Abstract

Using synchrotron radiation with a photon energy of 15 keV, the molecular structure of an adsorbed n-triacontanol layer at the n-hexadecane – water interface in different its phase states has been studied by the method of diffuse X-ray scattering. The analysis of the experimental data shows that a transition to the multilayer adsorption occurs at a temperature below the two-dimensional vapor – liquid transition at the interface. This transition has been attributed to a feature in the temperature dependence of the concentration of micelles in a surface layer ∼ 100 ÷ 200 Å thick.

Various reversible two-dimensional transitions between surface mesophases of fatty alcohols and acids (lipids) are possible in an adsorbed film at the n-alkane - water interface [1-7]. In particular, a solid – vapor phase transition is observed in a fluoroalkanol Gibbs monolayer [5, 8] and a solid – liquid phase transition is observed in a carbon acid monolayer [9]. It was briefly reported in [10] that a liquid – vapor thermotropic phase transition occurs in adsorbed n-triacontanol (C_{30}-alcohol) film at the n-hexadecane – water interface. In this work, the molecular structure of the neutral surface mesophases of this lipid is studied by diffuse (nonspecular) X-ray scattering and reflectometry with the use of synchrotron radiation. It is shown that a transition from the structure with a width of ∼ 3 Å to a monolayer with a thickness of ∼ 27 Å and, then, to a structure 100 ÷ 200 Å thick occurs with decreasing temperature in a relatively narrow temperature range. We attribute the latter transition to an increase in the concentration of micelles in the surface layer.

An adsorption film at the planar oilwater interface can be considered as a two-dimensional thermodynamic system with the parameters (p, T, c), where p is the pressure and c is the concentration of the lipid in the volume of the hydrocarbon solvent [11-13]. According to [10], the liquid-vapor transition in the adsorbed C_{30}-alcohol film at the n-hexadecane – water interface at p = 1 atm and c ∼ 0.6 mmol/kg is observed at T_c ∼ 300 K. The corresponding temperature dependence of the interfacial tension γ(T), measured by the Wilhelmy plate method, is shown by closed circles in Fig. 1 [10, 14]. A change in the slope of is due to a change in the surface enthalpy at the transition ΔH = -T_cΔ(∂γ/∂T)_p,c = 0.42 ± 0.04 J/m^2. At the same time, the transition to the C_{30}-alcohol monolayer at the n-hexane – water interface (open circles in Fig. 1) is characterized by the tripled value ΔH = 1.3 ± 0.1 J/m^2.

The reflection coefficient R and the intensity of diffuse surface scattering I_D of X rays at the n-hexadecane – water interface were measured at the X19C beamline of the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, United States) with the use of radiation with the wavelength λ = 0.825± 0.002 Å [15].

Let k_i and k_s be the wave vectors of the incident and scattered beams, respectively, with the amplitude k_0 = 2π/λ (see the inset of Fig. 2). In the coordinate system where the origin O lies at the center of the illuminated region, the plane xy coincides with the interface, the Oz axis is perpendicular to the beam direction, and the axis Ox is normal to the surface and is directed opposite to the gravitational force, the components of the scattering vector q = k_i - k_s in the interface plane are q_x ∼ k_0φ and q_y ∼ k_0(α^2 - β^2)/2 and the normal component is q_z ∼ k_0(α + β) (α, β << 1, φ ≈ 0).

According to the method described in [9, 16], the interface sample was prepared in a thermostatic cell, which was then placed on an optical table with active vibration isolation. Deionized water (Barnstead, NanoPureUV) with a volume of ∼ 100 mL was used as the bottom bulk phase. About ∼ 50 mL of the solution of n-triacontanol in n-hexadecane with c ∼ 0.6 mmol/kg was used as the top bulk phase. Saturated hydrocarbon C_{16}H_{34} (the melting temperature is 291 K, the boiling temperature is 560 K, and the density at 298 K is ≈ 0.77 g/cm^3) was preliminarily pu-
of the adsorbed n-triacontanol film. At 

\[ R \sim \alpha \]

and the natural divergence of the beam 

\[ \alpha \sim 6 \times 10^{-12} \text{ rad} \] for the n-hexadecane – water interface is determined by the difference \( \Delta \rho = \rho_w - \rho_h \) between the bulk electron densities in the hydrocarbon solvent \( \rho_h \approx 0.27 \text{ e}^+ / \text{A}^3 \) and in water \( \rho_w \approx 0.33 \text{ e}^+ / \text{A}^3 \).

Figure 3 shows data for the normalized intensity of diffuse surface scattering \( I_s(\beta) \equiv (I(\beta) - I_0(\beta))/I_0 \) (the normalization condition is \( I_s(\alpha) = 1 \)) obtained at the glancing angle \( \alpha \approx 3.3 \times 10^{-3} \text{ rad} (\approx 0.19^{\circ}) \) for various phase states of the interface. Here, \( I(\beta) \) is the number of photons scattered by the bulk of the sample and reflected ( specularly and diffusely) from the surface in the illuminated region with an area of \( A \approx 30 \text{ mm}^2 \) at the center of the interface in the \( \beta \) direction; \( I_0(\beta) \) is the normalization constant proportional to the intensity of the incident beam, which was controlled in the experiment immediately before entry of the beam into the cell; and \( I_s(\beta) \) is the number of photons scattered in the bulk of n-hexadecane on the path to the interface, which is determined by the method described in detail in [16]. The most intense peak on the curve \( I_s(\beta) \) corresponds to specular reflection at \( \beta = \alpha \), and the peak against the diffuse background at \( \beta \to 0 \) illustrates an increase in the scattering intensity at \( \beta = \alpha \). [19] The measurement of \( I_s(\beta) \) was performed with a collimated beam with the angular divergence in the vertical plane \( \Delta \alpha \approx 5 \times 10^{-5} \text{ rad} \) and \( \Delta \beta \approx 3 \times 10^{-4} \text{ rad} \).

From data for \( R(q) \) and \( I_s(\beta) \), we obtain information on the surface normal structure of the interface using the distorted wave Born approximation [20]. According to the model approach described in [16, 18], the interpretation of experimental data is reduced to determining the parameters of the structure factor function of the interface \( \Phi(q) \), which is in turn specified by the chosen model of the electron density distribution \( \rho(z) \) across the interface. Symmetric model profiles \( \rho(z) \) are constructed with the error function \( \text{erf}(x) \), which is used in the standard theory of capillary waves [21].

The qualitative model of the structure of the adsorbed C_{30}-alcohol film at the n-hexadecane – water interface shown in Fig. 4 provides a self-consistent interpretation of reflectometry and diffuse scattering data with a minimum number of fitting param-
The Gibbs monolayer is fairly well described within the qualitative wave nature [27].

$\rho$ is the maximum $qQ$ difference in $\Delta \beta > 0$, where $\rho$ accounts for the adsorbed film. Thinner diffuse scattering, which exceeds the calculated value for the capillary wave channel of elastic scattering for all phase states of the adsorbed film.

At $T > T_c$, the dependences $R(q_\rho)$ and $I_n(\beta)$ in the gas phase of the interface are fairly well described within a single-parameter model with the structure factor

$$\Phi(q)_V = e^{-\sigma^2 q^2/2}. \quad (1)$$

The minimum value of the parameter $\sigma^2$, which determines the width squared of the interface, is limited by the capillary width squared:

$$\sigma_0^2 = \frac{k_B T}{2 \pi \gamma(T)} \ln \left( \frac{Q_{\text{max}}}{Q_{\text{min}}} \right), \quad (2)$$

which is in turn specified by the short-wavelength limit in the spectrum of capillary waves $Q_{\text{max}} = 2\pi a$ (where $a \approx 10$ Å is the intermolecular distance) and $Q_{\text{min}} = q_{\text{max}}^* \Delta \beta/2$ (where $q_{\text{max}}^*$ is the maximum $q$ value in the experiment) [22-26].

The dependence $R(q_\rho)$ calculated by Eq. (1) for $T > T_c$ with the fitting parameter $\sigma = 3.4 \pm 0.2$ Å is shown by line 3 in Fig. 2. Within the error, $\sigma$ coincides with $\sigma_0 = (3.59 \pm 0.04)$ Å for this measurement. On one hand, this calculation without free parameters describes the dependence $R(q_\rho)$. On the other hand, the observed diffuse scattering intensity at $T > T_c$ is noticeably higher than that calculated by Eqs. (1) and (2) (solid line 3 in Fig. 3). To describe $I_n(\beta)$ by means of Eq. (1), the fitting value $\sigma \approx 6.5$ Å should be taken for the effective width (dashed line 3 in Fig. 3); Eq. (2) gives $\sigma_0 \approx 4.3$ Å taking into account the difference in $\Delta \beta$ and $q_{\text{max}}^*$ in measurements of $I_n$ and $R$.

This indicates that the interface has an internal structure with a width larger than $\sqrt{\sigma^2 - \sigma_0^2} \approx 5$ Å, which has a noncapillary wave nature [27].

At $T < T_c$, the reflection coefficient $R(q_\rho)$ in the liquid phase of the Gibbs monolayer is fairly well described within the qualitative two-layer model of the structure factor (lines 1 and 2 in Fig. 2):

$$\Phi(q)_L = e^{-\sigma^2 q^2/2} \left( \frac{1}{\Delta \rho} \sum_{j=0}^3 (\rho_{j+1} - \rho_j) e^{-iq(z+z_j)} \right), \quad (3)$$

where $z_0 = 0$, $\rho_0 = \rho_w$, and $\rho_3 = \rho_h$. The relative electron densities are $\rho_1/\rho_w = 1.10 \pm 0.03$ and $\rho_2/\rho_w = 0.90 \pm 0.03$ and the coordinates of the layer boundaries are $z_1 = 10 \pm 2$ Å and $z_2 \approx 27$ Å. The total thickness of the Gibbs monolayer is $z_2 - z_0 = (27 \pm 2)$ Å. The calculated values $\sigma_0 = 3.7 \pm 0.1$ Å and $\sigma_2 = 4.1 \pm 0.1$ Å for lines 1 and 2, respectively, coincide within the experimental error with the respective fitting values $\sigma = 3.8 \pm 0.2$ Å and $\sigma = 4.3 \pm 0.2$ Å.

The observed scattering intensity $I_n(\beta)$ in the range $T_c > T > T^* \approx 296$ K is insignificantly higher than the calculated value (solid line 2 in Fig. 3) and can be described by Eq. (3) with the effective width $\sigma \approx 5.9$ Å (dashed line 2 in Fig. 3), which is larger than $\sigma_0 \approx 4.3$ Å obtained from Eq. (2).

Finally, intensity $I_n(\beta)$ increases significantly at $T < T^*$ (see experimental points 1 in Fig. 3). Fitting Eq. (3) to all these data gives the width $\sigma \approx 30$ Å, whereas $\sigma_0 \approx 5.4$ Å.

The range of angles of observation of the diffuse background in scattering experiments is limited to $\beta < 0.006$ rad or $q_\beta < q_{\text{max}}^* \approx 0.07$ Å$^{-1}$, whereas the maximum value $q_{\text{max}}^*$ in reflectometry experiments is about 0.4 Å$^{-1}$. On one hand, the reflectometry data are quite well described by the parameter calculated by Eq. (2). On the other hand, the effective roughness of the surface according to diffuse scattering data is $> 6$ Å, which can reasonably be attributed to the existence of an extended near-surface structure (layer 3 in Fig. 4) thicker than $2\pi/q_{\text{max}}^* \approx 100$ Å. Then, a high grazing scattering intensity at $T < T^* \approx 296$ K can qualitatively be explained within a three-layer model (multilayer adsorption) [16]:

$$\Phi(q)_L + \frac{\delta \rho e^{-\sigma^2 q^2/2}}{\Delta \rho} e^{-iq(z+z_3)}. \quad (4)$$

Here, the second term describes the third layer with the thickness $z_3 - z_2$ and density $\rho_3 + \delta \rho$, the parameter $\sigma_3$ reflects the noncapillary wave structure of the boundary of layer 3 with the solvent, and $\Phi(q)_L$ is given by Eq. (3) with the substitution $\rho_3 = \rho_h + \delta \rho$.

The intensity $I_n(\beta)$ calculated by Eq. (4) is shown by dashed line 1 in Fig. 3. The estimated thickness of the thick layer is $z_3 - z_2 \approx 200$ Å, the parameter $\delta \rho/\rho_w = 0.02 - 0.09$, and the width is $\sigma_3 \approx 20 - 40$ Å. The density $\rho_3 + \delta \rho$ corresponds to the electron density in a high-molecular-weight alkane liquid [28]. The experimentally observed broadening of the central peak on line 1 is possibly due to small-angle scattering from micelles in the bulk of n-hexadecane, which was disregarded in the calculations of $I_n(\beta)$.

Model profiles of the electron density ($\rho(z)$) for mesophases of the adsorbed C$_{30}$-alcohol film in units of $\rho_w$ are shown in Fig. 5. At $T > T_c$, the gas phase of the Gibbs monolayer (structure 3), which is characterized by a single parameter, the interface width $\sigma \approx 3.4$ Å, is implemented in the adsorbed film. In the range $T^* < T < T_c$, the liquid Gibbs monolayer with the thickness $27 \pm 2$ Å (structure 2) is implemented. The observed diffuse scattering intensity in these phase states of the adsorbed film exceeds the calculated value for the capillary wave channel of elastic scattering and indicates the presence of the weakly contrast layer 3 with a thickness of $\sim 100$ Å in the surface structure. Structure 1 at $T < T^*$ differs from structure 2 in the presence of the dense ($\rho_3 \approx 0.9 \rho_w$) and thick ($\sim 200$ Å) layer 3. Such a structural change can be called multilayer adsorption.

We believe that the participation of n-triactanol–micelle aggregates in the formation of the structure of the adsorbed film can explain a surprisingly high background of diffuse scattering in all phase states of the n-hexadecane–water interface, which cannot be due to scattering on thermal fluctuations of the interface. The characteristic diameter of a spherical micelle is about two lengths of the C$_{30}$-alcohol molecule, i.e., $\approx 80$ Å ($\sim 2\pi/q_{\text{max}}^*$). The incomplete filling of surface layer 3 with a thickness of $\sim 200$ Å can be responsible for the observed blurring or a large width $\sigma_3 \approx 30$ Å.

Figure 4. Model of the transverse structure of adsorbed n-triactanol C$_{30}$H$_{62}$O film at the n-hexadecane–water interface.
of the interface between the adsorbed film and bulk.

The described structures of neutral surface mesophases of the C$_{30}$-alcohol at the n-hexadecane – water interface noticeably differ from the structure of both the solid phase of its Langmuir monolayer on the water surface and its mesophases at the n-hexane – water interface [29]. In particular, the observed thickness (27 ± 2) Å of the n-triacontanol Gibbs monolayer at the n-hexadecane – water interface (area per molecule is $A = (29 ± 3) \text{Å}^2$) is noticeably smaller than (36 ± 2) Å (area $A = (24 ± 1) \text{Å}^2$) at the n-hexane – water interface.

To conclude, the analysis of scattering data has shown that, with decreasing temperature $T$, a two-dimensional condensation transition of the C$_{30}$-alcohol to the Gibbs liquid monolayer at the interface at the temperature $T_c$ is followed at the temperature $T^*$ by a transition to its multilayer adsorption. We believe that this adsorption is caused by an increase in the concentration of micelles in the 100- to 200-Å-thick surface layer. The observation of such transitions in two-component adsorbed fluoroalkanol films and in C$_{30}$-alcohol and C$_{30}$-acid single-component films at the n-hexanewater interface was reported earlier [9,30,31].

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References

[1] N. Matubayasi, K. Motomura, M. Aratono, R. Matuura, Bull. Chem. Soc. Jpn. 51, 2800 (1978).

[2] M. Lin, J. L. Ferpo, P. Mansaura, J. F. Baret, J. Chem. Phys. 71, 2202 (1979).

[3] Y. Hayami, A. Uemura, M. Ikeda, M. Aratono, K. Motomura, J. Colloid Interface Sci. 172, 142 (1995).

[4] T. Takiue, T. Matsuuo, N. Ikeda, K. Motomura, M. Aratono, J. Phys. Chem. B 102, 4906 (1998).

[5] Z. Zhang, D. M. Mitinovic, S. M. Williams, Z. Huang and M. L. Schlossman, J. Chem. Phys. 110, 7421 (1999).

[6] M. L. Schlossman, M. Li, D. M. Mitinovic, A. M. Tikhonov, High Performance Polymers 12, 551 (2000).

[7] P. S. Venkatesh, T. Takiue, G. Guangming, A. M. Tikhonov, N. Ikeda, M. Aratono, M. L. Schlossman, J. Dispers. Sci. Technol. 27, 715 (2006).

[8] T. Takiue, A. Yanata, N. Ikeda, K. Motomura, M. Aratono, J. Phys. Chem. 100, 13743, (1996).

[9] A. M. Tikhonov, JETP Lett. 104, 309 (2016).

[10] A. M. Tikhonov, M. L. Schlossman, J. Phys.: Condens. Matter 19, 375101 (2007).

[11] J. W. Gibbs, Collected Works, Vol. 1, Dover, New York, 1961.

[12] R. S. Hansen, J. Phys. Chem. 66, 410 (1962).

[13] K. Motomura, N. Matubayasi, M. Aratono, R. Matuura, J. Colloid Interface Sci. 64, 356 (1978).

[14] A. W. Adamson, Physical Chemistry of Surfaces, 3rd ed.; John Wiley & Sons: New York, 1976.

[15] M. L. Schlossman, D. Synal, Y. Guan, M. Meron, G. She-McCarthy, Z. Huang, A. Acero, S. M. Williams, S. A. Rice, P. J. Viccaro, Rev. Sci. Instrum. 68, 4372 (1997).

[16] A. M. Tikhonov, JETP Lett. 102, 552 (2015).

[17] A. Goebel, K. Lunkenheimer, Langmuir 13, 369 (1997).

[18] A. M. Tikhonov, JETP Lett. 105, 775 (2017).

[19] Y. Yoneda, Phys. Rev. 131, 2010 (1963).

[20] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley, Phys. Rev. B 38, 2297 (1988).

[21] F. P. Buff, R. A. Lovett, F. H. Stillinger, Phys. Rev. Lett. 15, 621 (1965).

[22] A. Braslav, M. Deutsch, P. S. Pershan, A. H. Weiss, J. Als-Nielsen, J. Bohr, Phys. Rev. Lett. 54, 114 (1985).

[23] D. K. Schwartz, M. L. Schlossman, E. H. Kawamoto, G. J. Kellogg, P. S. Pershan, B. M. Ocko, Phys. Rev. A 41, 5687 (1990).

[24] A. M. Tikhonov, J. Phys. Chem. B 110, 2746 (2006).

[25] A. M. Tikhonov, J. Chem. Phys. 124, 164704 (2006).

[26] A. M. Tikhonov, J. Phys. Chem. C 111, 930 (2007).

[27] D. M. Mitinovic, A. M. Tikhonov, M. Li, Z. Huang, and M. L. Schlossman, Phys. Rev. Lett. 85, 582 (2000).

[28] D. M. Small, The Physical Chemistry of Lipids, Plenum Press, New York, 1986.

[29] A. M. Tikhonov, M. L. Schlossman, J. Phys. Chem. B 107, 3344 (2003).

[30] A. M. Tikhonov, JETP Lett. 106, 576 (2017).

[31] T. Takiue, T. Tottori, K. Tatsuta, H. Matsubara, H. Tanida, K. Nitta, T. Uruha, M. Aratono, J. Phys. Chem. B 116, 13739 (2012).