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Initial Contact Angles of Dispersion Droplets and Structure of Ring-Shaped Deposits Resulting from Capillary Self-Assembling of Particles

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Abstract—Initial contact angles have been measured for sessile droplets of dispersions, from which ring-shaped deposits are being formed. Factors that affect the initial contact angles, i.e., the regime of droplet application; droplet volume; method of substrate surface treatment; and the concentration, charge, and nature of dispersion particles, have been analyzed. It has been found that, depending on the method of substrate cleaning, the contact angle may be changed by 47°. At the same time, the regime of droplet application may change the contact angle by 13°. The presence of particles may either increase or decrease the contact angle by 5°, depending on their nature. The structure of a formed deposit has been shown to depend on the contact angle and the degree of chemical homogeneity of a substrate surface.

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INTRODUCTION

The evaporation of sessile droplets and films of dispersions is a prevailing method for realizing the self-assembling of colloidal particles into various structures [1–3]. There are different approaches to studying the processes of capillary self-assembling. At present, great attention is focused on the formation of ring-shaped deposits, i.e., the so-called "coffee ring effect" (CRE). The essence of the effect consists in the fact that, under certain conditions, the evaporation of small droplets of dispersions on solid substrates gives rise to the formation of a ring-shaped deposit of particles along the perimeter of the initial area of the droplet–substrate contact. Although this phenomenon has been known for a long time [4], the interest in it has greatly increased after publication of article [5], in which a nontrivial mechanism of deposit formation was shown, with capillary effects playing an essential role in the process. Then, CRE was observed for diverse systems containing rather large colloidal particles [6], as well as nanoparticles [7], and individual molecules [8].

At present, the influence of different factors on the structure of formed deposits is being intensely studied. For example, it was found [9] that the structure of a ring-shaped deposit is strongly affected by the pH of a dispersion medium. Detailed investigations showed that this effect is due to a change in the character of the interaction between colloidal particles. Using the ideas of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the authors established a relation between a change in the character of the interparticle interaction (the prevalence of electrostatic or dispersion forces) and a change in the structural organization of a deposit. The influence of the force particle–particle and particle–substrate interactions on the regularities of the formation of ring-shaped deposits from ellipsoidal hematite particles was studied in [10]. The experimental data were also analyzed using the ideas of the DLVO theory. It was shown that the structure of formed deposits can be controlled by varying the particle–particle and particle–substrate interactions. Ring-shaped deposits are formed when the interparticle repulsive interaction prevails over the particle–substrate attractive interaction. When attraction prevails in the particle–particle and particle–substrate interactions, ring-shaped deposits are not formed, but rather uniform films composed of nanoparticles are deposited. Therewith, the semiaxial ratio of ellipsoidal particles weakly affects the character of the self-organization of nanoparticles on a substrate. This work refines the results of previous studying the effect of the shape of nanoparticles on the formation of ring-shaped deposits [11]. The possibility to suppress the formation of rings with the used nanoparticle shape was only mentioned in that study; however, the character of the force interactions in the studied system was not discussed in detail.

The interrelation between the sizes of nanoparticles and the width of a ring-shaped deposit was discussed in [12]. It was noted that the minimum width of a ring-shaped deposit is determined by the relation between the rate of droplet evaporation and the mobility of suspended particles. When a liquid is rather rapidly evaporated from a droplet, particles do not have time to be packed into a regular structure and a ring-shaped deposit is not formed. These considerations have recently been confirmed in [13] for a large series of solutions of high-molecular-mass surfactants, the presence of which affects the hysteresis of the contact angle. It has been shown that the incorporation of such surfactants enables one to control the formation of a ring-shaped deposit up to the complete suppression of CRE. As has been proposed in [14], the three-phase contact line fixation, which is necessary for the formation of a ring-shaped deposit, may be reached only when the particle density in the zone of the three-phase contact is rather high. The authors have studied in detail the evaporation of the droplets of pure liquids and colloidal dispersions. An essential difference has been shown between the behaviors of evaporating droplets of these systems, and a mechanism for the fixation of particles at the three-phase contact line has been proposed based on the braking of liquid flows in thin films by particles.

Note that, going into details, in the majority of works ([14] may be an exception), the effect of the initial contact angle on the structures resulting from CRE has not been profoundly studied. At the same time, the existence of this interrelation seems to be quite clear. For example, in [15–18] it was shown that the formation processes of ring-shaped deposits on hydrophobic metal and hydrophilic glass substrates are essentially different. This difference causes substantial changes in the geometric parameters and structures of the deposits. In [15–18], the regularities of formation, structure, and electrical conductivity of nanocomposites resulting from evaporating droplets of aqueous dispersions of silver nanoparticles on glass and metal substrates were studied. The contact angles were nearly 25° and 90° on the glass substrate and metal substrates, respectively. It is obvious that the general regularities can hardly be established from these two values of the contact angle. Systematic studies are necessary for this purpose. This and subsequent works have been and will be devoted to such studies.

The goal of this work was to determine the influence of different factors relevant to the droplet application onto a substrate and the preliminary treatment of the latter on the value of the initial contact angle. Experiments were performed with the purpose to determine the possible scatter of the contact angle values at different regimes of droplet application, methods used for substrate cleaning, dispersion compositions, and droplet volumes. In a certain sense, the data presented in this article are of preliminary character, and the fine structure of the deposits will be discussed in subsequent communications.

EXPERIMENTAL

Experiments were carried out with droplets of aqueous dispersions of polystyrene latex particles having sizes of 250 ± 60 nm [19] and silica particles with sizes of 228 ± 10 nm obtained by hydrolyzing tetraethoxysilane in ethanol in the presence of ammonia as a catalyst [20]. Polystyrene particles had a concentration of NH^- and CO^- surface groups of 2×10^{-6} mol/m^2. All dispersions were prepared in deionized water.

Microscope slides with sizes of $75 \times 25 \times 1$ mm^3 (Heinz Herenz Medizinalbedarf GmbH, Germany), as well as microscope slides with the same sizes and cover glasses (CGs) with sizes of $24 \times 24 \times 0.17$ mm^3 (Menzel-Gläser, Germany), the surface of which was cleaned by different methods (see below), were used as substrates. The glasses were cleaned of dust and dried in a Spincoater P6700 setup (Specialty Coating Systems, United States).

Droplets were applied onto the substrates using a manual dosing pipette equipped with replaceable attachments, this pipette making it possible to form droplets with sizes of 2–40 μL, an *e*PET electronic dosing pipette (Biohit, Finland) equipped with replaceable attachments (droplets with volumes of 0.2–10 μL), and a Jetlab II setup (MicroFab Inc., United states). To increase the dimensional stability of the droplets obtained with the Jetlab II setup, the optimal shape of the pulse inputted to the piezoelectric element was selected in a series of preliminary experiments. It appeared that droplets with the most reproducible characteristics were obtained at a bipolar shape of the pulse with durations of 30 and 60 μs and amplitudes of 20 and 27 V for the stages of the "supply" and "recoil" of a droplet, respectively. The droplets generated in this way had the following parameters: velocity at the nozzle outlet of 2.3 ± 0.2 m/s, volume of 230 ± 25 pL, diameter of 78 ± 2 μm, and angle of droplet trajectory deviation from the vertical of no larger than 1°.

The droplets were monitored using a video camera supplied with the Jetlab II setup and a SolverBio scanning probe microscope (NT-MDT, Russia). The contact angles were measured with the help of an optical video stand (Photochemistry Center, Russian Academy of Sciences) [21] 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 droplets at different angles.

The droplets were applied onto horizontal substrates. Fourteen CGs with sizes of $24 \times 24 \times 0.17$ mm^3 were used after being cleaned by the following methods (two substrates for each method of cleaning).

Table 1. Contact angles θ (deg) measured in different series of experiments, their mean values *P*, and corresponding root-mean-square deviations *s*

Number Series	1	2	3	4	5	6	7	8	9	10	11	*P*	*s*
1	11.4	13.4	12.2	14.6	11.1	12.9	13.6	12.8	14.9	13.9	14.5	13.0	1.3
2	12.1	15.7	14.3	13.0	14.5	12.7	11.3	10.7	13.5	14.4	10.6	13.0	1.7
3	9.4	8.9	7.1	8.0	7.6	8.6	9.0	9.2	8.0	8.0	9.2	8.4	0.8
4	8.6	10.6	8.9	8.3	9.8	10.2	9.0	7.4	7.6	7.0	8.8	8.5	1.0

(1) A CG was cleaned of dust by centrifuging in a Spincoater P6700 setup at 6000 rpm for 2 min.

(2) A CG was exposed in acetone for 1 h, washed with a large amount of deionized water filtered through a 5-μm filter, and dried in the Spincoater P6700 setup.

(3) A CG was exposed in a 1.5% alkali solution (Hellmanex, Hellma GmbH & Co, Germany) for 3.5 h and washed with a large amount of deionized filtered water.

(4) A CG was exposed for 1 h in ethanol filtered through a 5-μm filter; then, the CG was washed with a large amount of ethanol.

(5) A CG was exposed for 1 h in 2-propanol filtered through a 5-μm filter; then, the CG was washed with a large amount of 2-propanol.

(6) A CG was exposed in acetone for 1 h, immediately washed with filtered deionized water, and exposed in chromic mixture for 1 h. Then, the CG was washed with a large amount of filtered deionized water.

(7) A CG was exposed in chromic mixture for 1 h and washed with a large amount of filtered deionized water.

All CGs cleaned by methods 3–7 were dried in the Spincoater P6700 setup.

Microscope slides with sizes of 75 × 25 × 1 mm^3 were cleaned by method 5.

INITIAL CONTACT ANGLES

Natural Scatter of Contact Angles

Let us present the data of four series of experiments, in which 10-μL droplets were applied with a manual dosing pipette onto the surfaces of microscope slides with sizes of 75 × 25 × 1 mm^3 produced by different manufacturers (Heinz Herenz Medizinalbedarf and Menzel-Gläser). Frontal images of the droplets were taken and initial contact angles were measured with the use of the horizontal camera of the optical video stand. Table 1 lists the contact angles measured for the droplets applied with the manual (series 1 and 3) and electronic (series 2 and 4) dosing units onto two substrates made of glasses produced by Heinz Herenz Medizinalbedarf (series 3 and 4) and Menzel-Gläser (series 1 and 2). The corrected root-mean-square deviation was calculated by the following formula:

$$s = \sqrt{\frac{n\sum_i \theta_i^2 - \left(\sum_i \theta_i\right)^2}{n(n-1)}}, \qquad (1)$$

where n is the number of the measurements and θ_i is the angle measured in an ith experiment.

The mean θ values were 13.0° and 8.4°, depending on the type of substrate. The maximum root-mean-square deviation was 1.7°. This value could be taken as the natural scatter of the contact angles. However, it should be taken into account that the application regime may somewhat vary for each specific droplet formed with the use of the dozing pipette. This problem will be discussed in the next section.

The Effect of the Application Regime on the Contact Angle

In addition, a series of experiments were performed in which the application regime was varied in a targeted fashion. The droplets were applied onto the same substrate from different distances, at different pipette orientation angles, in the presence and absence of a bubble, and at a varied velocity of dosing pipette approach to the substrate. In these experiments, an aqueous dispersion of polystyrene microspheres 250 nm in diameter was used; the volume of “macrodroplets” was 40 μL, while the surface of the microscope slides with sizes of 75 × 25 × 1 mm^3 was thoroughly purified from contaminants by method 5.

Figure 1 depicts typical micrographs of the applied droplets, while Table 2 lists the values of the contact angles measured for these droplets in a series of 19 experiments.

The mean θ value is 37°, while the corrected root-mean-square deviation is $s = 4.4°$.

It can be seen that variations in the application regime increase the root-mean-square deviation by more than two times. This indicates that the application regime affects both the mean value and the scatter of the contact angles. In order to reduce the scatter of

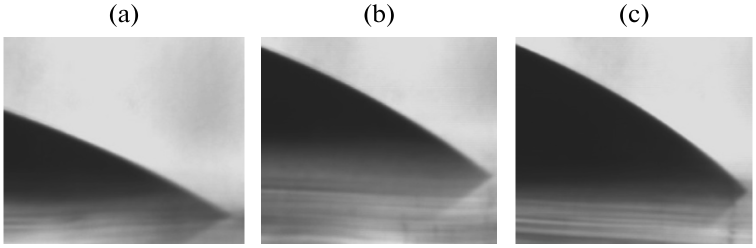

Fig. 1. Contact angles equal to (a) 33°, (b) 38°, and (c) 44° obtained for water droplets on microscope slides in one series of experiments.

the initial θ values, the tilt of the dosing pipette, distance to the substrate, and the velocity of the droplet escape from the nozzle must be kept constant. Moreover, in order to decrease the error, the spatial position of the dosing pipette relative to the substrate should be strictly fixed and an electronic dosing unit should be used.

As will be seen below, the initial contact angle fundamentally affects the structure of a formed deposit of particles; therefore, the scatter of its values must be minimized. This may be done by automating the droplet deposition process.

Effect of Droplet Volume

Water capillary constant $a = \sqrt{2\sigma/\rho g}$ (σ is the surface tension of a liquid, ρ is its density, and g is the free fall acceleration) is nearly 4 mm. Hence, the shape of droplets with volumes smaller than 200 μL is unaffected by gravity. This allows us to formally assume that the contact angle must be independent of the size of the droplets under investigation.

However, this assumption is valid for absolutely smooth substrates. In reality, substrates are both rough and chemically heterogeneous (see the next section). In the case of a rough surface, contact angle θ_r is determined by the following relation [22]:

$$\cos\theta_r = K_r \cos\theta_0,$$

where θ_0 is the contact angle on a smooth surface and K_r is the surface roughness coefficient. The roughness coefficient is known to increase with linear size L of an analyzed surface area in accordance with power low $K_r \sim L^\alpha$ [23, 24]. In our case, L coincides with the size of the contact spot, i.e., with the droplet size. The data reported in [23, 24] give grounds to assume that nearly the same effect of the contact spot size on the contact angle will also take place for a heterogeneous substrate. This circumstance is indicative of the necessity to measure the contact angles for droplets with different sizes.

We experimentally measured the contact angles for deionized water droplets with volumes of 2–10 μL on microscope slides with sizes of 75 × 25 × 1 mm^3. The dependence of the droplet contact angle on the droplet size is presented in Fig. 2. This dependence testifies that, in the studied range of droplet volumes, the contact angle remains unchanged. This leads us to conclude that the droplet volume will weakly affect the structure of a formed deposit.

Effect of the Method of Substrate Treatment

The method of substrate preparation has a stronger effect on the initial contact angle. We studied the contact angles on CG substrates treated by methods 1–7 (see above). Each method was used to treat two substrates. Two distilled water droplets with a volume of 8 μL were applied onto each substrate with the manual dosing pipette. Two values of the contact angle (on the left- and right-hand sides of a droplet profile) were measured for each droplet. Thus, eight values of the contact angle were obtained for each method of substrate cleaning. These values were averaged. The averaged results are presented in Table 3, from which it follows that, depending on the method of substrate cleaning, the values of the contact angle may differ by 47°.

Table 2. Contact angles for water droplets on microscope slides at different manners of droplet application

Experiment number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
θ, deg	44	37	35	36	39	41	33	40	32	38	33	41	31	44	43	44	38	44	40

Effects of Nature and Concentration of Particles

Since the targeted self-assembling of a structure from particles of a dispersion implies variations in the initial dispersion concentration, it is of interest to determine the dependence of the contact angle on the content of particles in it.

Experiments were carried out using dispersions of silica and polystyrene particles with particle concentrations of 1–50 wt %. Six 8-μL droplets of a dispersion with one concentration were applied using the dosing pipette onto a microscope slide with sizes of 75 × 25 × 1 mm^3, and the contact angles were measured. The averaged results of the measurements are illustrated in Fig. 3. As follows from Fig. 3, the presence of silica and polystyrene particles in water increases and decreases its contact angle, respectively. Therewith, a rise in the concentrations of the dispersions caused the θ values to reach plateaus in both cases. For both systems, the contact angle changed by at most 5°. Assuming that the particles are not deposited onto the glass/water interface and all variations are related to variations in the surface tension of a colloidal solution, it may be believed that silica particles are surface-inactive, while polystyrene particles are surface-active [25]. This may be related to different surface charges of these particles and their Hamaker constants, which characterize the particle–water dispersion interaction [26]. In order to unambiguously determine the contributions of these effects, it is necessary to study the stability of wetting films on particle surfaces, which is beyond the scope of this work.

The surface inactivity of silica particles, which leads to a rise in θ, may be related to rather efficient hydration thereof, which hiders their escape to water surface, similarly to the mechanism of negative adsorption of ions. For polystyrene particles, the hydration effect is less significant, and the common particle adsorption on water surface with a concomitant decrease in the surface tension takes place in this case.

Another important circumstance should be noted. The observed dependence of the contact angle on dispersion concentration c indicates that, as follows from the Gibbs equation

$$\Gamma_p = -\frac{c}{RT}\frac{d\sigma}{dc},$$

where R is the gas constant and T is temperature, particle adsorption Γ_p on a liquid surface reaches saturation rather rapidly. As will be shown in subsequent works, particles occurring on a liquid surface (adsorbed particles) play an important role in the formation of the deposit structure under certain conditions. The presented dependence of particle adsorption on dispersion concentration enables us to select the ranges of particle concentration in which the adsorption value and, in the long run, the deposit structure can still be controlled.

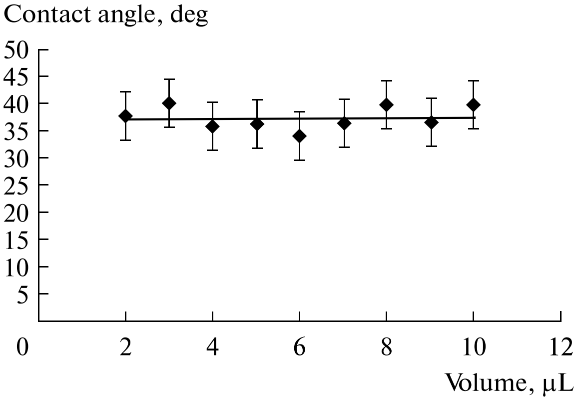

Fig. 2. Dependence of water droplet contact angle on droplet volume.

Effect of Particle Charge

Particle concentration is not the only factor affecting the contact angle. For a dispersion of the same concentration, the contact angle also varies with particle surface charge (Fig. 4). As can be seen from Fig. 4, an increase in the particle surface charge leads to a monotonic reduction in the contact angle. The data presented in Fig. 4 have been obtained for a 5 wt % dispersion of particles in water. The experiments were carried out with particles of ethylene glycol dimethacrylate (EGDM) and styrene–EGDM–methacrylic acid (MAA) copolymer. Their characteristics are presented in Table 4. In this series of experiments, microscope slides with sizes of 75 × 25 × 1 mm^3 were used after being successively treated with a detergent (Fairy) solution, acetone, and chromic mixture in an ultrasonic bath for 20 min and washed with deionized water. After the glasses were dried, 20-μL droplets of the dispersions were applied onto them and the initial contact angles were measured.

Solution ionic strength is known to be a factor affecting the contact angle. Its growth must increase the contact angle. Indeed, our measurements showed

Table 3. Contact angles of water droplets on CGs treated by different methods

Cleaning method	1	2	3	4	5	6	7
θ, deg	58	37	33	31	31	10	11

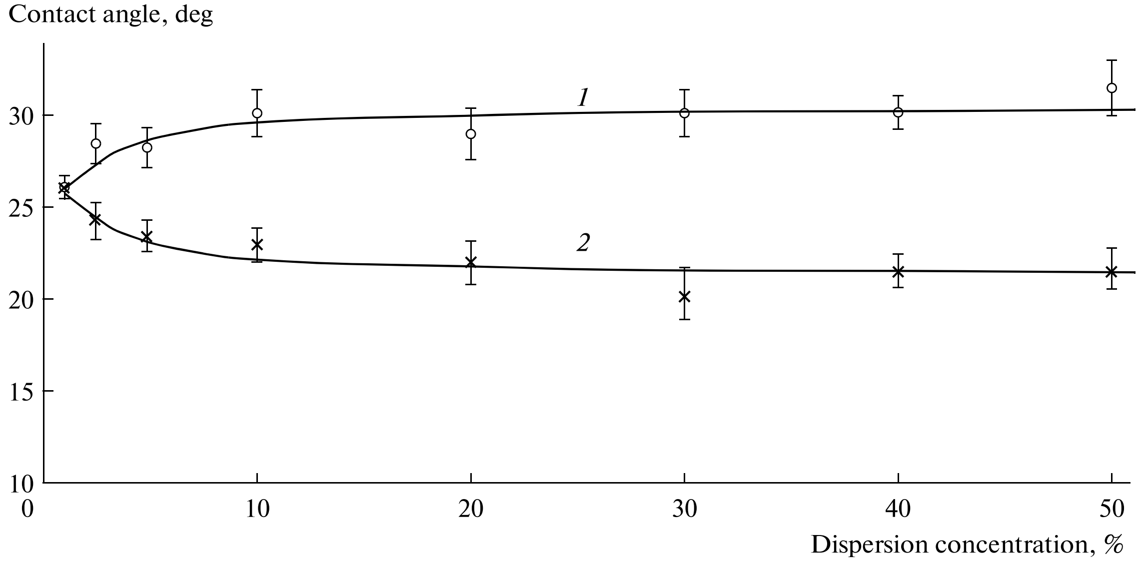

Fig. 3. Concentration dependences of contact angle for aqueous dispersions of (*1*) silica and (*2*) polystyrene.

that the addition of sodium chloride in concentrations up to 200 mM increases θ by nearly 3°.

INITIAL CONTACT ANGLE AND MACROSTRUCTURE OF RING-SHAPED DEPOSITS

The method used to clean a substrate strongly affects the macroscopic structure of a deposit resulting form dispersion droplet evaporation. The structure may be essentially different. We performed a series of experiments on the formation of deposits on substrates cleaned by methods 1–7. We used 0.5 wt % dispersions of polystyrene spheres with a size of 250 nm. In order to exclude the errors arising in the data due to the human element, the droplets were applied onto the substrates with the Jetlab II setup by arrays of 20 × 20 droplets. Note that the effect of the type of the surface treatment appeared to be stronger for the droplets applied in this manner than the effect for the macrodroplets applied with the dosing pipette. Therefore, we here consider the data on "microdroplets."

Remember that droplets escape from the nozzle of a Jetlab II setup at a velocity of 2–3 m/s. After the collision with a substrate surface, a droplet is deformed to acquire the shape of a disc. Then, capillary forces transform the droplet into a spherical segment. The subsequent droplet evolution due to the evaporation of the liquid is, to a substantial extent, governed by the state of the substrate surface (Fig. 5).

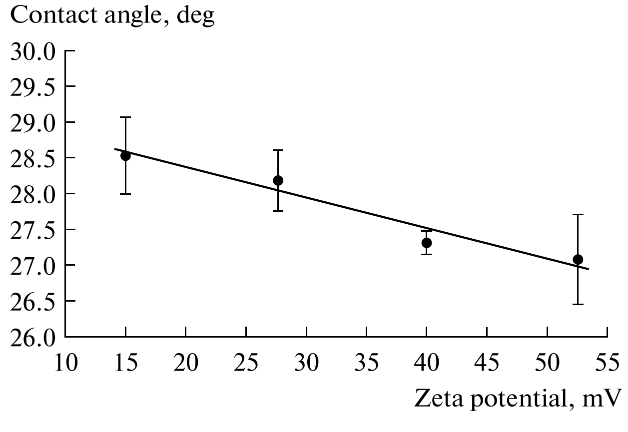

Fig. 4. Dependence of contact angle of aqueous polystyrene dispersion on particle ζ potential. Linear regression line is shown.

When a droplet evaporates on a hydrophobic glass surface, the area of its contact with the substrate remains unchanged; therefore, a spot composed of microparticles is, in the long run, formed on the substrate, with the spot shape, after the establishment of equilibrium, reproducing the shape of the droplet base. When a droplet is applied onto an "ideally" clean substrate, the equilibrium three-phase contact line and, hence, the spot of deposited particles have a regular roundish shape. When contaminants decelerating or accelerating the movement of the droplet boundary in the course of equilibrium establishment are present on a substrate, the three-phase contact line and the spot of deposited particles have an irregular deformed shape.

As regards the particle distribution inside the spot, when the substrate is ideally clean, it is uniform and centrally symmetric. In the course of the self-assembling of colloidal solution droplets, contaminants present on the substrate play the role of condensation sites; therefore, the particle distribution on a "dirty" substrate turns out to be nonuniform, and a set of particle clusters is formed.

The structures depicted in Fig. 5 show that the quality of a formed structure improves with increasing substrate hydrophilicity. The cleaner the surface, the more symmetric the formed structure. At the same time, the comparison of, e.g., Figs. 5f and 5g shows that the character of particle distribution inside the ring-shaped deposit is sensitive to slight variations in the contact angle. This circumstance illustrates the effect of the contact angle on the deposit fine structure, which is especially pronounced for microdroplets and will be discussed in subsequent articles. Here we only note that, after cleaning of the glasses by methods 1–3 and 6, contaminants remain on the surface, which lead to the formation of nonuniform deposits. Method 7 seems to ensure the best cleanness of the substrates. However, high-quality deposits are also formed at an initial contact angle of 31°, which is attained by cleaning methods 4 and 5 (with the use of ethanol and 2-propanol). The substrates treated by these two methods are of special interest, because we may state that they are highly clean at a markedly higher contact angle than that obtained on the substrate treated by method 7. Seemingly, when contaminants are removed from glass with chromic mixture, chromium cations are adsorbed on the surface, thereby decreasing the contact angle to 11°. At the same time, as can be seen from the comparison of the "almost ideal" samples shown in Figs 5d, 5e, and 5g, the deposit structure essentially depends on an initial contact angle.

Note that the influence of the degree of chemical homogeneity of a substrate on the structure of deposits resulting from evaporating dispersion droplets has not been discussed in the literature. Meanwhile, as can be seen from Fig. 4, it substantially affects the structure of ring-shaped deposits. This circumstance must also be taken into account when formulating theoretical models, which, as a rule, a priori assume homogeneity of a surface onto which a droplet is applied. Our results demonstrate the falseness of this assumption.

Table 4. Diameter D and ζ potential of polymer particles

Particle composition	D, nm	ζ, mV
EGDM	470	+14.7
EGDM	470	+39.6
EGDM	454	–52.6
Styrene/EGDM/MAA = 78/20/2	289	–27.8

CONCLUSIONS

The above-presented data show that a method of substrate surface treatment (the degree of its cleanness) has the strongest effect on the contact angle of a droplet. The state of the surface strongly affects the structure of a formed deposit. Moreover, the initial contact angle of a droplet depends on the manner in which it is applied onto a substrate; in this case, variations in the initial contact angle values may be as large as 13°. To a lesser extent, the contact angle is affected by the concentration and nature of dispersed particles. As the particle concentration is increased, the initial contact angle may both decline and grow.

Deposits with regular shapes are formed only on a clean surface. The presence of contaminants disturbs the symmetry of not only the external ring-shaped deposit, but also its internal region. Therefore, the study of the structure of a deposit formed via the CRE mechanism enable one to judge both the cleanness and the degree of homogeneity of a surface, because, in the absence of contaminants or other heterogeneities, a uniform centrally symmetric distribution of particles develops along the boundary and inside of a spot.

For microdroplets applied with the help of a Jetlab II setup, the method of surface cleaning also substantially affects the radial distribution of deposit particles in the internal region of the spot. In the case of microdroplets on clean homogeneous surfaces, the structure of a deposit depends on the initial contact angle more strongly than it does in the case of macrodroplets.

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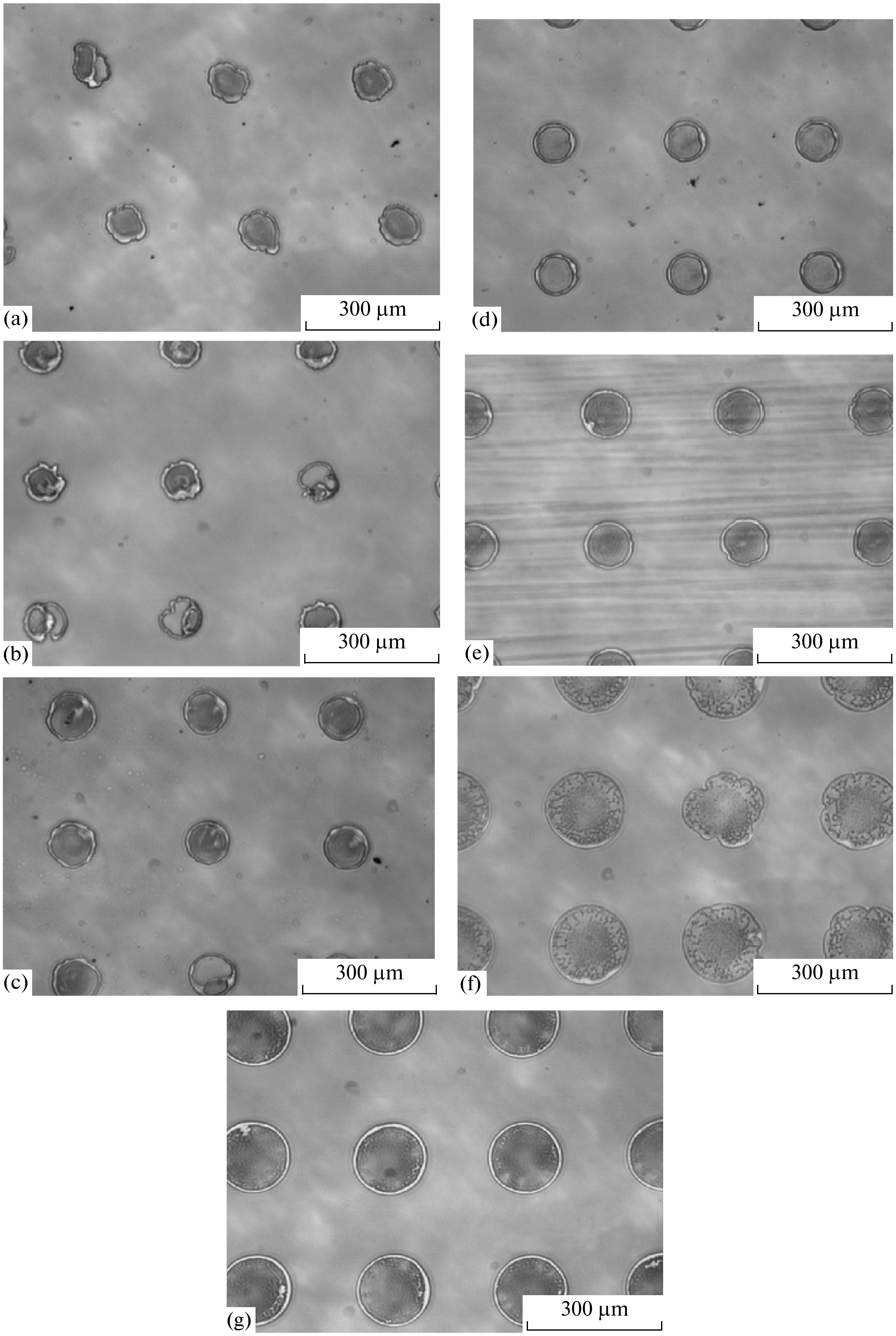

Fig. 5. Structure of deposits formed via CRE mechanism on substrates with different degrees of hydrophilicity: (a–g) substrates treated by methods 1–7, respectively.

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