Synchrotron X-Ray Reflectivity Study of the Adsorption Film of Octadecanamide at the Toluene – Water Interface

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Abstract

The structure of an adsorption octadecanamide film at the planar toluene – water interface is studied by X-ray reflectometry using synchrotron radiation with photon energy of 15 keV. The electron density (polarizability) profiles, according to which the interface structure is determined by the pH level in the water subphase, are reconstructed from experimental data with the help of a model-independent approach. For a high pH ≈ 11, the adsorption film is a crystalline octadecanamide monolayer with a thickness of about 26 Å, in which aliphatic tails of surfactant are extended along the normal to the surface. For low pH ≈ 2, the thickness of the surface structure consisting of the crystalline monolayer directly on the toluene – water interface and a thick layer of deposited octadecanamide micelles reaches about 500 Å. In our opinion, the condensation of nonionic surfactant micelles for which the surface concentration of the surfactant increases significantly is caused by a change in the polarization direction upon a decrease in the pH level in the electric double layer at the interface between the water subphase and the octadecanamide monolayer. The shape of the reconstructed electron density profiles also indicates the existence of a plane of the closest approach of surfactant micelles to the interface at a distance of about 70 Å from it.

INTRODUCTION

The experimental determination of the structure of the transition layer at the interface between two condensed phases (in particular, a nonpolar organic solvent (oil) and water) is an important problem in the physics of surface phenomena. A soluble adsorption film of a diphylic substance (surfactant) on this surface can be treated as a 2D thermodynamic system in which, for example, various barotropic, lytropic, and thermotropic phase transitions between surface mesophases can be observed [12, 14, 15]. The properties of epitropic liquid-crystal layers with a similar structure determine viscosity parameters of motor oils in the tribotriad [14, 15]. The application of synchrotron radiation in the hard part of the X-ray wavelength range in analysis of the structure of buried interfaces using the reflectometry and diffuse scattering methods provides basically new experimental tools for determining the nature of these and many other phenomena in surface layers [16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

Earlier, there were reports on the observation of transitions to multilayer adsorption in two-component adsorption fluoroalkanol films and in one-component triacontanol and triacontane acid films at the n-hexane – water interface (see, for instance, [30]). In our recent publication [29, 31], it was shown that upon a decrease in temperature $T$, the 2D condensation transition, for example, of triacontanol from the gas phase to the liquid Gibbs monolayer of thickness $z_1 \approx 27$ Å at the n-hexane – water interface is followed by its transition to the monolayer adsorption, which we attributed to the increase in the micelle concentration in the surface layer of thickness $z_2 \approx 200$ Å [32] (Fig. 1). The structural information is obtained from the results of these and other experiments based on the calculation of the X-ray reflectivity for model surface structures using available information, for example, on the geometrical sizes and structure of molecules, interfacial tension, etc.

In this study, we analyze experimental data for the interface using a model-independent approach that does not require any additional assumptions concerning the transverse structure of the surface [33, 34, 35, 36]. The X-ray reflectometry data are used for studying the structure of the octadecanamide adsorption film on the planar toluene – water interface depending on the composition of the water subphase (pH level in it). It is found that at a low pH level...
(not exceeding 7), the surface concentration and thickness of the adsorption film of the amphiphilic substance increase significantly (by several times), which we attribute to the condensation of its micelles, induced by their electrostatic interaction with the interface. The application of the new approach has made it possible, for example, to establish the existence and determine the position of the plane of the closest approach of micelles to the interface (see Fig. 1).

EXPERIMENTAL

We have earlier established experimentally that the minimal admissible thickness (along the beam) of the hydrocarbon phase in the experimental cell in analysis of the oil – water interface is about 75 mm [37, 38] (Fig. 2). For the normally incident photons (for example, with energy of 8 keV), the coefficient of transmission through such a hydrocarbon layer is about $10^{-11}$. In a direct beam with an input intensity of about $10^7$ photon/s (wide-focus X-ray tube with a copper anode), we obtain $10^{-3}$ photon/s at the sample exit, which is 2 - 3 orders of magnitude lower than the intrinsic noise level of a modern X-ray detector. For harder (e.g., 15 keV) photons, the transmission coefficient increases to approximately $10^{-2}$. However, a probe beam with a vertical width of smaller than 10 µm and an angular divergence of $10^{-5}$ rad is used in actual practice for correct measurement of the reflectivity factor from the interface. The preparation of a beam with such parameters inevitably leads to a considerable decrease in intensity. For this reason, laboratory sources for X-ray diffraction studies of buried planar interfaces are less attractive considering their low brightness as compared to synchrotron sources of hard radiation [39].

The samples with a planar toluene – water interface oriented by the gravity force were studied under standard conditions in a thermocycled stainless steel cell in accordance with the technique described in [40, 41]. X-ray-transparent windows of the cell were prepared from polyester; the geometrical sizes of the interface between bulk phases in such a cell are 75 mm × 150 mm along and across the beam, respectively.

All chemical components for experiments were purchased at the Sigma-Aldrich company. We used octadecanamide C18H37NO as a nonionogenic surfactant that is well-soluble in the aromatic hydrocarbon and is insoluble in water. The estimated length of this linear chain molecule is $L \approx 26$ Å ($= 17 \times 1.27$ Å (C-C) + 1.5 Å (CH3) + 2.5 Å (CONH2)) [42].

Toluene (C7H8 with a density of approximately 0.86 g/cm³ at $T = 298$ K; boiling point is $T_b = 384$ K) was purified in a chromatographic column [39]. The upper oil phase was a solution of octadecanamide in toluene about 75 ml in volume and with a volume concentration of about 5 mmol/L. Deionized water with pH≈ 7 (Barnstead, NanoPureUV), sulfuric acid solution (pH≈ 2), and NaOH solution (pH≈ 11) in it of about 100 ml in volume were used as the lower bulk water phase. Prior to experiments, liquids were degassed in an ultrasonic bath. During measurements of X-ray reflectivity $R$, the sample was subjected to “annealing”: the temperature of liquids in the cell was increased by 30 K above the room temperature and then the sample was brought to equilibrium at $T = 298$ K by thorough mechanical stirring for several hours [29].

Interfacial tension $\gamma$ was measured by the Wilhelmy plate method directly in the experimental cell [44]. For this purpose, we used a chromatographic paper (Whatman) sheet of size approximately $10 \times 5$ mm which was fixed to a platinum wire (of about 0.25 mm in diameter) passing through the holes (of diameter about 2 mm) in the upper lid of the thermostat and in the cell port cover. The covers were replaced by the lids consisting of two parts, which expectedly affected the leak tightness of the cell in tension measurements. Interfacial tension $\gamma \approx \Delta F/2L$ was determined from change $\Delta F$ in the weight of the plate during its separation from the toluene – water interface, which was measured by a NIMA PS-2 electric balance. After its separation from the interface, the plate remains completely sub-
merged in the hydrocarbon phase. At $T = 298$ K, the value of $\gamma$ for all toluene samples lies in interval $23 \pm 24$ mN/m, which is smaller by approximately 1/3 than a tension of $36.0 \pm 0.1$ mN/m at the toluene – water interface between pure liquids [43, 44].

The transverse structure of the toluene – water interface was studied by reflectometry at the X19C station of the NSLS synchrotron [47]. In experiments, a focused monochromatic photon beam of intensity about $10^{11}$ photon/s and energy $E = 15$ keV ($\lambda = 0.825 \pm 0.002$ Å) was used. The structure of the station made it possible to study the surfaces of solids as well as liquids [48, 50, 51]. For example, we have investigated earlier a transition of melting at the toluene – water interface in the adsorbed monolayer of octodecane acid using this setup [52].

In the case of specular reflection, scattering vector has only one nonzero component $q_z = (4\pi/\lambda) \sin \alpha$ along the normal to the surface (see inset to Fig. 3). For grazing angles $\alpha$ smaller than critical value $\alpha_c = \lambda/\sqrt{r_e \Delta \rho / \pi}$ (where $r_e = 2.814 \cdot 10^{-5}$ Å is the classical electron radius and $\Delta \rho = \rho_w - \rho_r$), the incident beam experiences total external reflection, and $R \approx 1$. Under standard conditions, the electron density is as much as $\rho_w \approx 0.333 e^{-1/\text{Å}^3}$ ($\text{Å}$ is the electron charge) in water and $\rho_r \approx 0.85\rho_w$ in toluene ($\Delta \rho \approx 0.15\rho_w$). Therefore, $\alpha_c \approx 0.03$ deg at the toluene – water interface.

Figure 3 shows the experimental dependences of reflectivity factor $R$ on $q_z$, which are normalized for better visualization by Fresnel function $R_F(q_z) \equiv \langle q_z - [q_z^2 - q_z^2(1/2)]^2/(q_z + \sqrt{q_z^2 - q_z^2(1/2)})^2 \rangle$, where $q_z = (4\pi/\lambda) \sin \alpha_c \approx 0.0085 \text{Å}^{-1}$. Triangles correspond to values of $R(q_z)/R_F(q_z)$ at a level of pH$\approx 2$, circles correspond to pH$\approx 7$, and squares, to pH$=11$. These data demonstrate a quite strong dependence of the interface structure on the pH level in the water subphase.

**THEORY**

According to experimental data on $R(q_z)$ in the interval from approximately 1 to $10^{-9}$, we reconstructed electron density distributions $\rho(z)$ along the normal to the surface using two fundamentally different approaches, viz., with the assumption concerning the monolayer structure of the adsorption film and without any assumption about the transverse structure of the surface. In the former case, we used a qualitative monolayer model based on the error function, which describes temperature-activated fluctuations of the interface (capillary waves) [53, 54, 55, 56]. In the first Born approximation of distorted waves (DWBA), reflectivity factor $R(q_z)$ for the toluene – water interface with the Gibbs monolayer is expressed as follows [57, 58]:

$$\frac{R(q_z)}{R_F(q_z)} \approx \exp\left(-\frac{\sigma^2 q_z^2}{\Delta \rho^2}\right) \times \left|\rho_1 - \rho_w + (\rho_1 - \rho_1) \exp\left(iz_1 \sqrt{q_z^2 - q_z^2(1/2)}\right)\right|^2,$$

where $q_z = \sqrt{q_z^2 - q_z^2(1/2)}$ and $\rho_1$ is the electron density in the octodecaneamide monolayer. The position of the monolayer – water interface corresponds to $z_0 = 0$, $z_1$ is the thickness of the Gibbs monolayer (see Fig. 1), and $\sigma$ is the standard deviation of the positions of the boundaries from their nominal values $z_0$ and $z_1$. In our calculations, we fixed the value of parameter $\sigma^2$ for the monolayer boundaries equal to the square of the capillary width: $\sigma^2 = (k_B T/2\pi \gamma) \ln(Q_{\text{max}}/Q_{\text{min}})$, where $k_B$ is the Boltzmann constant, the short-wavelength limit in the capillary wave spectrum is $Q_{\text{max}} = 2\pi / a$ ($a \approx 10$ Å is of the same order of magnitude as the intermolecular spacing, and the long-wavelength limit of fluctuations of the surface in the experiment is $Q_{\text{min}} = q_w^2 \Delta \beta$ (where $q_w^2 \Delta \beta \approx 0.275 \text{Å}^{-1}$ and the detector angular resolution is $\Delta \beta \approx 4 \cdot 10^{-4}$ rad) [59].

In our experimental conditions, the calculated value of the width for the toluene – water interface is $\sigma \approx 4.75 \pm 0.05$ Å. This approach to analysis of reflectometry data have been successfully used in our earlier investigation of structures and phase transitions in adsorption films of amphiphilic substances at the planar air – water interface, as well as at the interface between saturated hydrocarbon n-hexane and water [60, 61, 62, 63].

The results of calculations for the model monolayer based on expression (1) are shown by dashed curves in Fig. 3. For pH$\approx 11$, the electron density in the Gibbs monolayer at the toluene – water interface is $\rho_1 = 0.350 \pm 0.005 e^{-1/\text{Å}^3}$ and $z_1 = 26 \pm 1$ Å. Monolayer density $\rho_1$ corresponds to the closest packing of hydrocarbon chains in the crystalline "γ"-phase", and the monolayer thickness coincides (to within the error) with length $L$ of the octadecanamide molecule [64].

Such values of fitting parameters correspond to the area per molecule in the monolayer $A = \Gamma/(z_1 \rho_1) = 18 \pm 1$ Å$^2$, where $\Gamma = 160$ is the number of electrons in C$_{18}$H$_{37}$NO molecule. Therefore, we can conventionally refer to the monolayer as a crystalline layer in which aliphatic tails of the surfactant are extended along the normal to the surface.

For other pH levels, the value of fitting parameter $\rho_1$ is approximately the same as for pH$\approx 11$, but $z_1$ is noticeably smaller than $L$ ($z_1 = 17 \div 20$ Å). On the one hand, this could correspond to the solid hexatic phase of the monolayer with a large angle of inclination of aliphatic tails (their angle of deviation from the normal is $\theta = \arccos(z_1/L) \approx 40^\circ$) analogously to the phases of the Langmuir monolayer of octodecane acid on the water surface [65, 66]. On the other hand, the integral characteristic of the monolayer is the area per molecule $A = \Gamma/(z_1 \rho_1) \approx 26$ Å$^2$, which corresponds to liquid octodecane (C$_{18}$H$_{36}$). This obvious contradiction is undoubtedly because of a more complex structure of the adsorption film than a monolayer.

The fact that the square of structure factor $R/R_F$ exceeds unity for small gliding angles (see data for pH$\approx 2$) in the interval of $q_z$ values from approximately $1.5q_w$ to $5q_w$ indicates the presence of the region of excessive electron density of the adsorbed substance near the interface as compared to the density of the model monolayer, which we attribute to the condensation of octadeanamide micelles at the interface. To relate this peculiarity on the structure of the toluene – water interface, we applied the model-independent approach based on the extrapolation of the asymptotic behavior of reflectivity factor $R(q_z)$ to the region of large values of $q_z$ [67]. We successfully used this
approach earlier in describing the structure of phospholipid multiplayers on the colloidal silica sol [68, 69, 70, 71] and lipid monolayers on a water substrate [72, 73, 74].

The key advantage of this approach is that it does not require any a priori assumptions concerning the structure of the object under investigation and provides the absolute depth-wise distribution of polarizability of the medium $\delta(z)$ (the real part of the complex permittivity) and, accordingly, electron density $\rho(z) \approx \pi \delta(z)/(r_e \lambda)$. In the general case, distribution $\delta(z)$ is represented as a piecewise-continuous function containing singular points $\Delta(n)(z_j)$ at which its n-th derivative varies stepwise; the asymptotic form of the decrease of reflection curve in this case is $R(q_z \to \infty) \propto 1/q_z^{(2n+4)}$.

The procedure of further analysis was described in detail in [33, 67]. It should only be noted that all experimental curves in our case decrease in proportion to $\propto 1/q_z^n$, indicating the existence of singular points of the first order ($n = 1$). The mutual positions of the curves can be determined using the following procedure of modified Fourier analysis:

$$F^1(x) = \frac{64}{k^4(q'' - q')} \times \int_{q'} q''R(q) - C \cos(2qx) dq;$$

$$C = \frac{1}{q'' - q'} \int_{q''} q''R(q) dq,$$

where $k = 2\pi/\lambda$. The integration in Eq. 2 with respect to $q \equiv q_z/2$ is performed for different values of $q'$ and $q''$. Stable extrema of function $F^1(x)$ correspond to paired distances between singular points $x_{ij}$ at which $F^1(x_{ij}) \sim \Delta_1^1 \Delta_2^1$.

For example, Fig. 4 shows the set of $F^1(x)$ calculated from the reflection curve for pH$\approx 11$. The only stable minimum indicates the only pair of singular points opposite in sign and separated by distance $x = 15.6$ Å, which correspond to the toluene-Gibbs monolayer interface ($z_1$ in Fig. 1) and to the maximal electron density in the vicinity of polar groups -CONH$_2$ of the octadecanamide monolayer. Further, the $\delta(z)$ profile defined numerically by set $M \sim 100$ of thin homogeneous layers with fixed positions of singular points $z_j$ was reconstructed by fitting of the calculated angular dependence of reflectivity factor $R_{calc}(q_z, \delta(z))$ to experimental data $R(q_z)$ using the standard least-square minimization method. To ensure stability of the solution, the target function was supplemented with a regularization term of form $\sum_{m \neq j}^M (\delta_{m-1} - \delta_m) \to \min$, which determines the smoothness of profile $\delta(z_1, d, M)$ in the intervals between singular points.

The disregard of absorption in the medium in this approach imposes a limitation on the thickness $L \ll \lambda^2 q_{\text{max}}^2/4\pi \delta(z)$ of structure being reconstructed [33]. Since the value of polarizability for water at wavelength $\lambda = 0.825$ Å, $\approx 2 \times 10^{-6}$, the admissible thickness of the reconstruction region ($L \gg 1000$ Å) is quite sufficient for determining the structure of the adsorption layer correctly [75].

**RESULTS AND DISCUSSION**

The solid and dashed curves in Fig. 5 show electron den-
Figure 6. Reconstructed electron density profiles $\rho(z)$ for the monolayer adsorption octadecanamide film at the toluene – water interface normalized to the electron density in water under standard conditions ($\rho_w = 0.333 \text{ e}^{-/\text{Å}^3}$): (1) pH ≈ 11; (2) pH ≈ 7; (3) pH = 2. For convenience of comparison, profiles 2 and 3 are shifted along the ordinate axis by +0.01 and by +0.03, respectively. The position of the boundary between the polar region of molecules in the Gibbs monolayer and water is set at $z = 0$.

In a nonpolar organic solvent (toluene), the micelle core is formed by hydrophobic polar groups -N₃, while hydrophilic tails of octadecanamide -C₁₇H₃₅ form the outer shell (inverted micelle). The minimal radius of a spherical micelle is $L \approx 26 \text{ Å}$. If we assume that the packing density of octadecanamide molecules in micelles and in the Gibbs monolayer is approximately the same, the surfactant concentration in the micellar layer for pH ≈ 2 is smaller than in the model Gibbs layer by $(\rho_1 - \rho_0)/(\rho_2 - \rho_0) \sim 4 \div 5$ times. At the same time, the broad layer is thicker than the monolayer by $(z_2 - z_1)/z_1 \sim 15 \div 20$ times. Therefore, the amount of octadecanamide in the micellar layer is larger than its amount in the monolayer by 3 – 4 times. Consequently, the surface concentration of nonionogenic surfactant at the oil – water interface is determined by the pH level of the aqueous subphase, i.e., by the direction of polarization in the electric double layer at the boundary of the water phase or by the sign of the electric potential at the monolayer – electrolyte solution interface.

The shape of the reconstructed electron density profiles $\rho(z)$ also indicates the existence of the plane of the closest approach of micelles to distance $z' \sim 70 \text{ Å}$ from the interface, and the emergence of the depletion region in the interval $z_1 < z' < 70 \text{ Å}$ is a quite unexpected feature of the profile. Such an interface polarization pattern is probably a manifestation of specific electrostatic and steric effects in the interaction of micelles with the surface and requires a detailed investigation that is beyond the scope of this article. It should only be noted that the existence of the closest approach plane for micelles has not been discussed in earlier publications, because it is difficult to reliably establish its presence using the model approach to the reconstruction of the $\rho(z)$ profile [24, 30, 32]. This is primarily because with such an approach, the ambiguity in determining these parameters rapidly increases as a rule upon an increase in the number of model structure parameters.

Thus, the structure of the dissolvable adsorption octadecanamide film at the toluene – water interface strongly depends on the pH level of the water subphase. At a high pH level, the film has the state of a solid monolayer of a thickness of approximately 26 Å, in which aliphatic octadecanamide tails are extended along the normal to the surface. At a low pH level, the thickness of the surface structure increases to approximately $500 \text{ Å}$ due to condensation of surfactant micelles; as a result, the amount of the adsorbed substance increases by 3 – 4 times (i.e., significantly). According to our results, the structure of the Gibbs monolayer in this case is independent of the pH level of the subphase.

Using the model-independent approach, we could establish...
the existence of the plane of the closest approach of surfactant micelles to the interface, which lies at a distance of about $\sim 70 \AA$ from it in the pH interval from 2 to 11. In our opinion, the effect of micelle condensation at the interface upon a decrease in the pH level, which is demonstrated in this study, is caused by the change in the direction of polarization in the electric double layer at the water phase boundary.

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