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Dynamics of Complete Evaporation of a Sessile Droplet of 1-Propanol–Water Solution at Different Ambient Humidities

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Abstract—Experimental data have been obtained on the complete diffusion evaporation of a sessile microdroplet of an aqueous 1-propanol solution on a hydrophobized polished quartz substrate in air at atmospheric pressure and room temperature. During the evaporation of the sessile droplet, time dependences have been determined for its key thermodynamic and geometric parameters, i.e., the contact angle, base surface area, and volume. It has been revealed that the character of time variations in the contact angle depends on the initial alcohol concentration in the droplet and air humidity. At a high alcohol concentration and a low air humidity, the droplet contact angle monotonically decreases throughout the evaporation process. The contact angle of a solution droplet with a prevailing content of water varies in several stages. In this case, the monotonic reduction in the contact angle is, at a certain moment, replaced by a stage of its growth. The comparison of the maximum contact angle of an evaporating droplet with the contact angle of a sessile droplet of pure water enables one to determine the amount of alcohol in a studied droplet by the end of this stage. The residual alcohol amount governs the subsequent evolution of the droplet up to its complete evaporation.

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INTRODUCTION

There is increasing interest in the study of wetting solid surfaces by liquids and the behavior of contact angles of evaporating and growing sessile droplets due to the important role of such droplets in heterogeneous nucleation upon phase transitions and the feasibility of using hydrophobic and superhydrophobic surfaces in new microfluid technologies. Numerous experimental and theoretical studies devoted to the analysis of fundamental mechanisms of wetting and evaporation have been published in recent decades [1–7]. These studies mainly deal with the evaporation of one-component liquids, with particular attention being focused on water droplets on diverse solid substrates. Anderson et al. [8] have experimentally shown that water droplet evaporation on a nonideal surface is accompanied by wetting hysteresis. At the first stage of evaporation, the contact angle decreases, while the droplet base surface area remains unchanged until the contact angle reaches some critical value. At the second stage, the contact angle remains unchanged, whereas the base surface area monotonically diminishes. In other works [9–12], different stages of pure water droplet evaporation were also observed and theoretically described. For example, the problem of the due to stationary diffusion into gas phase isothermal evaporation of a one-component sessile droplet on a solid substrate was rigorously solved in [9]. Later, other authors used the theoretical results of this work, although as applied mainly to the first and second stages of droplet evaporation. In [11], we have presented a brief review of previous works devoted to the stationary evaporation of sessile droplets and compared new experimental data with the theory of the stationary evaporation at all three stages of sessile water droplet evaporation at different ambient humidities. In particular, it has been shown that the diffusion regime of droplet evaporation is realized at the first and second stages with allowance for a decrease in the droplet temperature. It also remains stationary at the third stage, when the droplet base surface area and contact angle decrease simultaneously; however, the gradual approach of the droplet temperature to the substrate temperature with a substantial decrease in the droplet height at the final stage of evaporation must be taken into account. The influence of thermal effects on the dynamics of droplet evaporation at all three stages was evaluated in [11].

The study of the roles of ambient medium properties (temperature, pressure, and humidity) and the state (hydrophobicity, hydrophilicity, smoothness, or roughness) and nature of a surface has resulted in the development of ideas about the influence of these factors on the contact angle of an evaporating water droplet. For example, aluminum, which is a metal very widely applied in industry, was used as a substrate for droplet evaporation in [12–15]. The authors of [13] have described the experimental study of the effect of temperature on the quasi-static advancing contact angle of a water droplet on an aluminum surface. This study has resulted in the determination of a temperature regime that changes the stability of the contact angle. The study of the effect of the microstructure of a rough aluminum surface on the contact angle with allowance for the Wenzel factor [15] has shown that the contact angle on such rough substrates may substantially vary upon displacement of the contact line. Chow has generalized the Dupre–Young equation [16] by introducing the wetting of a rough surface into it and has proposed a theory describing the shape of the contact line taking into account the nonuniform microstructure of the surface. Thus, the theoretical results obtained by many authors for one-component droplets have, on the whole, been confirmed by experimental observations of time variations in droplet parameters, such as contact angle, contact radius, and volume.

The evaporation of solution droplets has been studied to a substantially smaller extent. The regularities of the evaporation of mixed liquids must be markedly affected by the properties of pure components of a mixture, such as the partial pressures of saturated vapors, partial evaporation heats, and partial molecular volumes, as well as, obviously, the concentrations of the substances in a solution. For example, methanol, ethanol, and propanol are infinitely miscible with water; however, strongly different sizes of their molecules may play an important role in the evaporation of binary mixtures. The saturation vapor pressures of sulfuric acid and water differ from each other by several orders of magnitude. In [17], we considered the stationary diffusion evaporation of a sessile droplet consisting of two infinitely miscible liquids in the atmosphere of a noncondensable gas. A relation between the current values of the solution concentration and the droplet volume has been derived in an explicit form under the ideal solution approximation. It has been shown that the volume of a binary sessile droplet may vary nonmonotonically with time. The experimental data on time variations in the volume, base surface area, and contact angle of a sessile droplet of an aqueous sulfuric acid solution on a hydrophobized substrate were used in [17] to describe the evaporation of the droplet taking into account the nonideality of this solution.

A number of works devoted to studying the evaporation of droplets of alcohol solutions on solid substrates should also be noted. Chiang et al. [18] studied the effect of a smooth polished and superhydrophobic substrate on the evaporation of binary ethanol–water solution droplets. The authors have revealed that, as a result of droplet rolling, the wetting hysteresis on a homogeneous nanostructured surface is substantially smaller (1.5°–2°) than that on a smooth polished surface (18°–20°). The results of experiments with droplets of ethanol–water binary mixtures on a gold surface modified with a self-organized decanethiol monolayer and a rough polytetrafluorethylene surface have been presented in [19, 20]. It has been shown that the evaporation of a sessile solution droplet is affected by two factors, i.e., the wetting hysteresis and the initial evaporation of a more volatile component. Therefore, the initial alcohol concentration in a solution plays the key role. The authors of [19, 20] have noted the following general tendency: an increase in the droplet contact angle is accompanied by a decrease in the base surface area. This tendency differs a binary mixture from a pure liquid, for which the contact angle and the base surface area monotonically decrease with time. An analogous character of evaporating volatile mixtures was also observed for other alcohols—methanol and propanol [21, 22]. The authors of [22] studied the evaporation of a sessile droplet of a binary water–methanol mixture on a smooth polymer substrate in saturated vapors of the components. Concomitant mechanisms of the evaporation process—namely, the competition between the evaporation and a hydrodynamic flow—were revealed. Rowan et al. [23] studied the evaporation of a mixed 1-propanol–water droplet on a poly(methyl methacrylate) surface at an initial contact angle of about 20°. The authors have noted that propanol is less volatile than ethanol. They have found that, at an alcohol concentration of less than 67.5 wt %, an aqueous 1-propanol solution is an azeotrope. The evaporation of the azeotrope mixtures containing excess water was accompanied by an unstable behavior of a sessile droplet, which led to the failure of the three-phase contact line and to actual disappearance of the droplet itself, i.e., its spreading into a film followed by spontaneous formation of a new droplet.

In this work, we report the results of new experiments on the complete diffusion evaporation of a sessile microdroplet of an aqueous 1-propanol solution in air at atmospheric pressure and room temperature. The time dependences of the key thermodynamic and geometric parameters of the sessile droplet (contact angle, base surface area, and volume) have been determined in the course of evaporation. In contrast to [23], we performed our experiments with 1-propanol–water solution droplets on hydrophobized polished quartz, when initial contact angles were rather large and droplet failure in the course of evaporation was not observed.

EXPERIMENTAL

A hydrophobized quartz plate was mounted in a sealed chamber with controlled air humidity and temperature. Preliminarily, the plate had been thoroughly washed with the help of sonication. The temperature and humidity of air in the chamber were measured with an electronic hygrometer at accuracies of 0.1° and 0.1%, respectively. During an experiment, the humidity could vary within 1%.

Water–alcohol solutions of different concentrations with prevailing contents of either water (alcohol fraction of 35 wt %) or alcohol (72 wt %) were prepared from triply distilled water and pure (99.9%) 1-propanol. A droplet of an alcohol solution was placed onto the hydrophobized plate with a microsyringe, and the droplet evolution in the course of evaporation was monitored with a video camera recording a side view, with the images being inputted to a computer display. The processing of the images obtained in the course of evaporation yielded current values of droplet base radius $R(t)$ and height $h(t)$. The linear sizes obtained in this way were used to calculate the current values of droplet base surface area, contact angle θ, and volume V. The values of θ and V were calculated by the following equations for a ball segment: $\theta = 2\arctan\left(\frac{h}{R}\right)$ and $V = \frac{\pi h}{6}\left(h^2 + 3R^2\right)$, respectively. Thus, the time dependences were obtained for the geometric parameters of the evaporating droplets at different initial alcohol concentrations in them.

The hydrophobicity of the quartz substrate used in the experiments was estimated by measuring the contact angle of pure water. The value of this angle equal to 103° found in these experiments was also used as a reference, which made it possible to judge (at least qualitatively) the character of variations in the alcohol concentration in a droplet during evaporation when analyzing the experimental time dependences of alcohol solution contact angles.

RESULTS AND DISCUSSION

A series of experiments was performed on the evaporation of microdroplets of binary propanol–water mixtures with different initial concentrations, as well as the evaporation of pure propanol droplets. The measurements were carried out at both a low air humidity in the chamber and a high humidity, when the water vapor was almost saturated. In all cases, the dependences of droplet contact angle, base surface area, and volume on evaporation time were obtained. These dependences have appeared to be absolutely different for different initial alcohol concentrations in the droplets and different air humidities.

The experimental data on the evaporation of a droplet of a 35 wt % propanol solution at a relative air humidity of 26% are presented in Fig. 1. The time dependences of the contact angle (Fig. 1a) and the base surface area (Fig. 1b) during evaporation exhibit several characteristic successive stages of variations. In the course of approximately 1 min after the onset of evaporation, the contact angle monotonically decreases from the initial value of 70° to nearly 60°; then, it remains almost unchanged for about 1 min more. At the same time, the droplet base surface area remains actually unchanged for the first minute; then, it begins to decrease monotonically. Such behavior is similar to that observed for a one-component droplet evaporating under the conditions of contact angle hysteresis [11] and is most likely due to the fact that, in this experiment, the solution concentration in the droplet varies rather slowly in the beginning of the evaporation process. It is obvious that, under the condition of a constant solution concentration, the behavior of a binary droplet must be similar to the behavior of a one-component droplet with some effective values of the surface tension and other thermodynamic characteristics. As the alcohol concentration in the droplet decreases with time, the evaporation process passes to a new stage, at which the contact angle gradually increases to reach a maximum value of 96°. Judging by the value of the contact angle, by the end of this stage, we deal with a droplet containing predominantly water and some amount of the alcohol, because the contact angle still remains noticeably smaller than 103°, i.e., the value of the angle for pure water. At the same time, the droplet height somewhat increases, while its base surface area somewhat decreases.

Note that the observed duration of the stage of growing contact angle (about 4 min) is comparable with the characteristic time of diffusion mixing of a solution in a droplet. Indeed, for diffusion mixing time t_D, we have $t_D \approx h^2/D$, where h is the droplet height and D is the binary diffusion coefficient of alcohol and water in a droplet. Using value $D \approx 10^{-5}$ cm/s and taking into account that, in this experiment, $h \approx 0.5$ mm, we obtain $t_D \approx 250$ s. Thus, it may be supposed that, by the end of the stage of growing contact angle, the droplet solution becomes almost spatially homogeneous throughout the droplet bulk, including the region of the interface with the substrate. This, in turn, leads to a rise in the surface tension at the droplet–substrate interface, which also facilitates the growth of the contact angle. Upon the further evaporation, both the base surface area and contact angle of the droplet monotonically decrease with time, like they do at the final stage of the evaporation of a pure water droplet [11]. The volume of the evaporating droplet (Fig. 1c) monotonically decreases with time rather rapidly in the beginning of the evaporation process and very slowly at the end of the droplet lifetime.

The photographs obtained by video filming the successive variations in the droplet profiles (Fig. 2) obviously illustrate the above-described behavior of

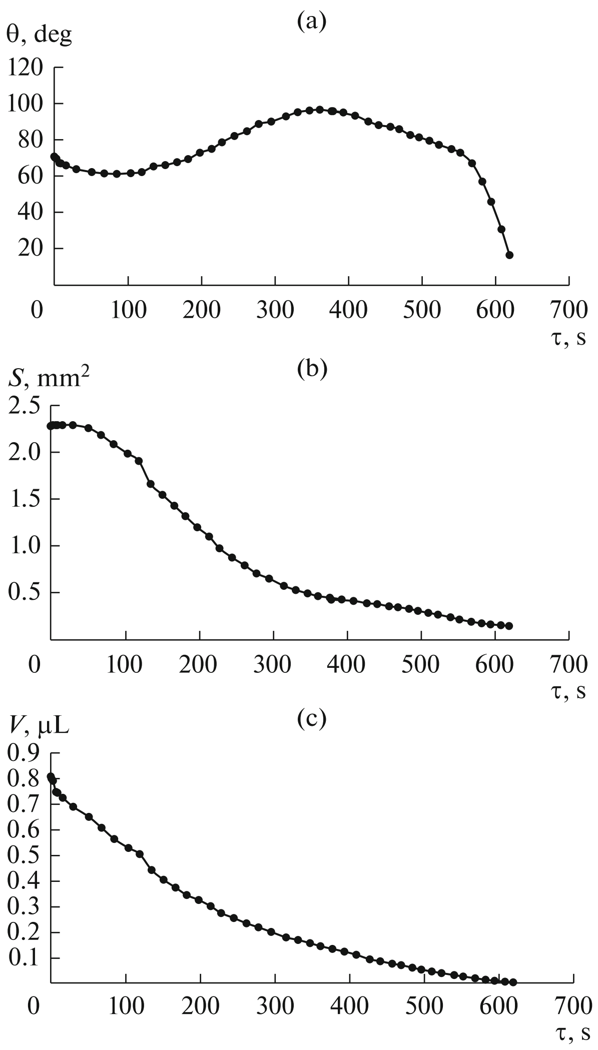

Fig. 1. Time variations in (a) contact angle, (b) base surface area, and (c) volume of a 35% propanol solution droplet evaporating at 26% humidity.

the droplet in the course of evaporation. The first profile (a) corresponds to the initial droplet with a contact angle of 70°. For the approximately 60 initial seconds of evaporation, the angle has decreased by 10° (b). The next photograph (c) shows that the diameter of the droplet base has diminished, while its height and contact angle have increased. Therewith, the contact angle approaches its maximum value of 96°; then, the droplet size begins to monotonically decrease (d, e) up to its complete evaporation.

The experiment on the evaporation of a droplet of a 35% propanol solution in water-saturated atmosphere has shown that the character of the binary mixture evaporation noticeably differs from the evaporation under the conditions of low humidity. A vessel with water was placed into the sealed chamber to saturate the atmosphere with water vapor. Figures 3a and 3b present the dependences of the droplet contact angle and base surface area on the time of evaporation at air humidity of 87%. A slight (about 3°) decrease in the contact angle for the initial 60 s of evaporation is followed by its rather abrupt growth; nearly 4 min later, the contact angle reaches its maximum value of 102°; i.e., it becomes almost equal to the corresponding value for a pure water droplet. Therewith, the time variation in the droplet base surface area (Fig. 3b) is similar to the behavior of the corresponding dependence in the case of low humidity; i.e., it remains constant during a short initial time period, and, then, it monotonically decreases. At the next stage, the droplet evaporates for some time in the regime of a constant contact angle; then, the final stage of evaporation begins, at which both the droplet base surface area and contact angle monotonically decrease with time.

This behavior is analogous to the behavior of a pure water droplet at corresponding stages of evaporation. In this case, the droplet volume monotonically decreases with time, although very slowly because of the high air humidity. The comparison between the initial contact angles of a droplet in an unsaturated atmosphere (Fig. 2a) and at a high humidity (Fig. 3a) shows that that they are equal; hence, the increased air humidity has no effect on the wetting of the hydrophobic substrate by an initial droplet. The role of the high humidity substantially manifests itself as a more pronounced increase in the contact angle and the appearance of a rather long (about 10 min) subsequent stage of evaporation at a constant contact angle, which is equal to its maximum value. The increase in the contact angle is distinctly seen in the droplet photographs depicted in Figs. 4b and 4c.

The dependences obtained in the above-described experiments show that, at the same initial alcohol concentration in a droplet, the character of evaporation significantly depends on the air humidity in the chamber. The observed increase in the droplet contact angle is much more pronounced at a high humidity than at a low one. Therewith, at low humidity, alcohol does not completely evaporates from the droplet, while, in the atmosphere saturated with water vapor, propanol is actually absent in the droplet already by the moment of reaching the maximum value of the contact angle; then, pure water evaporates slowly. Since, at the same initial alcohol concentration in the droplet, a decrease in the humidity decelerates the growth of the contact angle, it may be reasonable to suggest that, at equal air humidities, an increase in the initial alcohol concentration must also lead to suppression of the aforementioned effect. To verify this hypothesis, experiments were carried out on the evaporation of an aqueous pro-

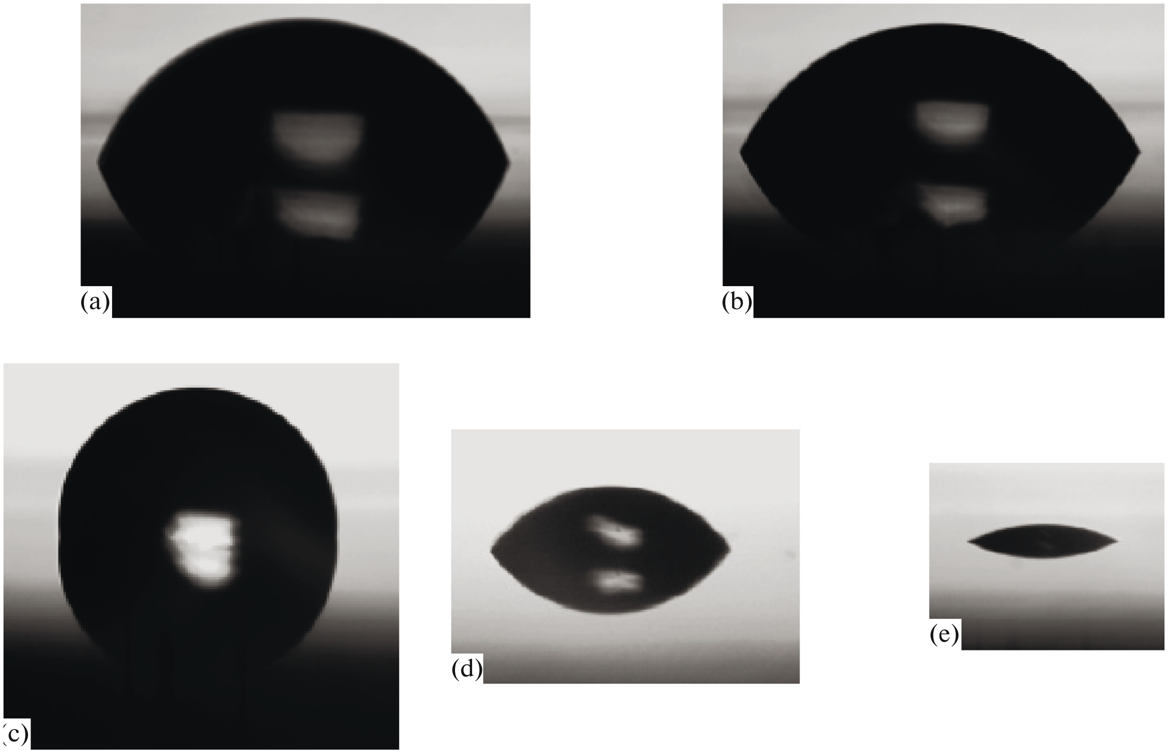

Fig. 2. Photographs of the gradually varying profile of a 35% propanol solution droplet evaporating in an unsaturated atmosphere at 26% humidity.

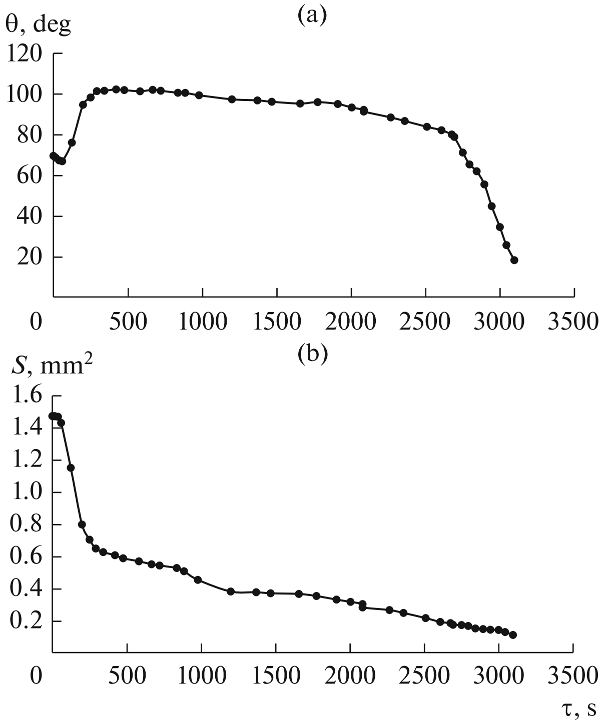

Fig. 3. Variations in (a) contact angle and (b) base surface area of a 35% propanol solution droplet evaporating at 87% humidity.

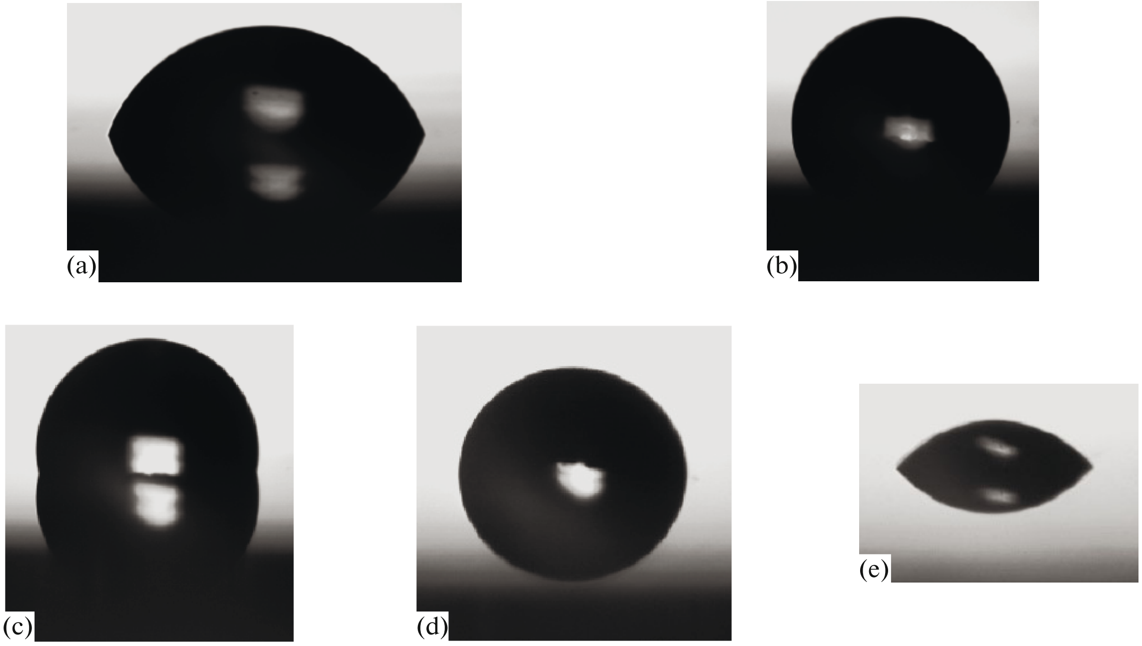

Fig. 4. Photographs of the gradually varying profile of a 35% propanol solution droplet evaporating in a saturated atmosphere at 87% humidity.

panol solution droplet with an alcohol concentration of 72 wt % at different relative air humidities. The results of these experiments are illustrated in Fig. 5. Figure 5a shows the time dependence of the contact angle at a humidity of 30%. It can be seen that, during the entire evaporation process, the contact angle monotonically decreases with time in this case. Recollect that, upon the evaporation of a droplet with an initial alcohol concentration of 35 wt % at almost the same humidity (26%), the corresponding dependence exhibited a stage of a noticeable increase in the contact angle (Fig. 1a). Thus, an increase in the initial alcohol concentration at the same air humidity, does suppress the possible growth of the contact angle. In this experiment, the droplet base surface area remained unchanged during initial ~50 s (while the contact angle monotonically decreased), due to, as has been mentioned above, the contact angle hysteresis in the beginning of the evaporation process; then, it monotonically decreased (Fig. 5b). When the humidity is increased, the time dependence of the contact angle becomes nonmonotonic. This dependence plotted for an initial alcohol concentration of 72 wt % and a humidity of 45% (Fig. 5c) exhibits a stage of growth, with the maximum angle value being nearly 82°, which is noticeably lower than the contact angle for a pure water droplet. Therefore, the droplet seems to contain a substantial amount of the alcohol at this moment.

This important effect of the air humidity on the dynamics of droplet evaporation is also evident from the results of the experiments on the evaporation of a concentrated propanol droplet. The time dependences of the contact angle plotted at different humidities are presented for this case in Fig. 6. In a rather dry air (23% humidity), a slight monotonic decrease in the contact angle was observed during the entire evaporation period (Fig. 6a). At a moderate humidity (63%), the time dependence of the contact angle (Fig. 6b) shows a stage of slight growth followed by a monotonic and rather rapid decrease. In the atmosphere of an almost saturated water vapor (90% humidity), the time dependence of the contact angle (Fig. 6c) is similar to the dependence observed for the evaporation of a droplet with an alcohol concentration of 72 wt % at 45% humidity (Fig. 5c). In both cases, a relatively short initial stage of a decrease in the angle due to the hysteresis is followed by the stage of evaporation at an almost constant contact angle; then, the angle begins to grow. The maximum angles observed in these experiments have close values, and, upon subsequent evaporation, they monotonically decrease with time in both cases.

Thus, the initial alcohol concentration and air humidity are the key factors that determine the dynamics of the evaporation of sessile droplets of propanol—water solutions and pure propanol in an air

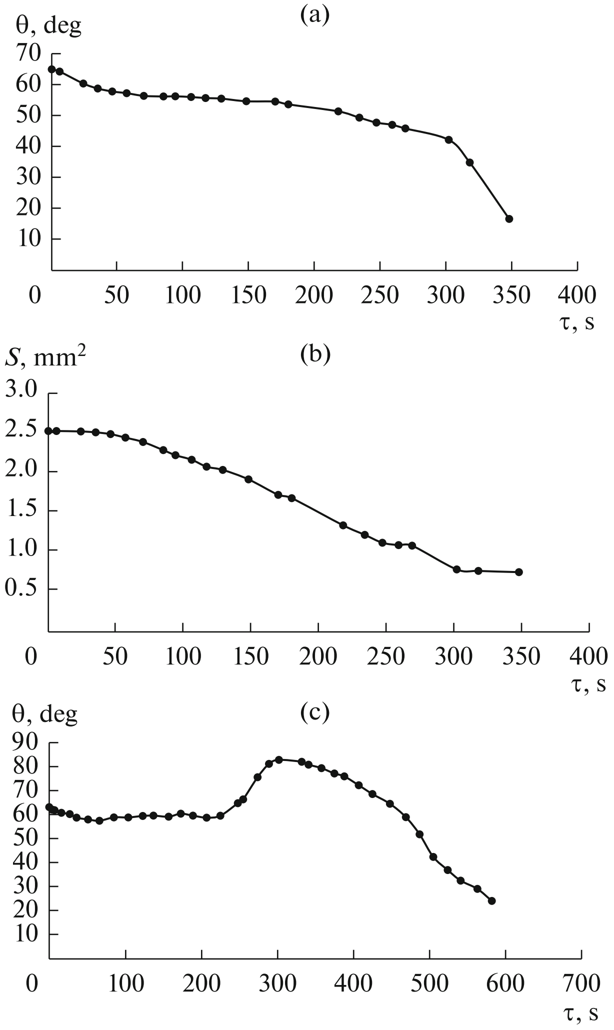

Fig. 5. Evaporation of a 72% propanol solution droplet: (a, c) variations in the contact angle at humidities of 30 and 45%, respectively, and (b) variations in the droplet base surface area at 30% humidity.

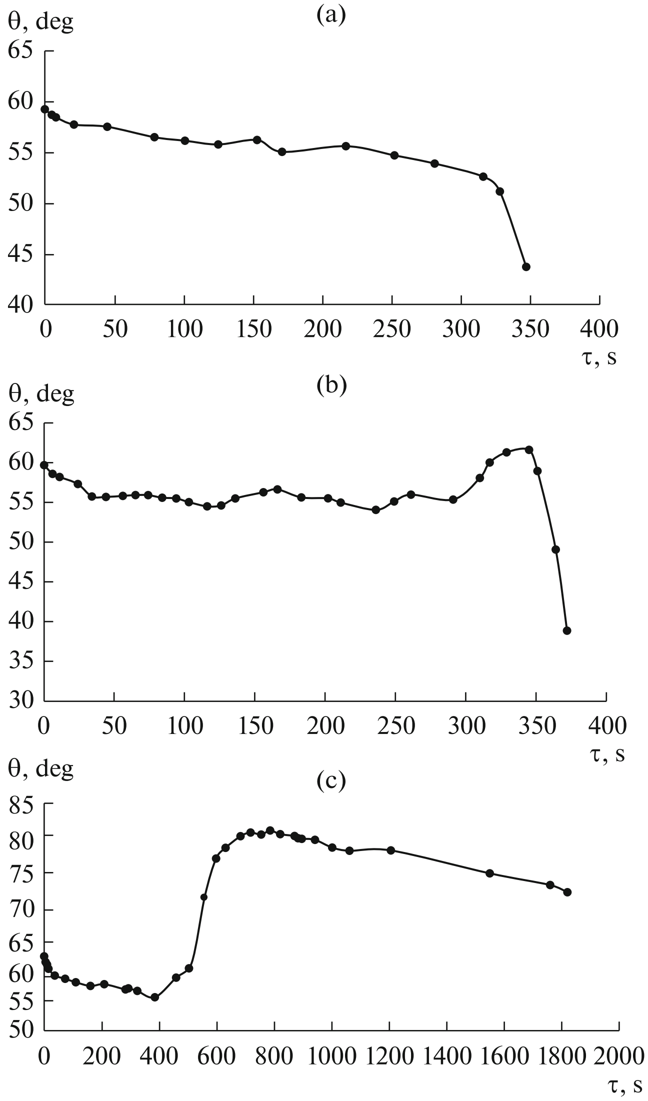

Fig. 6. Evaporation of concentrated propanol: variations in the contact angle at humidities of (a) 23, (b) 63, and (c) 90%.

atmosphere. Depending on the values of these parameters, different characters of the time dependences are observed for the contact angles and base surface areas of the droplets. In particular, the time variations in the contact angle of a droplet with a high alcohol concentration at a low air humidity fundamentally differs from the corresponding dependence obtained for the evaporation of a droplet with a prevailing content of water at a high humidity. The above-described analysis of the obtained experimental data qualitatively indicates the main tendencies and regularities of the evaporation and wetting with allowance for the concentrations of droplet components and air humidity. The refinement of these regularities and their possible quantitative description will require additional investigations.

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