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SOME PROPERTIES OF A PRECURSOR FILM

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The optical, rheological, and topological properties of a precursor film, which is created by a drop lying on a surface, were studied by means of ellipsometry. The investigated liquid is glycerin; the investigated substrates were type K8 and KU1 glass. The results are in good qualitative agreement with DLFO theory.

Heterogeneous dispersive media are used in many industrial processes, which creates heightened interest in the wetting and spreading phenomena, which play a defining role in such systems. It is known that an interphase liquid—vapor surface can form near the contact of a drop with the base. If wetting is incomplete, the contact angle is finite at equilibrium; if wetting is complete, the contact angle is negligibly small [1]. It has been observed [1-3] that a submicron thick film forms on a solid substrate for any type of wetting near the interphase contact line. This film, which is called the precursor film, starts at the boundary between the phases, where its thickness is at a maximum, and slowly thins away from the boundary. In the case of complete spreading, this film has the shape of a pancake, which contains all the initial volume of the liquid. In the case of incomplete wetting, that is, when some equilibrium contact angle θ is established in the system, this film also takes on a more complex equilibruim shape, which forms a transition region between the drop and the substrate. The shape and properties of this transition region are totally determined by the balance of forces which act on the interphase boundary and, consequently, are the most important characteristics of the liquid—solid body—vapor system.

The method of ellipsometry was used to study the optical, rheological, and topological properties of the precursor film, which arises in the case of incomplete wetting. Glycerin was chosen as the liquid to be studied. The substrates in the study were plane parallel plates of optical glass of type K8 and KU1. K8 glass is a single-component borosilicate glass, which contains additives of large cations and as a result has a large porosity in its structure. KU1 glass is a simple quartz silicate glass with no additional inclusions or developed porosity. From studies on glass surfaces [4], it is known that the surface of any silicate glass under normal conditions is covered with a layer of adsorbed water with inclusions of a depolymerizing silicon oxide grid. This "gel" has a chemical composition of the type $SiO_x(OH)_y$, where $x \to 2$ and $y \to 0$ with depth. We determined the effective values of these coating thicknesses for the glasses we used. The thickness was 50 Å for K8 glass, and 20 Å for KU1 glass, which is in good agreement with other investigations [5], which give values of 55 and 20 Å, respectively. The difference in the thicknesses is explained by the different glass porosities and

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therefore the different ability of the surface to accumulate water. Drops of glycerin which were placed on those surfaces did not wet them completely, but formed finite values of the equilibrium contact angles of 20° for K8 and 25° for KU1.

The surface was cleaned before each experiment, first mechanically with a pad moistened with alcohol and then with ultraviolet radiation [6]. This cleaning sequence guaranteed a high reproducibility of the surface, which was monitored with ellipsometry. The ellipsometer used in the investigations was a standard instrument LEF-3M which was equipped with a cap, which narrowed the measurement field to an area of 0.1 mm^2 and made it possible to measure the optical constants and the thicknesses with a high degree of spatial resolution.

The experiment was conducted as follows: an automatic microdispenser was used to place glycerin drops (2-mm diameter) on a base, which was in a thermostatic cell on the stage of the ellipsometer. Temperature of the drop itself was the same as the substrate, which was guaranteed by regulating the temperature of the dispenser. The cell was maintained at a temperature of 26°C with an accuracy of 0.1°C during the whole experiment. The optical constants and the thicknesses of the precursor film, which correspond to various distances from the edge of the drop, were determined immediately after flow started, using the methods discussed in [7].

In the experiments, it was observed that the film, which arose immediately after flow started, outpaced the motion of the drop. Therefore, in the first half hour, the liquid layer nearest the surface moved faster. This time is the time required to establish the equilibrium shape of the precursor film. The flow of the drop, which was recorded by measuring the radius and the contact angle, continued over one hour, but the from of the precursor film did not change (it moved along with the drop boundary). The equilibrium state in the drop—substate—vapor system was established in 1.5 h under the conditions described above. The profile of the precursor film under equilibrum is shown in Fig. 1. Here the beginning of the OY-axis coincides with the glass (without the "gel" layer) and the beginning of the OX-axis coincides with the optical boundary of the drop.

As can be seen from Fig. 1, the maximum thickness of the precursor film occurs at the same 8-nm mark on both glasses (if it is measured from the actual surface of the glass). The decrease in the thickness of the precursor film itself away from the boundary of the drop is rather slow, but nonetheless its slope can be divided into two parts. The first part, near the boundary, is characterized by a monotonic drop in thickness. The second part, on the periphery of the slope, has a stepwise character and falls even slower. The height of one step is estimated at roughly 1.5 Å by the ellipsometry method. The base of the film at all stages of flow was stepped, and in the first stage of the layer the liquid forming the step moved with various velocities, which increased closer to the surface.

The existence of such a structure on the slope of the precursor film, the nature of its motion, and also the ratio of the observed width to the height of a single step, which is comparable to the dimension of a "stacked" molecule, can lead to the hypothesis that here the liquid molecules are oriented and packed in monolayers. Actually, when glycerin, or for that matter any polar liquids, are adsorbed on sorbents with hydroxyl groups, molecular complexes are formed with stable hydrogen bonds [8]. The distribution of OH^- groups along the chain of a molecule favors its horizontal orientation along the solid substrate. Thus, the interaction of glycerin with the glass surface should be accompanied by structural changes of the boundary layers.

The fact that a decreased value of the polarization of the glycerin in the film is recorded in the experiment tends to substantiate this hypothesis. The index of refraction for the precursor film was $n = 1.22$ as opposed to $n = 1.47$ for bulk glycerin. A similar decrease indicates directly that the film is structured and that orientation effects occur in it.

The geometric form of the precursor film, which corresponds to the equilibrium drop—substrate—vapor configuration, can also be obtained by using the basic assumptions of the Deryagin—Landau—Fervei—Overbek (DLFO) stability theory of lyophobic colloids. According to this theory, the condition for equilibrium between a wetting film and the bulk liquid is determined by the equality of the disjoining pressure in the film $\Pi(h)$ and the drop in the capillary pressure P_0 on the surface of the bulk liquid. From these assumptions it follows that surface forces should continue to act in a transition region between the drop and the film which is in equilibrium with it.

In order to find the exact geometric form of the transition region, we can use the known equation which expresses the constant chemical potential of liquid molecules in any part of a layer with a variable thickness $h(r)$ [9]:

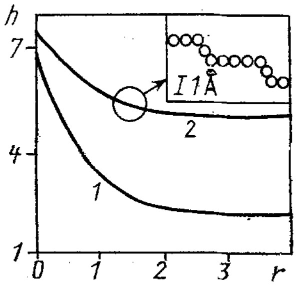

Fig. 1. Profile shape of the precursor film for a glycerin drop on substrates of K8 glass (1) and KU1 glass (2), where h is in nanometers and r is in millimeters.

$$\sigma K(r) + \Pi(h) = P_0 = \text{const},\ K(r) = h''/(1 + (h')^2)^{3/2}. \tag{1}$$

In order to solve this equation we use the method discussed in [10]. Starting from a typical form of the isotherm of the disjoining pressure, we use a typical function $\Pi(y)$:

$$\Pi(h) = \begin{cases} 0 & \text{for } h > t_1, \\ a(t_0 - h) & \text{for } 0 < h < t_1. \end{cases} \tag{2}$$

For a film with small curvature ($h' \approx 0$) and spherical drops, Eq. (1), with a consideration of (2), takes the following form

$$\sigma h'' + a(t_0 - h) = P_0.$$

Furthermore, we use the boundary condition $h \to h_0$ for $r \to \infty$ and introduce a new variable $h_0 = t_0 - P_0/a$. Then we obtain a solution to this equation in the form

$$h = h_0 - (h_0 - t_1) c \exp(-\sqrt{a/\sigma}\, r). \tag{3}$$

The constant C, which enters into the solution, can be determined from the joining condition of the transition region with the drop: $h(L) = t_1$ and $C = \exp(\sqrt{a/\sigma} L)$, where L is the radius of the base of the drop.

Equation (3) defines a precursor film geometry, which is similar to that observed experimentally and which makes it possible to evaluate a. Its value is slightly different for both glases $a = 10^6\text{-}10^7$ dyn/cm^3. However, it should be noted that the difference between the experimental value and the literature value is that the calculated value [10] only considers two components of the disjoining pressure: the dispersion and the molecular components, but we must consider the structural component. The contribution [3, 9] of this component slows the decrease in disjoining pressure with thickness, which indicates an increase in a, which we observed.

Equation (3) also makes it possible to estimate the equilibrium contact angle θ. If we assume that the radius of the base of the drop $L > \sqrt{\sigma/a}$, we can assume that the derivative h' taken at the boundary of the drop (r = L) will give the tangent of θ

$$h'(L) = \mathrm{tg}\,\theta \approx \sqrt{a/\sigma}\,(t_1 - h_0).$$

The contact angle turns out to be proportional to the difference ($t_1 - h_0$). Consequently, if the values of t_1 are close, θ will be larger for a drop which is in eequilibrium with a thinner film and vice versa. Actually, glycerin on KU1 glass covered with a 20 Å film has a 5° smaller contact angle than does K8 glass, which is covered with a 50 Å film, if the surface forces act over the same radius (~8 nm) for both glasses.

Thus, it can be concluded that the experimental data obtained here are related to the geometric form of the precursor film, which is in good qualitative agreement with DLFO theory. By using this theory it is possible to explain the observed difference in the contact angles for a glycerin drop on substrates made from different brands of glass. Based on these results it will be possible to conduct more precise investigations on the makeup of the disjoining pressure and especially to evaluate its structural composition.

NOTATION

θ, equilibrium contact angle; σ, surfacetension of liquid; $K(r)$, local value of the surface curvature; P_0, capillary pressure of the drop at equilibrium; R, radius of curvature; $h(r)$, variable film thickness; $\Pi(h)$, disjoining pressure; t_1, radius for the action of surface forces; h_0, thickness of the equilibrium film on the surface; a and t_0, parameters which determine the change of the disjoining pressure.

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NONSTEADY FLOW OF A VAPOR–DROP FLOW IN A HEATED CHANNEL

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Flow of a vapor–drop mixture in a heated channel is studied under steady and nonsteady conditions using a model which considers direct thermal interaction of drops with the heating surface.

In various heated channels using a two-phase working fluid as well as in accidental situations a vapor–droplet flow can develop, as has been mathematically modeled in a large number of studies – an overview can be found in [1]. A complete model for description of a vapor–drop flow in a heated channel under steady-state conditions was presented in [1]. That model considered direct thermal interaction of drops with the heating surface, and the temperature of the superheated vapor was found from the energy equation, including the thermal flux from the heating surface into the vapor and the thermal flux from the vapor to the drops. In the present study, using a model analogous to that of [1], we will consider the flow of a vapor–drop mixture under steady and nonsteady conditions. The system of equations for the flow of vapor–drop mixture [1] (assuming that the flow is not in thermodynamic equilibrium, the vapor velocity is equal to the drop velocity, and breakup and combination of drops are absent) has the form:

$$\begin{gathered}\partial(\rho_i^0\alpha_i)/\partial t+\partial(\rho_i^0\alpha_i v)/\partial z=J_{ij},\\ \partial(u_i\rho_i^0\alpha_i)/\partial t+\partial(u_i\rho_i^0\alpha_i v)/\partial z=-J_{ij}u_{is}+\alpha_i p/\rho_i^0\,d\rho_i^0/\partial t-Q_{i\sigma}+Q_{w1},\\ \partial n/\partial t+\partial(nv)/\partial z=0,\end{gathered}\tag{1}$$

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