Solid - Liquid Phase Transition in a Gibbs Monolayer of Melissic Acid at the n-Hexane - Water Interface

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Abstract

A sharp phase transition from a crystalline state with the area per molecule $A = (17 \pm 1) \, \text{Å}^2$ to a liquid state with $A = (23 \pm 1) \, \text{Å}^2$ at the n-hexane - water interface in a Gibbs monolayer of melissic acid has been revealed in data of X-ray reflectometry with the use of synchrotron radiation.

The solid - liquid phase transition on the surface of a high-molecular alkane is observed above the bulk melting temperature [1, 2]. The possibility of such a phase transition at an alkanewater interface has been discussed for a long time [3, 4, 5, 6, 7]. The observation of a solid - liquid phase transition at the n-hexane - water interface in the Gibbs monolayer of a surfactant is reported in this work.

Melissic acid (C$_{30}$-acid) is not solved in water and is weakly solved in n-hexane (C$_6$H$_{14}$, density $\approx 0.65 \, \text{g/cm}^3$ at 298 K, boiling temperature $T_b \approx 342 \, \text{K}$), which is hardly solved in water under normal conditions. At quite low temperatures, C$_{30}$H$_{60}$O$_2$ molecules of acid are adsorbed from a solution in a hydrocarbon solvent on the n-hexane - water interface in the form of a solid monolayer (Gibbs monolayer) with the thermodynamic parameters $(p, T, c)$, significantly reducing its energy [8]. According to our new data, with an increase in the temperature $T$ (at the pressure $p = 1 \, \text{atm}$), a phase transition occurs in the monolayer at a temperature $T_c$ that is determined by the concentration $c$ of the C$_{30}$-acid in the volume of the solvent serving

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Figure 1. Airtight sample cell for study of the planar liquid - liquid interface: (1) the removable cap of the hatch and (2) the transparent polyester (Mylar) window.

as a reservoir for the surfactant molecules.

A sample of a macroscopically flat n-hexane - water interface oriented by the gravitational force was studied in a stainless-steel cell (see Fig. 1). The dimensions of the interface were $75 \times 150 \text{ mm}$ \cite{9}. The surface tension of the interface $\gamma(T)$ was measured by the Wilhelmy plate method with the cell placed in a homemade single-stage thermostat \cite{10}. To this end, through holes with a diameter of $\sim 1 \text{ mm}$ were made in its upper cap and in the cap of the hatch of the cell. The reflectometry of the n-hexane - water interface was performed in the hermetically closed cell and its temperature $T$ was controlled in a homemade two-stage thermostat. For the entrance and exit of X rays, as well as for the convenient visual observation of the interface, the windows of the cell were fabricated from transparent polyester (Mylar).

A solution of sulfuric acid ($= 2$) in deionized water (Barnstead, NanoPureUV) with a volume of about 100 mL was used as the lower bulk phase. The solution of melissic acid in n-hexane with a volume of about 100 mL and the volume concentration $c \approx 0.2 \text{ mmol/kg} \left( \approx 2 \cdot 10^{-5} \right)$ was used as the upper bulk phase. C$_{30}$-acid and n-hexane were purchased from the Sigma-Aldrich Corporation. The alkane was preliminarily purified by multiple filtration in a chromatography column through a thick ($\sim 30 \text{ cm}$) layer of a fine-grained aluminum oxide powder with a particle diameter of $\sim 0.1 \text{ mm}$. C$_{30}$-acid was doubly purified by recrystallization at room temperature from a supersaturated solution in n-hexane, which was prepared by the solution of the acid in n-hexane at a temperature of $T \approx 333 \text{ K}$ \cite{11}. Before the measurements of the reflection coefficient $R$ from the interface, the sample was annealed: the liquids in the cell were heated
Figure 2. Temperature dependence of the surface tension of the n-hexane - water interface at the concentration \( c \approx 0.2 \text{ mmol/kg} \) of C30-acid in n-hexane. The bending point corresponds to \( T_c \approx 291 \text{ K} \). The inset shows the kinematics of scattering at the n-hexane - water interface. The \((xy)\) plane coincides with the interface; the \( Ox \) axis is perpendicular to the beam direction; the \( O\) axis is normal to the surface and is opposite to the gravitational force; \( k_{in} \) and \( k_{sc} \) are the wave vectors of the incident and scattered beams in the direction of the observation point, respectively; \( q = k_{in} - k_{sc} \) is the scattering vector; and \( \alpha \) and \( \beta \) are the grazing and scattering angles in the plane normal to the surface.

to \( T \approx T_b \) and were then cooled below \( T_c \). Thus, the formation of gas bubbles at the n-hexane - water interface at a change in \( T \) was prevented in subsequent experiments.

A Wilhelmy plate made of a chromatographic paper (Wattman) with a length of \( L \approx 10 \text{ mm} \) and a width of \( \approx 5 \text{ mm} \) was used in the measurements of \( \gamma(T) \). It was fastened to a thin (diameter \( \sim 0.25 \text{ mm} \)) platinum wire passing through holes in the caps of the thermostat and hatch of the cell (see Fig. 1). The maximum change in the weight of the plate \( \Delta F \) was fixed by an electric balance (NIMA PS-2) at its slow pulling from the lower phase. Figure 2 shows the dependence \( \gamma(T) \approx \Delta F/2L \), which exhibits a feature (kink) at the phase transition temperature \( T \approx 291 \text{ K} \). A change in the slope of \( \gamma(T) \) is related to a change in the surface enthalpy \( \Delta H = \)
Figure 3. Reflection coefficient $R$ versus $q_z$ for the n-hexane-water interface at (diamonds) 293.4, (triangles) 290.1, (squares) 289.2, and (circles) 288.3 K. The solid lines correspond to the two-layer model of the absorbed monolayer.

$$-T_c \Delta (\partial \gamma / \partial T)_{p,e} = 1.1 \pm 0.1 \text{ J/m}^2.$$

Methods based on the scattering of synchrotron X-ray radiation currently provide the main information on the microscopic structure of (nonpolar organic solvent-water) interfaces, which cannot be obtained from the measurements of such characteristics as the surface tension, capacity of the interface, and surface potential [10, 12]. Unfortunately, relatively strong scattering in the bulk of the hydrocarbon solvent at $\lambda \sim 1 \text{ Å}$ prevents the application of the grazing diffraction method to study the in-plane crystal order at the liquid-liquid interface. The transverse structure of the interface was studied by X-ray reflectometry with the use of synchrotron radiation at the X19C station of the NSLS synchrotron, which was equipped with a universal spectrometer for studying the surface of the liquid [13]. A bending magnet with a critical energy of $\sim 6 \text{ keV}$ was a source of radiation for the X19C station. In experiments, a focused monochromatic beam with an intensity of $\approx 10^{11} \text{ photons/s}$ and a photon energy of $E = 15 \text{ keV}$ ($\lambda = 0.825 \pm 0.002 \text{ Å}$) was used.
Figure 4. Reflection coefficient $R$ versus $q_z$ for the n-hexane - water interface at (diamonds) 334.2, (triangles) 317.9, (squares) 308.1, and (circles) 298.2 K. The solid lines correspond to the two-layer model of the absorbed monolayer described in the main text.

Since the n-hexane - water interface is oriented by the gravitational force, the scattering kinematics is conveniently described in the right-handed Cartesian coordinate system whose origin $O$ is at the center of the illuminated region, the $(xy)$ plane coincides with the interface between the monolayer and water, the $Ox$ axis is perpendicular to the beam direction, and the $Oz$ axis is normal to the surface and is opposite to the gravitational force (see the inset in Fig. 2). Let $\mathbf{k}_{\text{in}}$ and $\mathbf{k}_{\text{sc}}$ be the wave vectors of the incident and scattered beams in the direction of the observation point, respectively. In the case of mirror reflection, $\alpha = \beta$ and $\phi = 0$, where $\alpha$ is the grazing angle in the $(yz)$ plane, $\beta$ is the angle between the scattering direction and the interface in the vertical plane, and $\phi$ is the angle between the incident and scattered beams in the $(xy)$ plane. The scattering vector $\mathbf{q} = \mathbf{k}_{\text{in}} - \mathbf{k}_{\text{sc}}$ at mirror reflection has only one nonzero component $q_z = (4\pi/\lambda) \sin(\alpha)$.

The dependence of the reflection coefficient $R$ on $q_z$ contains in-
Figure 5. Temperature dependence of the normalized reflection coefficient $R/R_1$ at $q_z = 0.05 \text{Å}^{-1}$, where $R_1$ is the reflection coefficient at $T \approx 292.2$.

formation on the electron density distribution $\rho(z)$ across the n-hexane - water interface averaged over a macroscopic area of the illumination region ($\sim 100 \text{mm}^2$). The measurements of $R$ at low $q_z$ values are restricted by the transverse dimension and natural divergence ($\sim 10^{-4} \text{rad}$) of a synchrotron radiation beam incident on the sample. The distance between the center of the cell and the nearest slits limiting the vertical dimension of the incident beam is $\sim 120 \text{mm}$. At the smallest grazing angles of $\sim 6 \cdot 10^{-4} \text{rad}$ ($q_z \approx 0.01 \text{Å}^{-1}$), the vertical dimension of the beam should be $\approx 15 \mu\text{m}$ for the illumination region to not exceed the flat segment of the interface ($\sim 20 \text{mm}$). This can be achieved only by suppressing the natural divergence of the beam to $\sim 10^{-5} \text{rad}$, e.g., by means of two entrance slits with a dimension of $\sim 10 \mu\text{m}$ at a distance of $\sim 600 \text{mm}$. At large grazing angles ($q_z > 0.2 \text{Å}^{-1}$), the maximum vertical dimension of the entrance slits, 0.4 mm, is limited by the chosen vertical angular resolution of the detector, $2\Delta\beta \approx 10^{-3}$ (a slit with a vertical dimension of 0.8 mm at a distance of $\approx 680 \text{mm}$ from the center of the sample). The measurements were performed with the resolution $\Delta\phi \approx 10^{-2} \text{rad}$ of the detector in the horizontal
Figure 6. Model electron density profiles for a monolayer of melissic acid normalized to the electron density in water under normal conditions \( \rho_w = 0.333 \text{e}^{-/\text{Å}^3} \) obtained within the two-layer model of (solid line) the low-temperature phase of the monolayer \( (T = 293.4 \text{K}) \) and (dashed line) the high-temperature phase of the monolayer \( (T = 317.9 \text{K}) \).

Figures 3 and 4 show the dependences \( R(q_z) \) for the n-hexane-water interface at various temperatures above and below the phase transition, respectively. At \( q_z < 4\pi/\lambda \alpha_c \approx 0.01 \text{Å}^{-1} \), the incident beam undergoes the total external reflection \( R \approx 1 \). The critical angle \( \alpha_c \) is determined by the difference \( \Delta \rho \approx 0.11 \text{e}^{-/\text{Å}^3} \), between the volume electron densities of n-hexane and water: 
\[
\alpha_c = \lambda \sqrt{r_e \Delta \rho / \pi} \approx 10^{-3} \text{rad},
\]
where \( r_e = 2.814 \cdot 10^{-5} \text{Å} \) is the classical radius of the electron. The data presented in Figs. 3 and 4 clearly demonstrate that the reflection curve changes sharply near \( T_c \). In addition to the dependences \( R(q_z) \), we measured the temperature dependence of the reflection coefficient near \( T_c \) at a fixed value of \( q_z = 0.05 \text{Å}^{-1} \) (see Fig. 5) with the same spatial resolution of the detector.

The analysis of Figs. 3 and 4 shows that \( \text{C}_{30}\text{H}_{60}\text{O}_2 \) molecules are absorbed in the form of a monolayer on the n-hexane-water plane.
interface. In order to obtain detailed information on the structure of the interface from \( R(q_z) \), we used the simplest qualitative two-layer model (slab model) of an adsorbed layer with five fitting parameters in which the density profile \( \rho(z) \) is based on the error function [14].

The lower limit of the standard deviations \( \sigma_j \) of the positions of the \( j \)th interfaces of the bilayer (\( j = 0, 1, 2 \)) from the reference value \( z_j \) is determined by the capillary width \( \sigma_{cw}^2 = (k_B T/2\pi\gamma) \ln(Q_{max}/Q_{min}) \) (\( k_B \) is the Boltzmann constant), which is specified by the short-wavelength limit in the spectrum of capillary waves \( Q_{max} = 2\pi/a \) (where \( a \approx 10 \) Å is the order of magnitude of the molecular radius) and \( Q_{min} = q_z^{max}\Delta \beta \) (where \( q_z^{max} \approx 0.45 \) Å\(^{-1} \)) [15, 16, 17]. Under the assumption that \( \sigma_j = \sigma_0 \) for all \( j \) values, the structure factor of the surface in the first Born approximation has the form [18]

\[
\frac{R(q_z)}{R_F(q_z)} \approx \left| \frac{1}{\Delta \rho} \sum_{j=0}^{2} (\rho_{j+1} - \rho_j)e^{-iq_z z_j} \right|^2 e^{-\sigma_0^2 q_z^2}, \tag{1}
\]

where \( \rho_j \) is the electron density in the \( j \)th layer; \( \rho_0 \) and \( \rho_3 \) are the electron densities in water and \( n \)-hexane, respectively; and \( R_F(q_z) \approx (q_z - [q_z^2 - q_c^2]^{1/2})^2/(q_z + [q_z^2 - q_c^2]^{1/2})^2 \) is the Fresnel function. The calculated reflection curves are shown by solid lines in Figs. 3 and 4. The model profiles \( \rho(z) \) for monolayers of (solid line) low- and (dashed line) high-temperature phases are shown in Fig. 6.

The variation of the parameters in the model of the monolayer is in agreement with the molecular structure of melissic acid, which has a hydrophilic head part and a hydrophobic hydrocarbon tail. The first hydrophilic layer of the monolayer for the low-temperature phase, which is in direct contact with water, includes polar groups and has the density \( \rho_1 = (1.16 \pm 0.05)\rho_w \) and the thickness \( L_1 = z_1 - z_0 = (15 \pm 2) \) Å (\( \rho_w = 0.333 \) e\(^-\)/Å\(^3 \) is the electron density in water under normal conditions). If the width of this layer is fixed \( L_1 < 10 \) Å at fitting, the quality of fitting at high \( q_z \) values worsens significantly. The second layer with the thickness \( L_2 = z_2 - z_1 = (29 \pm 2) \) Å is formed by hydrocarbon chains with the density \( \rho_2 = (1.01 \pm 0.02)\rho_w \). The fitting parameter \( \sigma_0 \) varies from 3.6 Å to 4.5 Å, which coincides within the errors with the calculated \( \sigma_{cw} \) value. The total thickness of the monolayer is \((42 \pm 3) \) Å, which also coincides within the errors with the calculated total length \((40.8 \) Å = \( 29 \times 1.27 \) Å(C-C) + \( 1.5 \) Å(-CH\(_3\)) + \( 2.5 \) Å(-COOH)) of the C\(_{30}\)H\(_{60}\)O\(_2\) molecule (it contains 256 electrons). Thus, all molecules in this
phase of the monolayer are elongated along the normal to the surface and the area per molecule of C_{30}-acid is \( A = \frac{256}{(\rho_1 L_1 + \rho_2 L_2)} = (17 \pm 1) \, \text{Å}^2 \). This value corresponds to the densest crystal phase of alkanes [19].

The hydrophilic layer in the high-temperature phase has the density \( \rho_1 = (1.12 \pm 0.02) \rho_w \) and thickness \( L_1 = (18 \pm 2) \, \text{Å} \). The electron density in the second layer with the thickness \( L_2 = (18 \pm 2) \, \text{Å} \) is \( \rho_2 = (0.77 \pm 0.02) \rho_w \). The fitting value \( \sigma_0 = 4.0 \pm 0.2 \, \text{Å} \) coincides within the errors with the value \( \sigma_{cw} \approx 3.6 \, \text{Å} \) calculated with the data for \( \gamma(T) \). The value \( A = 23 \pm 1 \, \text{Å}^2 \) for the high-temperature phase corresponds to a high-molecular weight hydrocarbon liquid [19].

The monotonic temperature dependence \( R(T) \) at a fixed \( q_z \) value (see Fig. 7) indicates incoherent reflection from the in-plane structure of the interface. Since our data show that the relative contribution from diffuse scattering at the interface to the reflected power is small \( \sim 10^{-3} \), \( R \) in the first approximation can be represented in the form of a linear function of the coverage of the surface \( C(T) \) by domains of the low-temperature phase of C_{30}-acid [20]:

\[
R \approx C(T) R_1 + (1 - C(T)) R_2,
\]

where \( R_1 \) and \( R_2 \) are the \( R \) values for low-temperature \( (C(T) = 1) \) and high-temperature \( (C(T) = 0) \) phases, respectively. Circles in Fig. 7 represent the calculated dependence for \( C(T) \approx (R - R_2)/(R_1 - R_2) \) at \( q_z = 0.05 \, \text{Å}^{-1} \). According to this dependence, the phase transition in the monolayer at \( T_c \approx 293.5 \) is sharp: the surface is rearranged in the temperature interval \( \leq 0.5 \). A small difference \( \sim 2 \, \text{K} \) of the \( T_c \) value for this sample from the temperature of the bending point \( \gamma(T) \) in Fig. 2 is due both to uncertainty in its determination and to a small difference in the volume concentration \( c \) between the samples.

The analysis of the experimental results reveals two important features of the critical behavior of the crystalline monolayer of melissic acid at the interface. First, a phase transition associated with melting occurs in this monolayer with an increase in the temperature. Such a behavior differs from the critical behavior of monolayers of high-molecular saturated and fluorocarbon alcohols at this interface, where an increase in the temperature is accompanied by phase transitions of evaporation and sublimation of monolayers, re-
Figure 7. Temperature dependence of the coverage of the interface by domains of the low-temperature phase $C$. The points are obtained from the data presented in Fig. 5 with the use of Eq. (2), where $R_1$ and $R_2$ are the reflection coefficients at $T \approx 292\, \text{K}$ and $T \approx 295\, \text{K}$, respectively.

respectively [6]. Second, according our data, the total electron density in the monolayer at $T_c$ decreases stepwise by $\Delta A/A \approx 30\%$. This behavior is significantly different from the critical behavior of monolayers of high-molecular weight alcohols at the n-hexane - water interface, where phase transitions occur in a certain temperature range, as well as from the crystallization of monolayers of CTAB and STAB cationic surfactants, where two critical temperatures were observed [7].

To conclude, the reported data illustrate the solid - liquid phase transition in the Gibbs monolayer at the n-hexane - water interface. With an increase in the temperature in a narrow vicinity of $T_c$, a significant fraction of adsorbed molecules of C$_{30}$-acid leave the interface and are solved in the bulk of n-hexane. In this case, the thickness of the monolayer $L_1 + L_2$ decreases by $\approx 15\%$ and $A$ increases by $\approx 30\%$.

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