

# Mechanisms of Depinning Accompanying Evaporation of Colloidal Dispersion Droplets

S. P. Molchanov<sup>a, c</sup>, V. I. Roldugin<sup>b, \*</sup>, I. A. Chernova-Kharaeva<sup>c</sup>, and I. N. Senchikhin<sup>b</sup>

<sup>a</sup>*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119071 Russia*

<sup>b</sup>*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia*

<sup>c</sup>*Photochemistry Center, Russian Academy of Sciences, Moscow, 119421 Russia*

\**e-mail: vroldugin@yandex.ru*

Received January 24, 2017

**Abstract**—Experiments have been performed to clarify the mechanism of depinning, i.e., the onset of the movement of the menisci of evaporating dispersion droplets under the conditions of the formation of ring-shaped deposits (the coffee-ring effect). The influence of the nature and concentration of dispersed particles on depinning has been studied. It has been shown that there are three main effects responsible for depinning. The first effect is due to the hysteresis of droplet contact angle, the second one results from the influence of the particles on the surface tension of a dispersion, and the third effect is caused by the formation of a dense gel in the meniscus region. A relation has been revealed between the mechanisms being realized and scenarios of droplet evaporation.

DOI: 10.1134/S1061933X1704010X

## 1. INTRODUCTION

In [1–4], we have systematically studied the regularities of the formation of ring-shaped deposits upon the evaporation of dispersion droplets, i.e., the so-called “coffee-ring” effect (CRE). This phenomenon, which was, for the first time, considered in [5, 6], appears to have a rather complex mechanism, although the studied system seems, at first sight, to be almost trivial. A complex mechanism of ring-shaped deposit formation may explain why numerous studies have not resulted in a common opinion concerning the factors that govern the phenomenon under consideration. The performed studies have led to the clear conclusion that a set of phenomena responsible for the diversity of the formed structures underlies the examined effect. It may only be stated that the formation of ring-shaped deposits combines both individual and collective actions and behaviors of colloidal particles.

Previous investigations have shown that the structure of formed deposits depends on the properties of a dispersion medium [7], as well as on the state of the surface [8], shape, and size of particles [9, 10]. The presence of surfactants in a dispersion has a strong influence on the structure of a ring-shaped deposit [11], because they affect the interparticle interaction, the state of the surface of a liquid dispersion, and the degree of hydrophilicity/hydrophobicity of a substrate. The state of a substrate has appeared to be a key factor predetermining the structure of a formed deposit [1–4, 12–17]. In addition to the degree of sub-

strate hydrophilicity/hydrophobicity, the influence of its thermophysical characteristics has appeared to be unexpectedly strong [18, 19]. That is, heat-transfer processes play a noticeable role in the formation of a deposit structure. The evaporation rate of droplets and the temperature distribution in them are unambiguously related to the heat transfer. In turn, the temperature field predetermines the rates of convective flows, to which the process of the formation of ring-shaped deposits is unambiguously related. The influence of the droplet-evaporation rate and other dynamic effects on the self-organization of ensembles of colloidal particles has also been observed in other situations [20–24].

This work represents a continuation of our previous works on the regularities of the formation of ring-shaped deposits [1–4]. We shall consider a key stage of the process: depinning, which is the beginning of meniscus movement. This phenomenon follows another basic effect, pinning, which was considered in [4]. Pinning and depinning predetermine three main scenarios of ring-shaped-deposit formation, which were discovered in [2]. Let us recollect these scenarios: “droplet evaporation from the center to the periphery with the formation of a ring-shaped deposit,” “droplet evaporation from the periphery to the center with the formation of a ring-shaped deposit,” and “droplet evaporation from the periphery to the center with the formation of a disk-shaped deposit.” These scenarios comprise the following regimes of droplet evaporation

as key elements: “with an unchanged radius,” “with an unchanged shape,” and the combined regime “with both radius and shape being changed.”

It was previously noted [25] that only two main scenarios of droplet evaporation could be realized under the conditions of CRE. It was shown [3] that, under certain conditions, droplet-evaporation scenarios may replace each other, with the pinning and depinning effects playing a key role in the “switching” of the realized scenarios. Therefore, pinning and depinning undoubtedly predetermine the structure of formed deposits. In this work, the mechanisms responsible for depinning will be studied.

## 2. PRELIMINARY CONSIDERATIONS

We believe that it would be useful to analyze the traditional view of depinning. In [25], this view has been taken as a basis of two scenarios experimentally observed for droplet evaporation. The author suggested that the meniscus movement occurs in two stages.

At the first stage, a deposit of closely packed particles must be formed in the region of the meniscus, with the external profile of the deposit corresponding to the profile of the liquid surface. As the thickness of the deposit (its cross section has a rather complex shape of an asymmetric “hill”) grows, the meniscus moves along its external surface toward the hilltop. The value of the contact angle plays no role in this movement. The second stage of the movement begins when the contact angle of the droplet with respect to the internal side of the “hill” becomes smaller than receding angle  $\theta_{rp}$  for the liquid on a planar layer of the closely packed deposit. The onset of this movement essentially depends on the  $\theta_{rp}$  value: the two observed scenarios of droplet evaporation correspond to the small and large values of this angle.

In [25], the problem of droplet evaporation was solved numerically. The Navier–Stokes equation, thermal-conductivity equation, and the equation for the diffusion transfer of vapor in the atmosphere were used. Convective flow of a liquid related to the Marangoni effect, movement of the three-phase contact line, variations in the particle concentration in a dispersion due to the evaporation of the dispersion medium and the deposition of particles, and their transfer due to the advection and diffusion were taken into account. The movement of the three-phase contact line was expectedly realized in accordance with the above scheme. The solutions obtained showed that, at small and large  $\theta_{rp}$  values, a droplet evaporates via the “from the center to the periphery” and “from the periphery to the center” scenarios, respectively.

Below, we shall present experimental data showing that the “reasonable suggestions concerning depinning” put forward in [25] conflict with its real character. Therewith, the deviations from the real situation

are observed at the very early stage when the meniscus begins to “climb” onto a deposit. This work is mainly devoted to studying this initial stage. It should be noted that we have failed to find other communications devoted to studying this stage of depinning and its relation to the structure of a formed deposit.

Previously [2], we have shown that the suggestions of the authors of [25] do not survive experimental testing: larger and smaller receding angles correspond to the evaporation scenarios “from the center to the periphery” and “from the periphery to the center,” respectively. Before discussing the mechanisms responsible for the realization of this or that scenario, it is necessary to clarify in detail the second key element of CRE, i.e., depinning, to which this article has been devoted.

## 3. EXPERIMENTAL

Experiments were performed with droplets of a dispersion of polystyrene latex particles (DPSP) with diameter  $d = 250 \pm 60$  nm [26] and a dispersion of silica particles (DSP-1) with  $d = 255 \pm 10$  nm obtained by tetraethoxysilane hydrolysis in ethanol in the presence of ammonia as a catalyst [27]. Polystyrene particles contained surface  $\text{NH}^-$  and  $\text{CO}^-$  groups in a concentration of  $2 \times 10^{-6}$  mol/m<sup>2</sup>. In addition, Levasil particles (H.C. Starck GmbH & Co., Germany) with a diameter of 50 nm (DSP-2) were used.

Particle sizes were determined by dynamic light scattering with a Photocor Complex spectrometer (Fotocor Ltd, Russia).

Particles were dispersed in deionized water obtained by sorption and ion-exchange filtration followed by mechanical microfiltration in a D-301 deionizer (Akvilon, Russia).

Thermo Scientific SuperFrost microscope slides (MSs) (Menzel-Claser, Germany) with sizes of  $76 \times 26 \times 1$  mm<sup>3</sup> preliminarily cleaned from contaminants were used as substrates. The MSs were cleaned as follows:

- (1) initially, they were washed with tap water and, then, with distilled water to remove the main contaminants;

- (2) the MSs were placed into a glass beaker and successively treated with Fairy detergent, acetone, and chromic mixture in an ultrasonic bath for 10–20 min;

- (3) the treated MSs were washed with deionized water and dried.

Microdroplets were applied onto the MSs using a Lenpipet Digital one-channel dosing pipette equipped with replaceable heads, which enabled us to obtain droplets with volumes of 10–100  $\mu\text{L}$ .

The droplets were monitored and their contact angles were measured with the help of an optical video stand (Photochemistry Center, Russian Academy of Sciences, Russia) [23] consisting of a measuring table

for a substrate onto which a droplet was applied, as well as vertical and horizontal long-focus microscopes equipped with video cameras, which monitored the droplet at different angles. Before a droplet was applied, an MS was placed onto the measuring table. Then, the images were begun to be recorded (the top and side views) with preset time intervals. After that, a droplet of a specified volume was applied onto the MS. The droplet images were taken until it was completely evaporated. The obtained images were used to determine all necessary parameters, i.e., the initial and current contact angles, as well as the angle and time of depinning. Special software (Photochemistry Center, Russian Academy of Sciences, Russia) was employed to determine accurately the contact angle of a droplet from the parameters of its side-view image.

The experiments were carried out under standard laboratory conditions: the temperature of the solutions, substrates, and environment was 20°C, and the relative humidity was 25%.

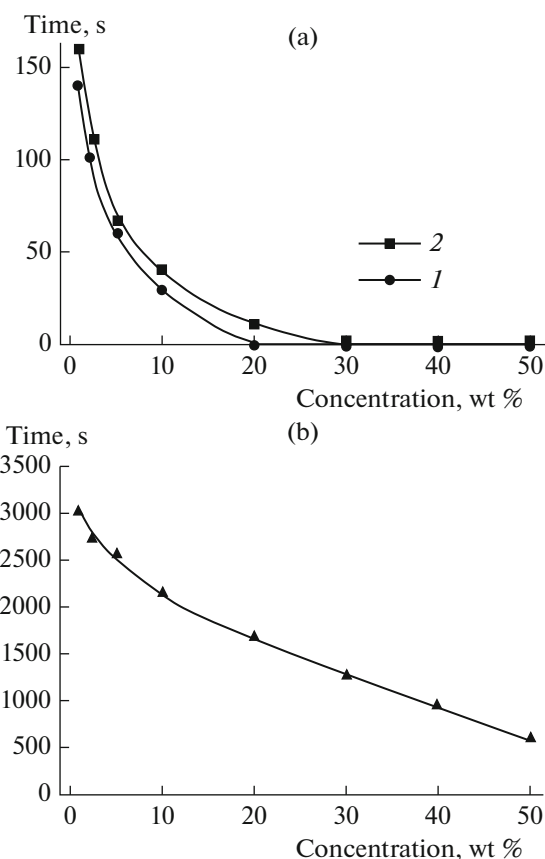
#### 4. DEPINNING TIME AND PARTICLE CONCENTRATION

The experiments have shown that depinning follows pinning in different time periods (depinning time) depending on the concentration of particles in a dispersion. Previously [2], it has been shown that the scenarios of droplet evaporation are closely related to the depinning time. Therefore, the dependences of the depinning time on the particle concentration were determined for three dispersions relevant to different scenarios of droplet evaporation [2]: DPSP (“evaporation from the center to the periphery with the formation of a ring”), DSP-1 (“evaporation from the periphery to the center with the formation of a ring”), and DSP-2 (“evaporation from the center to the periphery with the formation of a planar disk”).

Dispersions of the aforementioned particles with concentrations of 1, 2.5, 5, 10, 20, 30, 40, and 50 wt % were used in the experiments. Dispersion droplets with a volume of 20  $\mu\text{L}$  were applied onto the MSs. Top- and side-view images were taken from evaporating droplets with an interval of 2 s. Since pinning began (the droplet boundary was quiescent) immediately after a droplet was applied, the time elapsed between the moment of droplet application (actually, pinning) and the moment at which the meniscus began to move was taken to be the depinning time.

Figure 1a shows the dependences of the depinning time on the particle concentration. It can be seen that, for DPSP and DSP-1, these dependences have a similar pattern close to a hyperbolic one, thus indicating that diffusion is the main rate-limiting step.

At a DPSP concentration of nearly 20 wt %, the depinning time is, actually, equal to zero. For DSP-1, the zero depinning time is reached at a particle concentration of 30 wt %. The presented dependences

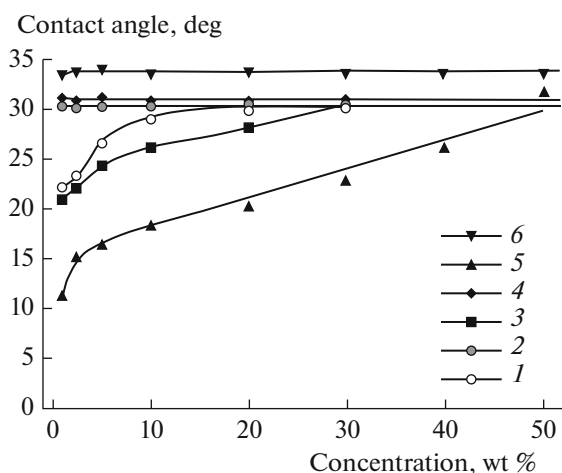


**Fig. 1.** Dependences of depinning time on particle concentration for 20- $\mu\text{L}$  droplets of (a) (1) DPSP and (2) DSP-1 and (b) DSP-2.

show that, in both cases, the depinning time is actually determined by the characteristic time of some process (or processes) developing in the pinned meniscus.

For DSP-2, the concentration dependence of the depinning time has an essentially different character (Fig. 1b). First, the depinning time has increased by more than an order of magnitude (by nearly 20 times), thereby indicating that the interactions in the substrate/dispersion system are substantially different. Second, the character of the occurring processes has obviously been changed: a small abrupt decrease in the depinning time at low concentrations, which is also inherent in other dispersions, is followed by an almost linear dependence of the depinning time on the particle concentration. Since the diffusion coefficient of particles in DSP-2 is markedly higher than in other dispersions, the increase in the depinning time indicates that diffusion is not the rate-limiting step of these processes. Everything is governed by the processes that occur in the meniscus and are relevant to its pinning on a substrate.

It is quite clear that, in the limiting case of small concentrations, all three dependences presented in Fig. 1 must converge at one point that corresponds to



**Fig. 2.** Dependences of (1, 3, 5) depinning angle and (2, 4, 6) initial contact angle on particle concentration for (1, 2) DPSP, (3, 4) DSP-1, and (5, 6) DSP-2.

a pure solvent on a clean substrate. However, the fact that this is not observed indicates the presence of particles that have almost instantaneously been attached on the substrate. This almost instant attaching of particles at the droplet periphery was already mentioned in [4]. The interaction between the solvent and these particles “retains” the droplet meniscus at the initial stage of the evaporation. The interaction between the meniscus and these particles determines, to a great extent, the character of dispersion-droplet evolution. There are, however, other factors the action of which is rather veiled.

## 5. DEPINNING CONTACT ANGLE AND PARTICLE CONCENTRATION

It is of obvious interest to study the dependence of the depinning contact angle on particle concentration. The results of the performed experiments are shown in Fig. 2. For visualization, the same figure presents the initial contact angles for droplets of dispersions with different concentrations. It can be seen that the initial contact angles may, within the experiment error, be considered to be constant. Let us note once again the contradiction with the scheme proposed in [25]: scenario “from the center to the periphery” corresponds to larger angles of DPSP, while scenario “from the periphery to the center” corresponds to smaller angles of DSP-1 and DSP-2.

The depinning angles of all three dispersions increase with their concentration. For DPSP and DSP-1, the coincidence of the initial angle with the depinning angle is observed at concentrations of 20 and 30 wt %, respectively. For DSP-2, the depinning angle remains to be smaller than the initial contact angle even at a concentration of 50 wt %. Hence, the depinning mechanism for this dispersion differs from

that for the first two dispersions because, in particular, of different interactions in the adsorbed particles/dispersion system.

We should also note the existence of some “critical” concentration for DSP-2 in the region of 10 wt %, where the patterns of the concentration dependences of the depinning time and contact angle abruptly changes (Figs. 1b, 2).

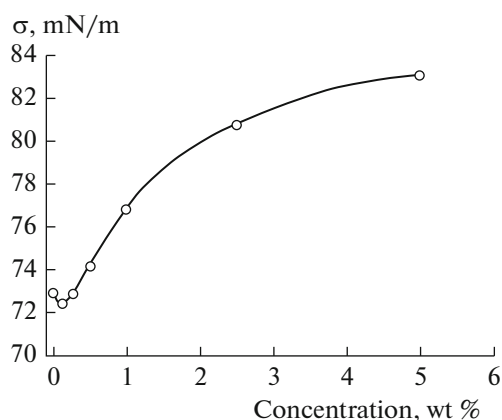
The almost instant onset of the meniscus movement upon reaching certain (critical) concentrations of DPSP and DSP-1 indicates that the onset of the depinning requires reaching some “critical” concentration in the meniscus region. A certain time is required to reach this concentration if the initial concentration is lower than the critical one. Therewith, it should be noted that the initial contact angle weakly depends on the particle concentration (this dependence has been considered in detail elsewhere [1]). Hence, at the initial moment of time, the presence of particles in a colloidal solution does not affect significantly the interfacial surface energies.

The disagreement shown between the depinning angles of the dispersions and the scenarios of droplet evaporation enables us to state that the “reasonable suggestions” [25] concerning the depinning mechanism are not in correspondence with reality. It is necessary to perform special experiments aimed to determining the behavior of particles in the region of evaporating droplet meniscus, in particular, to establishing the existence of a region with an increased particle concentration. In addition, it seems of interest to compare receding contact angles with depinning angles.

## 6. FACTORS AFFECTING DEPINNING

### 6.1. Surface Tension and Particle Concentration

To begin with, let us discuss the formal effect of particle concentration on depinning. As has been noted previously [1], the particle concentration affects the surface tension and initial contact angle of a dispersion. Since the receding contact angle must be reached for the onset of depinning, the particle concentration may influence it by varying the dispersion surface tension because of the necessity to reach its critical value in the meniscus region. The intensity of this influence was estimated by measuring surface tension  $\sigma$  of DPSP. These measurements have distinctly shown that the particle concentration in a dispersion rather strongly affects its surface tension, and that this factor must be taken into account when comparing the experimental data with the results of model calculations. Here, we have presented only data on DPSP, because the effect of the difference between the densities of the dispersed phase and the dispersion medium is weakest in this system. DPSP with a particle diameter of 250 nm was used in the experiment. The surface tension was measured with the help of stalagmometry. The measurement results are presented in Fig. 3.



**Fig. 3.** Dependence of DPSP surface tension on particle-weight concentration.

Figure 3 shows that the surface tension increases with the particle concentration; i.e., polystyrene particles are surface-inactive. This is, in principle, explainable, because the particles are negatively charged, with the concentration of  $\text{NH}^-$  and  $\text{CO}^-$  surface groups being of nearly  $2 \times 10^{-6}$  mol/m<sup>2</sup>. An increase in the surface tension of the dispersion must lead to a growth in the receding angle on both “clean” and deposit-containing surfaces. That is, a rise in the particle concentration of a dispersion may affect the depinning time via the surface tension.

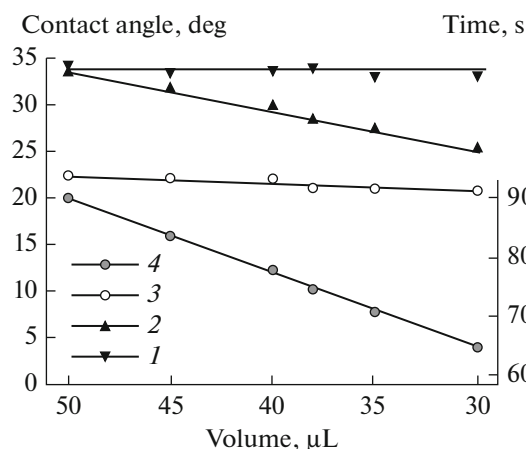
The growth of surface tension with particle concentration (Fig. 3) indicates that the depinning contact angle must also grow. Thus, the accumulation of particles in the meniscus region substantially contributes to the increase in the depinning angle with particle concentration.

Attention should be focused on the fact that the contact angle drastically increases and rapidly reaches a constant value. The dependences in Fig. 2 have such a pattern. It is reasonable to assume that the accumulation of the particles in the meniscus region has a fundamental effect on the depinning angle.

### 6.2. Depinning and Initial Contact Angle

The experiments described in Section 5 showed that the initial contact angles were almost the same for dispersions with different particle concentrations. Therewith, by virtue of different depinning times, the depinning began at different contact angles and particle concentrations. The absence of the simultaneous monitoring of both these factors made the separation of their roles impossible.

It seemed to be reasonable to carry out experiments on varying the value of the initial contact angle at the same particle concentration. For this purpose, we used the previously proposed method [3], in which the initial contact angle was decreased by removing some



**Fig. 4.** Dependences of contact angle and depinning time on residual volume for particles obtained by partial removal of dispersion from them: (1) initial droplet and (2) after partial removal of dispersion; (3) depinning angle and (4) depinning time after removal.

volume of a dispersion from a droplet already applied onto a substrate.

DSP-2 with a concentration of 10 wt %, which corresponded to the nonlinear region of dependences presented in Fig. 2, was selected for these experiments. Droplets of DSP-2 with a volume of 50 μL were applied onto a substrate. Dispersion volumes of 5, 10, 12, 15, and 20 μL were removed from the droplets in 30 s after their application. One 50-μL droplet was used as a reference one. The contact angle was determined at an initial moment and after the partial removal of the colloidal solution, as well as the depinning angle.

Curve 1 in Fig. 4 shows the identity of the droplets applied onto the substrate. The pattern of curve 2 shows that, after the partial removal of the dispersion, the contact angles of the formed droplets have decreased, while their menisci were pinned at the initial moment. Note that the particle concentration of the dispersion was the same for all droplets.

Curve 3 indicates that the menisci begin to move at almost equal contact angles. At the same time, curve 4 exhibits some dependence of the depinning time on the initial contact angle. This dependence is obviously due to a decrease in the volume of the dispersion medium, which must be evaporated to reach the depinning angle. It is obvious that the particle concentrations in the droplets with different initial volumes are different at the moment of the depinning.

Note that the depinning time (90 s) of the reference droplet with a volume of 50 μL is much shorter than that (2000 s) for the 20-μL droplet (Fig. 1). This difference is explained by a rather strong dependence of the depinning time on the droplet volume. This dependence will be discussed in Section 8.

Thus, it may be stated that the factor that triggers the depinning is reaching a certain critical value of the contact angle. Now, let us consider the role of the particle concentration in the depinning.

### 6.3. Depinning and Critical Particle Concentration

General considerations and the data on numerical simulation indicate that there is a substantially increased particle concentration in the meniscus region. This increase in the concentration affects the depinning in several ways, i.e., via the aforementioned variation in the surface tension of a colloidal solution and a variation in the “phase” state of a dispersion in the meniscus region. The latter factor has not previously been discussed. It will be shown here that the particles of a colloidal dispersion form a gel in the meniscus region.

It is commonly thought (see, e.g., [25]) that, in the meniscus region, the particles immediately pass from the freely dispersed state into a solid deposit. This passage was not discussed in detail; it was just believed that the particles transferred by a compensatory flow could be accumulated up to a concentration corresponding to their dense package. As has been mentioned above, the meniscus moves together with the “top” of the deposit.

The solid deposit has appeared to be formed in, at least, two stages. Initially, particles in the meniscus region form a gel, which has a low yield stress and reproduces the droplet shape. The gel volume grows at the internal side of the meniscus. By virtue of the low yield stress, the gel has almost no effect on the value of the depinning angle.

The presence of the gel in the meniscus region was found for many dispersions, including those considered in this work, i.e., DPSP, DSP-1, and DSP-2. Below, we shall present the data from experiments performed with DSP-2. The data confirming the existence of the gel in other dispersions will be presented in subsequent communications.

Unfortunately, the particle concentration in the meniscus region of an evaporating droplet is difficult to measure directly. Therefore, we present the data of an experiment that has enabled us to detect a rise in the concentration of DSP-2 particles in the region of a meniscus being formed on a glass plate immersed in the dispersion.

In this experiment, we used namely DSP-2, because, according to the data obtained in [2], the largest growth of the concentration in the meniscus region should be expected for this dispersion. The dispersion concentration was 70 wt %.

Preliminarily, for a 20- $\mu$ L droplet of this dispersion, the depinning angle and time were determined; they appeared to be 32° and 36 s, respectively.

Then, a glass plate was immersed vertically into the same dispersion occurring in a 2-mL cylindrical ves-

sel. The position of the plate was regulated in a manner such that the contact angle coincided with the initial contact angle of the droplet (37°). The plate was exposed for a time period (4 min) markedly longer than the depinning time of the droplet; then the plate was slowly withdrawn. The side view of the meniscus was recorded at intervals of 2 s during the entire experiment.

While the plate was quiescent, the position of the meniscus remained unchanged. After the plate was withdrawn from the dispersion, a small hill of particles was seen on it (Fig. 5).

The formation of the “hill” of particles which had not “flowed down” together with the dispersion was obviously due to the region of increased particle concentration located in the vicinity of the meniscus. Since the duration of the plate exposure was substantially longer than the depinning time of a droplet, it could be confidently stated that the particle concentration, at which the depinning began in the experiments with droplets, was reached in the meniscus region.

Note that the formed “hill” was easily washed out when the plate was repeatedly immersed; i.e., it was not a solid deposit, which would be strongly fixed on the substrate (see above).

It may also be inferred from this experiment that reaching the limiting concentration in the meniscus region is not the necessary condition for the onset of depinning.

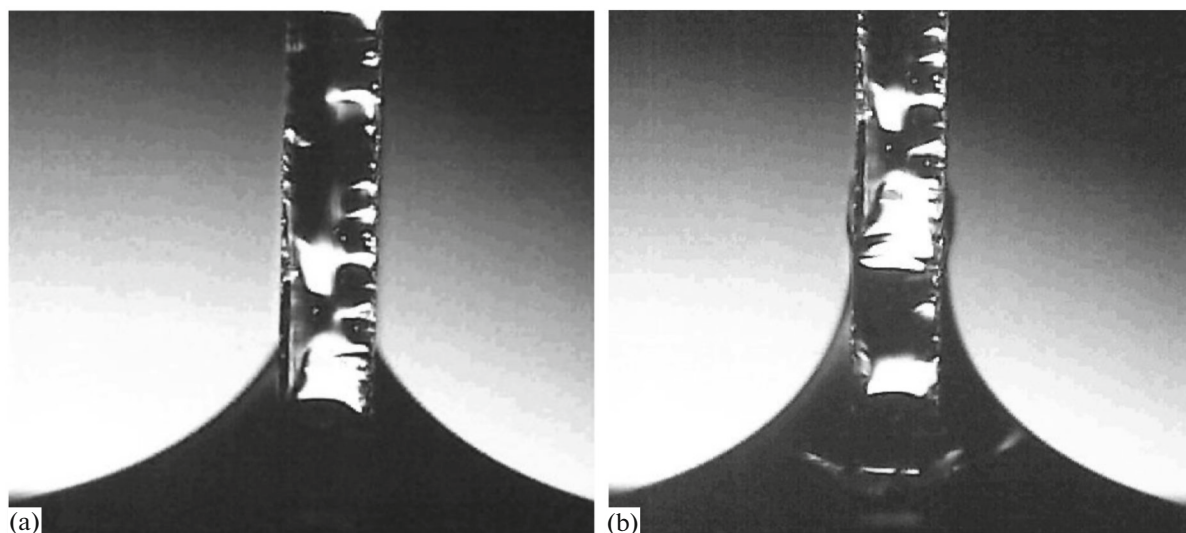
Below, we shall describe experiments showing the roles of the main factors affecting depinning.

## 7. DEPINNING ANGLE AND RECEDING CONTACT ANGLE

As can be seen from the aforementioned data, the depinning angle of a droplet and the receding contact angle of a dispersion on a planar substrate are the key factors in the phenomenon under consideration. However, the question of their equivalence remains open. There is some difference between them: upon the depinning, the three-phase contact line may move along the plane of the liquid/gas interface, while, upon receding, it moves only in the plane of the liquid/substrate interface. It should also be noted that, strictly speaking, the depinning angle is often rather difficult to determine experimentally, especially when its value is close to or larger than the equilibrium value of the contact angle of a droplet. It is much more convenient to measure the receding angle for a planar substrate immersed vertically into a corresponding colloidal solution, i.e., by the so-called “receding meniscus method.”

We performed experiments simultaneously with both dispersion droplets applied onto substrates and the same substrates immersed into a corresponding dispersion.





**Fig. 5.** Meniscus profiles on a glass plate immersed into DSP-2 (a) at the initial time moment and (b) after withdrawal of the meniscus region from the solution.

To determine the receding angles on glass plates, they were immersed vertically into a 200- $\mu$ L cylindrical vessel filled with a corresponding dispersion. Then, the plate was slowly withdrawn with the help of a micrometer screw, and the contact angle was measured at the moment, when the three-phase contact line began moving. This angle was considered to be the receding angle for this dispersion.

### 7.1. Receding Angle of a Dispersion on a Clean Plate

Three series of experiments were carried out for each of the three dispersions. In the first series, the time between the moment of plate immersion into a dispersion and the onset of its withdrawal was as short as possible. It was assumed that, in this case, particles had not time to be transferred to the meniscus and form the region of an increased concentration. The dependences of the receding angles on the particle concentration plotted in this series of the experiments for different dispersions are shown by curves 1 in Fig. 6.

It can be seen (Figs. 6a, 6b, curves 1) that, for DPSP and DSP-1, the receding angle is independent of both the concentration and nature of the particles. Hence, the angle thus measured on the plate is just the receding angle of a (virtually) pure solvent on a clean substrate.

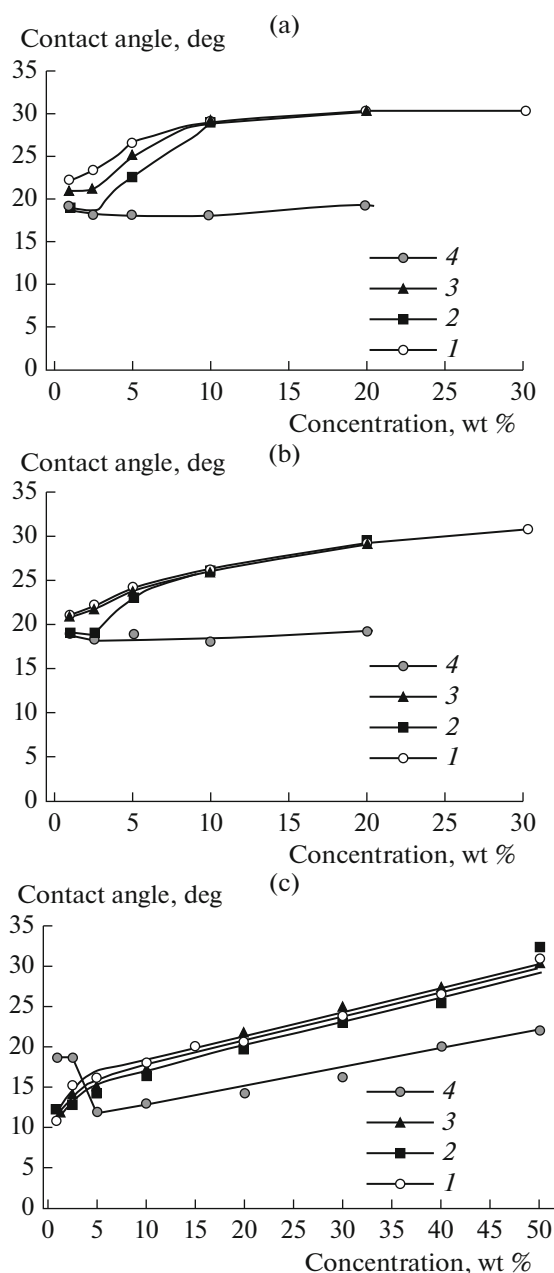
For DSP-2 (Fig. 6c, curve 1), the constancy of the angle is observed only at low concentrations, i.e., beginning from some concentration, the angle drastically decreases; then, it begins to gradually grow. It may be stated that, at some threshold concentration, the number of particles bonded to a substrate is sufficient to retain the three-phase contact line.

The comparison between curves 1 and 4 in Fig. 6 shows that the receding angles of all dispersions on the plate appear to be much smaller than their depinning angles. Hence, the processes, which are responsible for the onset of meniscus movement at contact angles larger than the receding angle of a dispersion on a clean substrate, develop in the region of the droplet meniscus. In principle, two main factors causing the difference between the aforementioned angles have been noted above: they are an increase in the particle concentration and the formation of a deposit at the limiting concentration. Both these factors are of a dynamic character, because, the longer the time delay of the depinning, the larger the corresponding value of the contact angle (see Figs. 1, 2). In the experiments with the plates, the time delay is absent according to the experimental conditions.

### 7.2. Effect of the Preliminary Contact Time on the Receding Angle of Dispersion

In the next series of experiments, we studied the receding of dispersions on plates that were immersed into them and withdrawn in time intervals equal to the depinning times of corresponding dispersion droplets. The obtained dependences are shown in Fig. 6 (curves 2).

It can be seen that, under these conditions, the curves for low-concentration DPSP and DSP-1 coincide with those plotted in the previous series (curves 1). That is, the menisci may be believed to occur on virtually clean substrates. As the concentration grows (from 2.5 to 10 wt %), the meniscus movement regime changes and the contact angle coincides with the corresponding depinning angle of a droplet (curves 4).



**Fig. 6.** Dependences of receding contact angles on (1) a clean plate, (2) a plate being exposed in a dispersion, (3) a plate with a layer of adsorbed particles being exposed then in a dispersion, and (4) depinning angle on particle concentration for (a) DPSP, (b) DSP-1, and (c) DSP-2.

The existence of the “transitional” concentration range indicates that an important role is played by particle concentration in depinning. The differences observed between the depinning and receding angles may be explained by differences in the formation of monolayers of the particles in the meniscus regions in the cases of a droplet on a plate and the plate in the corresponding liquid. The droplet evaporation is accompanied by an increase in the average concentra-

tion of particles in a dispersion as a whole, while, in the case of the plate, this increase may be ignored because of the large volume of the liquid. As a consequence (e.g., due to the lower concentration gradients in the meniscus region and a weaker diffusion efflux of particles or because of different rates of evaporation from convex and concave menisci), in the case of a droplet, the concentration of particles in the meniscus region appears to be higher than that near the meniscus on a plate. This results in a higher surface tension of the dispersion, which affects the value of the depinning angle.

Moreover, the higher concentration accelerates the development of the conditions for the meniscus movement. The absence of the transitional zone in the case of DSP-2 (Fig. 6c, curve 2) may be explained by a higher mobility of these particles and a substantially longer time of the contact.

All of the aforementioned is, to some extent, confirmed by the following series of experiments.

### 7.3. Receding Angle of a Dispersion on a Plate with a Layer of Adsorbed Particles

The differences observed in the previous series between the values of the receding angles and the depinning angles of DPSP and DSP-1 droplets (under seemingly the same time conditions) may, in addition to the aforementioned reasons, be explained by different rates of “delivering” particles to the meniscus region. It is quite obvious that the rate of compensatory flows in the case of a plate is much lower than in the case of a droplet. In order to substantiate the observed differences by namely “incompleteness” of the adsorbed layers, a third series of experiments were performed, in which layers of adsorbed particles were preliminarily applied onto the plates (by their repeated immersion into a dispersion). The concentration dependences of receding angles for the modified plates are illustrated by curves 3 in Fig. 6.

After modification of the plates, the receding and depinning angles almost completely coincide with each other. Slight deviations take place only for DPSP (Fig. 6a, curve 3). In this case, the receding angle remains almost unchanged at the first two concentrations. This may be due to the slower development of the conditions corresponding to depinning in the meniscus. It may be stated that the adsorbed layer plays an important, but not the decisive, role in depinning. A “special” state of a colloidal dispersion in the meniscus region is necessary to provide the conditions for the meniscus movement.

## 8. DEPINNING AND DROPLET VOLUME

Dependences of the depinning time and angle on droplet volume may be found by comparing curves 1 and 2, as well as 3 and 4, in Fig. 7. The dependences of the depinning time and angle on the particle concen-



tration described by these curves have been plotted for droplets with volumes of 20 and 8  $\mu\text{L}$ , respectively. The comparison between these dependences leads us to the following unambiguous conclusion: a reduction in the droplet size causes a decrease in both the depinning time and the concentration, at which the depinning time becomes equal to zero (remember that the zero depinning time was observed in [2] for a 40- $\mu\text{L}$  DPSP droplet with a concentration of 5 wt %). This may be explained by the fact that, in larger droplets, the particle concentration at the meniscus increases faster because of the higher rate of the compensatory flows (a lower geometric constraint) and a lower concentration gradient, which lead to a faster decrease of the curves. Therewith, both the depinning angle and the initial contact angle remain almost unchanged.

## 9. RESULTS AND DISCUSSION

The aforementioned experimental data indicate that the depinning mechanism proposed in [25] (and, seemingly, the conventional one) does not reflect the processes that really take place. In the meniscus region, the particle concentration may be close to the limiting one; however, a solid deposit (with the exception of a monolayer) is not formed, while the meniscus remains quiescent. The attainment of the contact-angle value corresponding to the receding contact angle for a dispersion on a substrate composed of densely packed particles also does not, per se, force the meniscus to move, while the delivery of particles by the compensatory flows to the meniscus region does not lead directly to the growth of the solid deposit. An important role is played by the formation of a gel in the meniscus region and the relevant effects.

Before considering the main effects relevant to the gel formation, it should be noted that, for the onset of gelation, the particle concentration must reach a certain value, while the increase in the concentration is governed by various processes. The main process is the delivery of particles by the compensatory flows. It is predetermined by the evaporation rate and the development of the compensatory flows, the intensity of which depends on the value of the contact angle. The contribution of the opposite diffusion flows is also obvious, with their intensity being determined by the particle concentration in the system as a whole. Moreover, it is necessary to take into account the transfer of particles onto the liquid/gas interface, as well as the passage of particles from a dispersion, in which they are mobile, to a solid densely packed deposit. This passage seems to reduce the concentration of mobile particles in the meniscus region. However, this passage itself requires a special consideration. The issue is that the particles that have been accumulated in the meniscus region and have already formed a gel do not undergo "aggregation" with the particles composing a monolayer on a substrate. The height of the barrier that hinders the aggregation is rather large (which, in

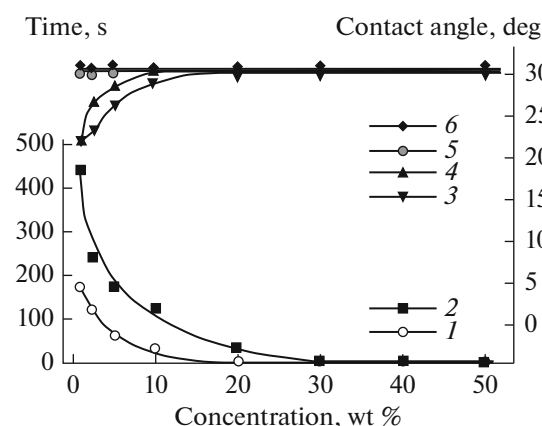


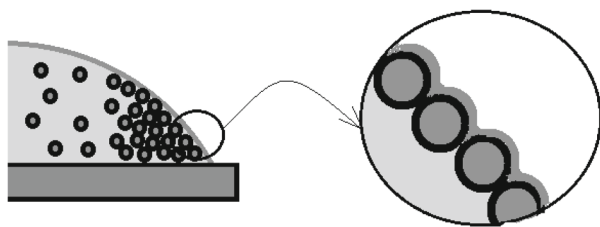
Fig. 7. Dependences of (1, 2) depinning time, (3, 4) depinning angle, and (5, 6) initial contact angle on dispersion concentration for DPSP droplets with volumes of (1, 3, 5) 20 and (2, 4, 6) 8  $\mu\text{L}$ .

fact, provides dispersion with the stability to aggregation), and additional forces are necessary to make the particles to pass from the state of the gel into the state of a solid structure.

The gel state of the system of colloidal particles plays an important role in this passage. The gelation in the meniscus region is an effect that has not been discussed by anyone. This effect is most pronounced for DSP-2. This is due to the well-known experimental fact that silica particles may form network (coagulation) structures already at relatively low concentrations (silica is widely used as a thickener). The described experiments distinctly show the formation of a gel structure in the region of an evaporating meniscus (the corresponding data are not presented, but the gel is formed in all studied systems). The presence of the gel requires to radically revise the process the deposit formation, the mechanism of depinning, and the entire process of droplet evaporation.

For example, it is obvious that in the presence of a gel, the solvent mass transfer to the surface dramatically decreases, thus affecting the state of particles near a surface, especially in the vicinity of the three-phase contact line. The decrease in the mass transfer is related to the rigidity of the gel through which the solution must flow. Note that free colloidal particles cannot substantially hinder the mass transfer because of their mobility, although they affect this process via the osmotic effect.

The deceleration of delivering an evaporating liquid to the surface of evaporation and a certain rigidity of the gel may result in the fact that the "surface" layer will begin to "dry" and the liquid surface will acquire a complex relief (Fig. 8). When the relief shown in Fig. 8 has been formed, tightening interparticle capillary forces arise, which may cause particle aggregation with the formation of a strong solid structure. In addition, the gel-decelerated mass transfer also concerns



**Fig. 8.** Dispersion-droplet surface profile corresponding to the onset of the formation of a solid structure from particles.

low-molecular-mass solutes, an increase in the concentration of which also may decrease the interparticle potential barrier. Indeed, a solid structure is formed in manner such that the external profile of the deposit reproduces the current shape of the liquid/gas interface. This leads us to assume that, in correspondence with the situation presented in Fig. 8, the solid deposit is formed beginning from the liquid/gas interface and from the three-phase contact line rather than from the substrate (in spite of the obviousness of this process).

The generally accepted erroneous opinion of the formation of the deposit has obviously been generated by the fact that it, nevertheless, begins to grow from the three-phase contact line. However, this character of the growth is just due to the highest evaporation rate in this region. The fallibility of the generally accepted opinion is easy to substantiate by indicating that the external profile of the solid deposit corresponds to the depinning angle rather than the initial contact angle of the droplet, as it would be with the “obvious” mechanism of its formation.

It should once more be noted that, when speaking of depinning, we mean the onset of the meniscus movement over the deposit, which grows along the liquid/gas interface. The considered depinning mechanism indirectly implies that the character of the movement of the three-phase contact line will also differ from the generally accepted one. We shall analyze this stage of the deposit formation in the next communication.

Now, let us note another fact that has not yet been explained. As can be seen from Fig. 6, the receding contact angle on a plate almost coincides with the depinning angle of a droplet. However, in the case of droplet depinning, the meniscus moves at an angle to the substrate rather than along it, while the movement on the plate occurs along the substrate. We hope to explain the aforementioned coincidence of the angles after the consideration of the meniscus movement.

## 10. CONCLUSIONS

The performed studies have shown that, when a ring-shaped deposit is formed, depinning occurs via a mechanism different from the generally accepted one.

The main difference is associated with the fact that a solid deposit begins to grow from the liquid/gas interface and the three-phase contact line. The realization of this mechanism requires an increase in the particle concentration on the droplet surface and the formation of a gel from particles in the meniscus region. Both these factors govern, in the long run, the formation of the solid deposit. The main factor is precisely the gel formation.

The formation of a gel with a certain strength hinders the transfer of a solvent to the surface of evaporation. As a result, the surface layer begins to “dry,” thus providing the possibility of aggregation of colloidal particles and the formation a solid structure. The growth of the solid structure begins from the three-phase contact line, at which the evaporation rate and the deceleration of the solvent flow are highest. The meniscus movement follows the deposit growth.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 16-08-00554a and 15-03-02300a) and the Program of Basic Research of the Presidium of the Russian Academy of Sciences (no. P1.8).

## REFERENCES

1. Molchanov, S.P., Roldughin, V.I., and Chernova-Kharaeva, I.A., *Colloid J.*, 2015, vol. 77, p. 761.
2. Molchanov, S.P., Roldughin, V.I., and Chernova-Kharaeva, I.A., *Colloid J.*, 2015, vol. 77, p. 770.
3. Molchanov, S.P., Roldughin, V.I., Chernova-Kharaeva, I.A., and Yurasik, G.A., *Colloid J.*, 2016, vol. 78, p. 633.
4. Molchanov, S.P., Roldughin, V.I., Chernova-Kharaeva, I.A., and Yurasik, G.A., *Kolloidn. Zh.*, 2017, vol. 79, p. 182.
5. Deegan, R.D., Bakajin, O., Dupont, T.F., Huber, G., Nagel, S.R., and Witten, T.A., *Nature (London)*, 1997, vol. 389, p. 827.
6. Deegan, R.D., Bakajin, O., Dupont, T.F., Huber, G., Nagel, S.R., and Witten, T.A., *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, vol. 62, p. 756.
7. Bhardwaj, R., Fang, X., Somasundaran, P., and Attinger, D., *Langmuir*, 2010, vol. 26, p. 7833.
8. Dugyala, V.R. and Basavaraj, M.G., *Langmuir*, 2014, vol. 30, p. 8680.
9. Yunker, P.J., Still, T., Lohr, M.A., and Yodh, A.G., *Nature (London)*, 2011, vol. 476, p. 308.
10. Shen, X., Ho, C.-M., and Wong, T.-S., *J. Phys. Chem. B*, 2010, vol. 114, p. 5269.
11. Li, Y.-F., Sheng, Y.-J., and Tsao, H.-K., *Langmuir*, 2013, vol. 29, p. 7802.
12. Vysotskii, V.V., Roldughin, V.I., Uryupina, O.Ya., and Zaitseva, A.V., *Colloid J.*, 2011, vol. 73, p. 176.
13. Vysotskii, V.V., Uryupina, O.Ya., Senchikhin, I.N., and Roldughin, V.I., *Colloid J.*, 2013, vol. 75, p. 142.

14. Vysotskii, V.V., Uryupina, O.Ya., Senchikhin, I.N., and Roldughin, V.I., *Colloid J.*, 2013, vol. 75, p. 634.
15. Vysotskii, V.V., Roldughin, V.I., Uryupina, O.Ya., Senchikhin, I.N., and Zaitseva, A.V., *Colloid J.*, 2014, vol. 76, p. 531.
16. Nazarov, V.G. and Stolyarov, V.P., *Colloid J.*, 2016, vol. 78, p. 75.
17. Huang, W., Cui, L., Li, J., Luo, C., Zhang, J., Luan, S., Ding, Y., and Han, Y., *Colloid Polym. Sci.*, 2006, vol. 284, p. 366.
18. Sefiane, K. and Bennacer, R., *J. Fluid Mech.*, 2011, vol. 667, p. 260.
19. David, S., Sefiane, K., and Tadrist, L., *Colloids Surf. A*, 2007, vol. 298, p. 108.
20. Vysotskii, V.V., Roldughin, V.I., Uryupina, O.Ya., Senchikhin, I.N., and Zaitseva, A.V., *Colloid J.*, 2015, vol. 77, p. 431.
21. Roldughin, V.I., *Usp. Khim.*, 2004, vol. 73, p. 123.
22. Terekhin, V.V., Dement'eva, O.V., and Rudoy, V.M., *Usp. Khim.*, 2011, vol. 80, p. 477.
23. Lebedev-Stepanov, P.V., Kadushnikov, R.M., Molchanov, S.P., Ivanov, A.A., Mitrokhin, V.P., Vlasov, K.O., Rubin, N.I., Yurasik, G.A., Nazarov, V.G., and Alfimov, M.V., *Nanotechnol. Russ.*, 2013, vol. 8, nos. 3–4, p. 137.
24. Vysotskii, V.V., Roldughin, V.I., and Uryupina, O.Ya., *Colloid J.*, 2004, vol. 66, p. 777.
25. Bhardwaj, R., Fang, X., and Attinger, D., *New J. Phys.*, 2009, vol. 11, p. 075020.
26. Men'shikova, A.Yu., Shabsel's, B.M., Evseeva, T.G., Shevchenko, N.N., and Bilibin, A.Yu., *Russ. J. Appl. Chem.*, 2005, vol. 78, p. 159.
27. Stöber, W., Fink, A., and Bohn, E., *J. Colloid Interface Sci.*, 1968, vol. 26, p. 62.

*Translated by A. Kirilin*