germany). In the case of 12-hydroxystearic acid monolayers, pH 3 subphase water adjusted by the addition of 0.1 M HCl was used. The monolayer-forming substances were dissolved in a 9:1 (v:v) mixture of heptane (for spectroscopy, Merck) and ethanol (p.a. Merck) to a 1 mM spreading solution. The experimental setup for the surface pressure—area (π – A) isotherm and the BAM studies consisted of a self-made computer-interfaced film balance coupled with a Brewster angle microscope (BAM1+, NFT, Göttingen). The surface pressure measured with the Wilhelmy method and using a roughened glass plate was reproducible to ±0.1 mNm⁻¹. The monolayer morphology was studied by BAM. An image-processing software was used to correct the distortion of the digitized images as the BAM images are distorted due to the observation at the Brewster angle. The lateral resolution of the BAM1+ is approximately 4 μ m. More detailed information on the experimental setup and BAM method is given elsewhere; see, e.g., refs 1 and 15.

The GIXD experiments were performed using the liquidsurface diffractometer on the undulator beamline BW1 at HASYLAB, DESY, Hamburg, Germany. To reduce the background in the X-ray scattering experiments, the film trough was located in a sealed He-flushed container. A monochromatic synchrotron X-ray beam was adjusted to strike the helium/water interface at a grazing incidence angle $\alpha_i = 0.85\alpha_c$, where α_c is the critical angle for total reflection. The diffracted intensity is detected by a linear position-sensitive detector (PSD) (OED-100-M, Braun, Garching, Germany) as a function of the vertical scattering angle α_f . A Soller collimator located in front of the PSD provides the resolution for the horizontal scattering angle $2\theta_{xy}$. The scattering vector Q = $k_{\rm f} - k_{\rm i}$ has 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.^{16,17} The diffracted intensities are corrected for polarization, effective area, and Lorentz factor. The lattice parameters are obtained from the peak positions. The lattice spacing is given by $d(hk) = 2\pi/2$ Q_{xy}^{hk} , where (h,k) denotes the order of the reflection. 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,¹⁸ according to $Q_z^{hk} = Q_{xy}^{hk} \cos \psi_{hk} \tan t$. The lattice parameters *a*, b, and γ were calculated from the lattice spacing d_{hk} , and from these the unit cell area $A_{xy} = ab \sin \gamma$. The cross section per alkyl chain $A_0 = A_{xy} \cos t$ is related to the unit cell area A_{xy} (area per molecule parallel to the interface) and the tilt angle t.



Figure 2. Surface pressure-area isotherms of 1-monostearoyl-rac-glycerol monolayers at different temperatures.



Figure 3. Surface pressure—area isotherms of 12-hydroxystearic acid monolayers at different temperatures.

Results and Discussion

The large effect of the OH substitution in the 12 position of the alkyl chain on the thermodynamic monolayer properties can be demonstrated by a comparison of the π -A isotherms of 1-(12-hydroxy)monostearoyl-rac-glycerol with nonsubstituted 1-monostearoyl-rac-glycerol and 12-hydroxystearic acid, which has the same alkyl-chain substitution but another headgroup (a carboxyl group instead of glycerol). Figure 1 shows the π -A isotherms of 1-(12-hydroxy)monostearoyl-rac-glycerol monolayers at 5, 10, 15, 20, 25, and 30 °C. The characteristic shape of these isotherms is noteworthy. For all temperatures, a flat "plateau" over a large area region between about 90 and 30 Å²/molecule at 5 °C and about 80 and 25 Å²/molecule at 30 °C indicates a broad two-phase coexistence region between the fluidlike and the condensed phase. The phase-transition pressure increases with the temperature, as expected. It is interesting to note that a small overshoot of the surface pressure around the break point of the transition to the condensed phase indicates a small supersaturation with fluid phase.

The π -A isotherms of the nonsubstituted 1-monostearoylrac-glycerol monolayers are completely different (Figure 2) and show the characteristic monolayer features of usual amphiphiles

consisting of a nonsubstituted alkyl chain and a headgroup with a somewhat larger cross section area. In particular, this concerns the temperature dependence of the "plateau" (two-phase coexistence) region. The coexistence region of the nonsubstituted 1-monostearoyl-rac-glycerol monolayers is essentially smaller than that of 1-(12-hydroxy)monostearoyl-rac-glycerol and shows an increasing inclination with increasing temperature. The nonhorizontal phase transition of the π -A isotherms and its dependence on the temperature has been theoretically described by consideration of the formation of two-dimensional aggregates on the basis of new equations of state.^{19,20} Also the phasetransition pressures are in a completely different temperature region. It is seen in Figure 2 how the phase-transition point changes with temperature; at 30 °C $A_c = 0.64 \text{ nm}^2/\text{molecule}$ and $\pi_c = 1.4$ mN/m, at 35 °C $A_c = 0.55$ nm²/molecule and π_c = 4 mN/m, at 40 °C $A_c = 0.48$ nm²/molecule and $\pi_c = 7.7$ mN/m, and at 45 °C $A_c = 0.44$ nm²/molecule and $\pi_c = 11.9$ mN/m.

The remarkable effect of the alkyl-chain substitution on the thermodynamic behavior of amphiphilic monolayers can be demonstrated by the π -A isotherms of 12-hydroxystearic acid monolayer (Figure 3). Despite the large differences in the monolayer properties of 1-monostearoyl-*rac*-glycerol and stearic acid, the π -A isotherms of both 12OH-substituted amphiphiles show striking similarities. The π -A isotherms of 12-hydroxy-stearic acid have a similar flat "plateau" over an even larger area region between about 110 and 30 Å²/molecule at 5 °C and between about 95 and 30 Å²/molecule at 30 °C as those of 1-(12-hydroxy)monostearoyl-*rac*-glycerol. At all temperatures, the isotherms show also a small overshoot of the surface pressure around the break point of the transition to the condensed phase, indicating a small supersaturation with fluid phase.

The dominating effect of the OH substitution in the 12 position of the alkyl chain on the thermodynamic behavior of the amphiphilic monolayers is corroborated by the direct comparison of the π -A isotherms of the three amphiphiles at the same temperature (e.g., 30 °C in Figure 4) and by the dependence of their break point for the main phase transition on temperature (Figure 5). Figure 4 shows that the shape of the π -A isotherms of the two 12OH-substituted amphiphiles is very similar; only the phase-transition pressure of the 12-hydroxy-



Figure 4. Surface pressure—area isotherms of the monolayers of 1-(12-hydroxy)monostearoyl-*rac*-glycerol, 1-monostearoyl-*rac*-glycerol, and 12-hydroxystearic acid at 30 °C.



Figure 5. Dependence of the main phase-transition point of 1-(12-hydroxy)monostearoyl-*rac*-glycerol, 1-monostearoyl-*rac*-glycerol, and 12-hydroxystearic acid monolayers on temperature.

stearic acid monolayer is somewhat lower than that of the 1-(12hydroxy)monostearoyl-rac-glycerol monolayer. On the other hand, it is clearly seen that there exist considerable differences between the 12OH-substituted and the nonsubstituted monostearoyl-rac-glycerol. In the same way, the presentation of temperature dependence of the break point for the main phase transition demonstrates the similarity of both the 12OHsubstituted amphiphiles, despite the essential difference of the headgroups, and the complete difference between the 12OHsubstituted and the nonsubstituted monostearoyl-rac-glycerol (Figure 5). In all cases, it exists a linear increase of the phasetransition pressure with temperature. For the two 12OHsubstituted amphiphiles, the slope is notably small and nearly the same in the same temperature range. The break point of the main phase transition is obviously shifted to lower temperatures by 12OH substitution of the alkyl chain. In the case of the nonsubstituted 1-monostearoyl- rac-glycerol monolayers, the much stronger increase of the break point for the main phase transition is convincingly demonstrated by the stronger slope of the adequate straight line.

The BAM studies provide information on the morphological features of the condensed phase domains formed in the twophase coexistence region. So, it is interesting to show in which way the 12OH substitution of the alkyl chain affects the morphology of the condensed phase domains of 1-monostearoylrac-glycerol. For a comparison, a single domain of 1-monostearoyl-rac-glycerol formed in the two-phase coexistence region at 30 °C is shown in Figure 6. It is seen that the domain is subdivided into seven segments of different uniform brightness that meet approximately in the center. The domain morphology is generally the same as that of the homologous 1-monopalmitoyl-rac-glycerol.^{21,22} On the basis of the geometric analysis of the domain texture performed for 1-monopalmitoyl-rac-glycerol, it can be concluded that, in each segment, the alkyl chains have the same azimuthal tilt along the bisector jumping with a defined angle ($\sim 51^{\circ}$ for same segment size) at the segment boundaries.

The domain morphology of the 1-(12-hydroxy)monostearoylrac-glycerol monolayers is completely different. At all temperatures, the domain shapes consist of several arms more or less curved, sometimes forming closed rings. This is demonstrated in Figure 7, which shows selected domain shapes for different temperatures between 6 and 25 °C. The tendency to form



Figure 6. BAM image of a characteristic 1-monostearoyl-*rac*-glycerol domain. T = 30 °C.

curvatures and to develop main arms from a center decreases somewhat with increasing temperature. Despite the curvature of the arms, the domain morphology looks more crystalline than that of the nonsubstituted monogycerol. However, the rather irregular domain shapes combined with differences in the growth direction indicate rather low line tension. All domains reflect homogeneously, which means the molecules within the domains have the same azimuthal orientational order. According to the racemic character of 1-(12-hydroxy) monostearoyl-*rac*-glycerol, domains with clockwise and anticlockwise curvatures of the domain arms have been found; see Figure 8. It is interesting to note that all arms within a domain have the same direction of curvature.

The 12OH substitution affects various monolayer properties, as demonstrated by comparison with the domain morphology of 12-hydroxystearic acid. Figure 9 shows typical domain textures of 12-hydroxystearic acid monolayers measured at 30, 20, and 10 °C. In agreement with the similarities of the π -A isotherms, the morphological features of both 12OH-substituted amphiphiles resemble each other considerably, despite the different headgroups. Also, the domains of 12-hydroxystearic







10°C





15°C

20°C





Figure 7. BAM images of typical domain shapes of 1-(12-hydroxy)monostearoyl-rac-glycerol monolayers at different temperatures.

acid are homogeneously reflecting, develop several arms, especially in the medium temperature region, and grow rather irregularly with differences in the growth direction. On the other hand, the tendency to form curvatures is not so strongly pronounced as in the case of 1-(12-hydroxy)monostearoyl-*rac*-glycerol.

The GIXD data confirm the conclusions on the dominant effect of the 12OH substitution on the structure of the condensed monolayer phase. In earlier work, evidence has been provided that the microscopic textural features of the condensed monolayer phases are related to the two-dimensional lattice structure.^{23–25} The contour plots of the GIXD measurements reveal



Figure 8. 1-(12-hydroxy)monostearoyl-rac-glycerol domains with counterclockwise (left) and clockwise (right) curvatures at 6 °C.



30 °C

20 °C



10 °C

Figure 9. BAM images of typical domain shapes of 12-hydroxystearic acid monolayers at different temperatures.

considerable differences between the nonsubstituted and the 12OH-substituted monostearoyl-*rac*-glycerol (Figure 10). According to the two reflexes of 1-monostearoyl-*rac*-glycerol ($Q_z = 0$ and $Q_z > 0$), the alkyl chain pack in a centered rectangular lattice tilted toward the NN direction. On the other hand, the three reflexes ($Q_z > 0$) of 1-(2-hydroxy)monostearoyl-*rac*-glycerol indicate that, in this case, the alkyl chains form an oblique lattice. In agreement with the π -A isotherms and the

BAM results discussed above with respect to the dominant effect of the 12OH substitution of the alkyl chain, the contour plots of the 12-hydroxystearic acid monolayers show also three reflexes ($Q_z > 0$) characteristic of the oblique lattice structure. The structure data calculated for different surface pressures of the three amphiphiles 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



Figure 10. Contour plots of 1-monostearoyl-*rac*-glycerol at 30 °C (top) and 1-(12-hydroxystearoyl)-glycerol at 16 °C (middle) and 12-hydroxystearic acid at 10 °C (bottom) monolayers.

 TABLE 1: Lattice Structure Data of

 1-(12-Hydroxy)monostearoyl-rac-glycerol,

 1-Monostearoyl-rac-glycerol, and 12-Hydroxystearic Acid

 Monolayers^a

| | a (Å) | b (Å) | γ (deg) | $egin{array}{c} A_{\mathrm{xy}} \ (\mathrm{\AA}^2) \end{array}$ | Ψ_a (deg) | t (deg) | A ₀ (Å ²) |
|--|----------|----------|------------|---|-------------------|------------|-------------------------------------|
| 1-(12-hydroxy)stearoyl-rac-glycerol, 16 °C | | | | | | | |
| 12 mN/m | 4.817 | 4.980 | 112.3 | 22.2 | 21 | 27 | 19.8 |
| 18 mN/m | 4.752 | 5.010 | 113.3 | 21.9 | 21 | 25 | 19.9 |
| 25 mN/m | 4.731 | 5.005 | 113.5 | 21.7 | 21 | 24 | 19.8 |
| 35 mN/m | 4.721 | 5.007 | 113.7 | 21.6 | 21 | 24 | 19.8 |
| 1-monostearoyl-rac-glycerol, 31 °C | | | | | | | |
| 10 mN/m | 5.095 | 5.623 | | 23.9 | NN | 33 | 20.0 |
| 20 mN/m | 5.039 | 5.525 | | 22.9 | NN | 29 | 20.1 |
| 30 mN/m | 4.991 | 5.227 | | 22.2 | NN | 26 | 19.9 |
| 40 mN/m | 4.928 | 5.099 | | 21.5 | NN | 22 | 20.0 |
| 12-hydroxyoctadecanoic acid, 10 °C | | | | | | | |
| 6 mN/m | 4.61 | 5.00 | 112.3 | 21.3 | 25 | 20.0 | 20.0 |
| 10 mN/m | 4.53 | 5.00 | 112.9 | 20.9 | 26 | 15.8 | 20.0 |
| 20 mN/m | 4.43 | 5.01 | 113.9 | 20.3 | | 5.8 | 20.2 |

^{*a*} *a*, *b*, γ are lattice constants, *t* is the polar tilt angle, A_{xy} is molecular area, A_0 is cross-section area of alkyl chain, and ψ_a is the angle between the azimuthal tilt direction and the *a* axis.

the polar tilt angle, and A_0 is the cross-section area of alkyl chain. The characteristic lattice data show clearly the funda-



Figure 11. Reflex profiles of 1-monostearoyl-*rac*-glycerol at 31 °C, 10 mN/m (top image) and 1-(12-hydroxystearoyl)-glycerol at 16 °C, 12 mN/m (bottom image).

mental differences in the lattice structure between the nonsubstituted and the 12OH-substituted monostearoyl-*rac*-glycerol, whereas most of the characteristic two-dimensional structure data of the two 12OH-substituted amphiphiles are very similar. In the latter case, solely some differences exist in the change of the polar tilt angle with the surface pressure in agreement with differences of the adequate nonsubstituted amphiphiles. Whereas the alkyl chains of stearic acid can be erected to the normal at high surface pressures, those of the 1-monostearoyl*rac*-glycerol remain tilted even at highest pressures.²³ Steric effects may be the main reason for this difference because of the smaller cross-section area of the -COOH headgroup compared with that of monoglycerol.

The changes of the lattice data of the substituted and nonsubstituted monoglycerols in dependence on the surface pressure are also different. This concerns particularly the polar tilt, t, the change of which is much smaller in the case of the 12OH-substituted monoglycerol. The hydroxyl group reduces, obviously, the erection of the alkyl chains. Accordingly, hydrogen bonds between the hydroxyl groups of adjacent alkyl chains may be formed. Such a possibility is indicated by the reflex profile of the GIXD measurements. Figure 11 shows the reflex profiles of 12OH-substituted and the nonsubstituted 1-monostearoyl-rac-glycerol monolayers. It is seen that one of the three reflexes of 1-(12-hydroxy)stearoyl-rac-glycerol has a lower width than the other one. That would be expected for the lattice direction along which the hydrogen bonds run. In agreement with the BAM studies, a more crystalline packing of the 1-(12-hydroxy)stearoyl-rac-glycerol monolayers can be concluded from a comparison of the different reflex profiles of the two monoglycerol monolayers because of the fact that the intensity distribution of 1-monostearoyl-*rac*-glycerol is close to a Lorentzian, whereas the intensity distribution of 1-(12hydroxy)stearoyl-*rac*-glycerol is close to a Gaussian. Finally, it is interesting to note that, despite the 12OH substitution, the cross-section area of the alkyl chain is not increased compared to that of the nonsubstituted alkyl chain.

Conclusions

Substitution of the alkyl chain in the 12 position by an OH group has a dominating effect on the main characteristics of long-chain 1-monoalkanoyl-*rac*-glycerol monolayers. This is demonstrated by a comparison of the monolayer features of 1-(12-hydroxy)monostearoyl-*rac*-glycerol with nonsubstituted 1-monostearoyl-*rac*-glycerol. The conclusions can be corroborated by the results of an amphiphile of another homologous series such as fatty acids but with the same alkyl-chain length and the same OH-substitution in the 12 position (12-hydroxy-stearic acid in the present work).

In case of OH substitution in the 12 position of the nonsubstituted amphiphile 1-monostearoyl-rac-glycerol, a complete change of phase behavior and ordering of the monolayer has been demonstrated. On the other hand, the two 12OHsubstituted amphiphiles have a similar phase behavior different to that of the usual nonsubstituted amphiphiles. The bipolar character of the OH-substituted amphiphile in midposition of the alkyl is obviously responsible for the special monolayer characteristics deviating from those of typical amphiphilic monolayers. Striking characteristics of the monolayers of 12OHsubstituted amphiphiles are an extended flat phase-transition (plateau) region of the π -A isotherms related with a small temperature dependence of the main phase-transition points, whereas the nonsubstituted 1-monostearoyl-rac-glycerol behaves as a typical amphiphile with stronger temperature dependence of the phase-transition point as well as the phase coexistence region.

Analogous conclusions concerning the effect of 12OH substitution of the alkyl chain can be drawn from the domain morphology and the two-dimensional lattice structure. 1-Mono-stearoyl-*rac*-glycerol monolayers form well-shaped circular domains subdivided by sharp boundaries into seven segments for different reflecting. They have a centered rectangular lattice tilted toward NN. The domains of both 12OH-substituted amphiphiles develop several arms which reflect homogeneously

and grow rather irregularly with different tendency to form curvatures. They have oblique lattices with very similar characteristics. The analysis of the reflex profiles suggests hydrogen bonds between the hydroxyl groups of adjacent alkyl chains.

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