

Deposition of Oil Drops on a Glass Substrate in Relation to the Process of Washing

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The attachment of emulsion drops to glass substrates is investigated in relation to the redeposition of oil drops in the process of washing. It turns out that the drops of a surfactant-stabilized oil-in-water emulsion cannot be attached to an immersed glass plate simply by the buoyancy force. However, the same drops can be deposited on the plate when the latter is pulled out of the emulsion, i.e., when the drops are pressed against the substrate by a receding meniscus. We measured the amount of the oily deposit as a function of the pH, ionic strength, and composition of an amphoteric-anionic surfactant mixture. The enhanced oil deposition at low pH correlates with the domain in which the emulsion drops and the solid substrate bear opposite electric charges. This was established by zeta-potential measurements with oil drops and glass particles. The anionic surfactant brings negative surface charge to the oil droplets and suppresses the oil deposition on the negatively charged glass. With the increase of the fraction of the amphoteric surfactant in the mixture, the zeta-potential is converted from negative to positive, and the oil deposition grows almost linearly with the potential. In general, the deposition of oil drops by a receding meniscus is governed by an interplay of electrostatic and hydrodynamic factors.

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1. INTRODUCTION

The removal of oily soils from a solid substrate (say in the usual dishwashing) can be considered as the reverse process of coagulation (1, 2). It is not a spontaneous process and requires some input of energy. The addition of detergents reduces the amount of input energy and promotes the removal of the oily deposit. The latter is transferred from the solid surface into the bulk of the aqueous phase in the form of small oil drops. However, the drops can be deposited again on the substrate. Hence, the efficiency of washing is determined by the competition between the removal and redeposition of the oil drops. The redeposition can be reduced or prevented by means of the same factors, which are known to bring about stability of dispersions (3–6). One could

expect that the oil drop redeposition can be suppressed if the electrostatic or steric repulsion between the oil drops and the solid substrate is increased. The electrostatic (double-layer) interaction strongly depends on the surface charge of the oil drops and the solid substrate. A steric repulsion appears in the presence of nonionic surfactants and/or water-soluble polymers.

The (re)deposition of oil drops on a solid substrate in the real washing process can be influenced by many different factors such as the type and concentration of the surfactants, the presence of other additives, including electrolytes, the nature of the oil phase and the substrate, and the temperature, size, and polydispersity of the oil drops (7). It is important to have in mind that the washing process takes place under dynamic conditions, in the presence of hydrodynamic flow. Therefore, studies of colloid stability at quasi-equilibrium conditions (for instance, in experiments with equilibrium emulsion and wetting films) might be incomplete regarding the main factors governing the oil redeposition.

In this paper we present experimental results for the deposition of soybean-oil drops on glass substrates under dynamic conditions (receding meniscus). The amount of deposited oil is directly measured. The effects of the concentration of an amphoteric surfactant, and its mole fraction in mixtures with an anionic surfactant, are examined. To elucidate the possible role of the electrostatic interactions in the deposition process, the ionic strength of the solution is also varied by adding NaCl. The ζ -potential of the oil drops and the glass surface is determined by means of electrophoretic measurements. The pH of the aqueous phase, which affects the ionization state of the amphoteric surfactant (8, 9), is also varied. The results demonstrate the crucial role of the electrostatic (double-layer) interaction between the oil drops and the glass surface in the process of oil deposition. We hope the experimental results and their interpretation will be helpful for a better understanding and control of this process.

2. EXPERIMENTAL

2.1. Preliminary Experiments

In our first attempts to study the process of oil drop deposition on solid substrates we used the experimental cell presented

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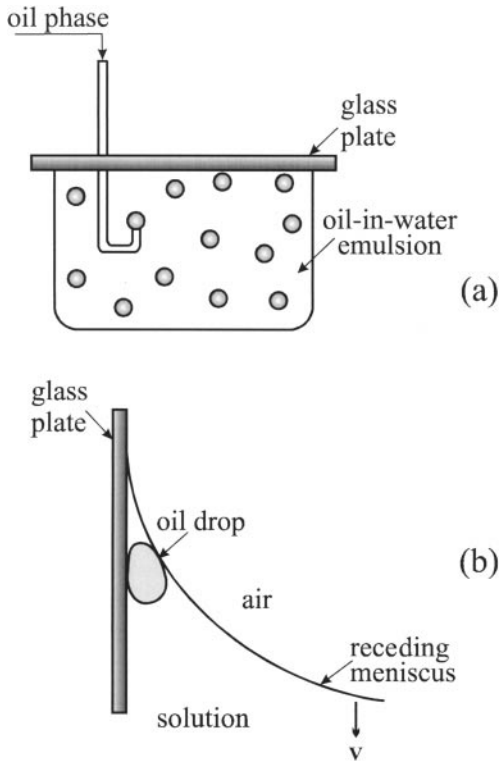


FIG. 1. Schematic representation of the experimental systems for studying oil drop deposition on a glass plate (a) under the action of buoyancy force and (b) by a receding meniscus moving downward with velocity v .

schematically in Fig. 1a. The oil drops were formed in the bulk of the aqueous surfactant solution by injection of soybean oil through the needle of a syringe. Driven by the buoyancy force, the drops approached the surface of the solution, which was covered by a glass plate. One might expect that at least some of the oil drops resting below the glass plate would be deposited on it. However, no oil deposition took place under these conditions—a thin aqueous film always remained between the drops and the glass surface. It turned out that the buoyancy force was not strong enough to cause attachment of the oil drops to the glass substrate. Then a question arises: which is the driving force of the oil redeposition in the real washing process?

The following observation gives a possible reply to this question. If the same oil-in-water emulsion flows out of a glass container (i.e., the level of the emulsion in the container gradually decreases), then one observes deposition of oil drops on the walls of the container. The same result can be obtained if a glass plate is pulled up out of the suspension. It seems that the receding meniscus presses some of the oil drops against the glass wall in the zone of the moving three-phase contact line and thus causes the oil deposition (Fig. 1b). In other words, it turns out that the deposition is due to the confinement of oil drops in the narrow wedge between the meniscus and the wall with a subsequent entrapment of drops in the wetting film remaining after the receding meniscus. Irrespectively of whether that wetting film is stable or unstable, the entrapped drops are firmly pressed against the

solid substrate by capillary forces, and they eventually stick to the substrate after the drainage and/or evaporation of the water. In summary, our preliminary experiments demonstrate that no deposition occurs under “static” conditions (Fig. 1a), whereas under dynamic conditions deposited oil drops remain on the substrate after the passage of a receding meniscus (Fig. 1b).

2.2. Experimental Setup and Procedure

Based on the observations from our preliminary experiments, we constructed an experimental setup for studying the oil deposition, which is sketched in Fig. 2. A glass plate is immersed vertically in a glass container filled with an oil-in-water emulsion. The glass plate is drawn out from the emulsion with a constant velocity using a step motor. The speed of the plate motion, and hence the velocity of the receding meniscus, is controlled by varying the speed of the step motor. Deposition of oil drops is observed during this experiment just like in the process presented schematically in Fig. 1b.

All experiments were carried out using hydrophilic glass plates. The glass surface was cleaned using chromic acid. Prior to the experiments the plates were rinsed gently with deionized water and dried at 100°C for 15 min. After the plates cooled down to room temperature (25°C) they were immediately used in the experiment.

The volume fraction of the soybean oil in the used emulsions was 6.7%. The emulsions were prepared by using a blade homogenizer (MLW ER10, Prugerate-Werk Germany), ca. 2000 rpm; the period for homogenization was 1 min. Owing to the presence of surfactant a large amount of foam is generated during the emulsification, which is subsequently separated from the emulsion with the help of a funnel. Since the emulsion

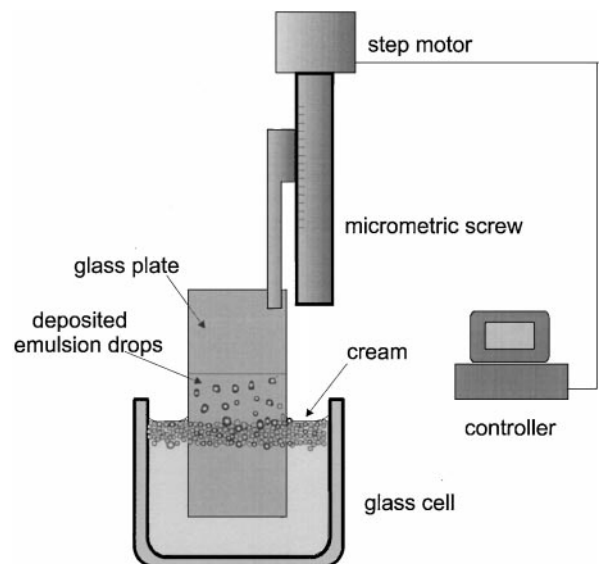


FIG. 2. Experimental setup for studying the process of oil drop deposition on a solid surface. The vertical glass plate is immersed in a glass cell containing oil-in-water emulsion. The plate is pulled up with a controlled speed driven by a step motor.

droplets in the samples are comparatively large (of average diameter between 20 and 100 μm) and very polydisperse, a cream is formed in the upper part of the aqueous phase within a period of 6–8 min. If the experiment on droplet deposition is performed during this period of time, the reproducibility of the results is very poor (i.e., the data are very scattered). This can be easily understood: the droplet size and concentration at the liquid surface change with time. To avoid this problem we carried out the deposition experiments after the complete creaming of the emulsion, which took about 15 min.

In each experiment the glass plate was fixed to a holder driven by the step motor (see Fig. 2). The immersion of the plate in the emulsion was performed at fixed velocity (0.63 mm/s). When the plate touched the bottom of the glass cell we started to pull it upward with the same velocity. Some of the oil drops entrapped by the receding meniscus were pressed against the solid surface and were deposited on the glass plate.

After the complete withdrawal of the glass plates out of the solution (with some oily deposit), they were left for a few hours at room temperature until the water completely evaporated from their surfaces; however, the deposit of soybean oil remained, since soybean-oil is not volatile at room temperature. The amount of deposited oil was determined by measuring the weight of the glass plates before and after the experiment. With each emulsion we performed between six and ten parallel experiments; the experimental points and the error bars in the plots of the data (see below) were calculated by averaging.

2.3. Materials

Two types of surfactants were used in the experiments, (i) the amphoteric surfactant lauryl-dimethyl-aminoxide, $\text{CH}_3(\text{CH}_2)_{11}(\text{CH}_3)_2\text{N}^+\text{O}^-$, which will be called Aminoxide (AO), and (ii) an anionic surfactant sodium polyoxyethylene-3 sulfate (SDP3S), $\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_3\text{OSO}_3\text{Na}$. The samples were provided by Colgate–Palmolive Co. and were used without additional purification.

The investigated emulsions were prepared from soybean oil, which was purified from polar contamination by passing through a column filled with Florisil (Sigma Co., USA). In this way possible impurities from mono- and diglycerides, free fatty acids, and phospholipids were removed.

The pH of the aqueous phase was varied by adding small portions of aqueous solutions of HCl and NaOH (analytical grade, Sigma Co.). The ionic strength was altered by addition of NaCl (analytical grade, Sigma Co.).

The glass substrates used in our experiments were microscope plates of dimensions $25 \times 75 \times 1$ mm. To measure electrostatically the ζ -potential of the glass–water interface we used small glass particles of the same material. For that purpose a glass plate was crushed to powder which was afterward dispersed into water. The obtained suspension was left at rest for several hours, and during that period the largest particles sedimented. Then the upper liquid was filtered through a Millipore filter with an average pore size of 450 nm. The permeate con-

tained only Brownian glass particles of mean hydrodynamic diameter of about 300 nm, measured by dynamic light scattering. No sedimentation of these small particles was observed over a period of 2 h.

2.4. ζ -Potential of Oil Drops and Glass Particles

To determine the surface electric potential of the oil–water and glass–water interfaces we measured the electrophoretic mobility of emulsion droplets and glass particles by means of a Zetasizer IIC (Malvern Ins. Ltd., UK). It includes an He–Ne laser and a Multibit-8 correlator. This method enables one to measure the electrophoretic velocity of the particles (or drops), u , under the action of an applied electric field of intensity E . Then the electrophoretic mobility, μ_E , is calculated from the relationship (10)

$$\mu_E = \frac{u}{E}. \quad [1]$$

The ζ -potential of particles with thin electric double layers can be calculated using the Smoluchowski equation (10)

$$\zeta = 4\pi\eta\mu_E/\varepsilon, \quad [2]$$

where η and ε are the viscosity and dielectric permittivity of the aqueous phase.

The Zetasizer IIC is designed for measurements with dispersions containing particles (drops) between 0.05 and 5 μm at a low particle volume fraction. To obtain dispersions suitable for electrophoretic measurements we prepared oil-in-water emulsions with the same composition as in the oil-drop-deposition experiments; however, a longer period of homogenization (10 min) was applied in order to obtain drops of smaller size than those in the deposition experiments. After some period of creaming a small portion of the emulsion phase below the cream was taken and diluted with the same aqueous solution which had been used to prepare the emulsion. The emulsion obtained in this way was very stable and contained drops of mean diameter about 0.5 μm ; it was used in the ζ -potential measurements. The pre-equilibration of the oil and water phases was found to have no effect on the measured ζ -potentials. Electrophoretic measurements, carried out 5–10 min, 2 h, and 24 h after the sample preparation gave the same results for ζ in the framework of the experimental accuracy.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Effect of pH on Oil Drop Deposition

First we studied the deposition of soybean-oil drops on glass plates at various pH, but at fixed concentration (2 mM) of the amphoteric surfactant Aminoxide (AO). The results for the amount of deposited oil as a function of pH are shown in Fig. 3. It is seen that for $\text{pH} < 6.0$ the amount of oil deposited on the glass surface increases markedly with the decrease of pH. In acidic solutions AO is present in both zwitterionic and cationic

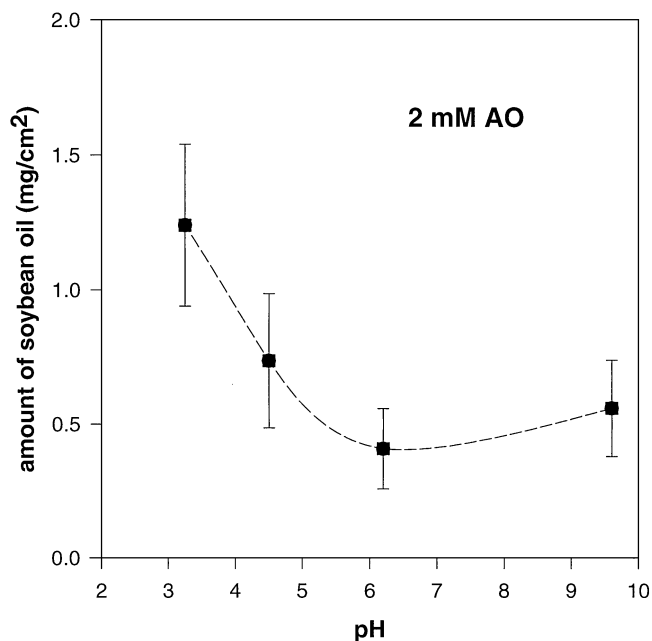
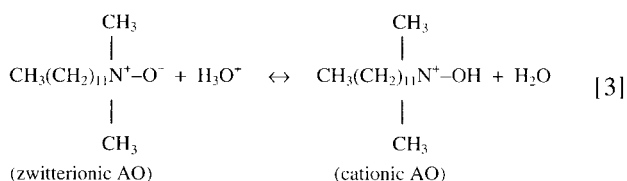


FIG. 3. Experimental data for the amount of deposited oil vs pH of the aqueous phase at fixed concentration (2 mM) of Aminoxyde (AO); pH is varied by addition of small portions of 0.1 M solutions of HCl and NaOH.

forms; the following reaction takes place.



The fraction of the cationic form of AO increases with the decrease of pH. At pH 3.0 almost all of the dissolved AO is in cationic form (9).

The ζ -potential of *pure* soybean-oil drops (no surfactant in the emulsion) is negative in the whole investigated range of pH and increases in magnitude with the increase of pH, from -23 mV at pH 3.0 up to -88 mV at pH 9.0. The latter values are close to those measured with pure xylene drops at the same pH and ionic strength (11). In both systems (xylene and soybean oil) the negative ζ -potential was found to increase in magnitude with the increase of pH in the absence of surfactant; this finding can be attributed to the adsorption of hydroxyl (OH^-) ions on the oil-water interface (11).

To elucidate the reasons for the observed dependence of oil deposition on the pH of the aqueous phase (Fig. 3), we measured the electric potential of the oil drops in the presence of amphoteric surfactant. Figure 4 shows the ζ -potential of soybean-oil drops measured as a function of pH in the presence of Aminoxyde (1 and 2 mM) and 1 mM added NaCl. The results obtained in the presence of 1 and 2 mM Aminoxyde (the solid and empty circles in Fig. 4) coincide in the framework of the experimental accuracy. This observation indicates that the surfactant

adsorption monolayer at the oil-water interface is saturated at Aminoxyde concentrations ≥ 1 mM.

The measured ζ -potential of the soybean-oil drops covered with Aminoxyde monolayer (Fig. 4) is negative at high pH; however, its magnitude is about two times smaller than that of the pure oil-water interface. A possible explanation is that the AO molecules, which are predominantly electroneutral (zwitterionic) for $\text{pH} > 7.5$, upon adsorption displace part of the hydroxyl ions bound to the bare oil-water interface. The decrease of pH leads to a reduction of the negative ζ -potential of the oil drops until it becomes zero at a pH of about 7.5. The ζ -potential becomes positive for lower pH, and its magnitude increases with the acidity of the aqueous phase due to the increase of the fraction of the cationic form of Aminoxyde; see Eq. [3]. At pH 3 the ζ -potential is $+95 \pm 8$ mV.

The pH dependence of the ζ -potential of *soybean-oil droplets* covered with Aminoxyde (Fig. 4) is very similar to the respective curve for *latex particles* covered with Aminoxyde reported in Ref. (9). Probably in both cases similar dense surfactant adsorption monolayers are formed, which determine the interfacial electric charge and potential.

One may expect that the glass surface remains negatively charged over the studied pH range due to the partial ionization of the SiOH-groups. This expectation was checked by measuring the ζ -potential of glass particles at different acidity of the solution in the *absence* of surfactant. The results are presented by the solid boxes in Fig. 4. The ζ -potential of the glass particles is negative and slightly increases in magnitude (from -40 to -60 mV) with the increase of pH. The ζ -potential of the glass particles in

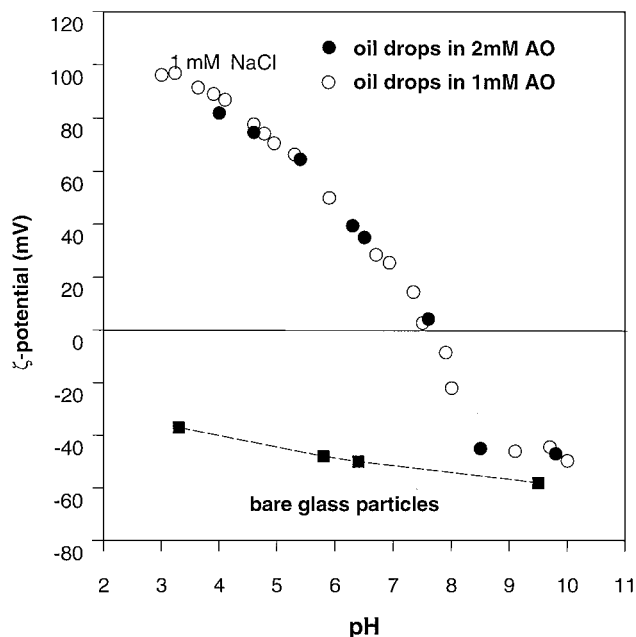


FIG. 4. Data for ζ -potential vs pH of the aqueous phase measured with bare glass particles (the boxes) and soybean-oil drops covered with an adsorption layer of Aminoxyde (the circles). The solution contains 1 mM added NaCl; the temperature is $25 \pm 0.1^\circ\text{C}$.

the presence of Aminoxide was also measured and its relevance to the deposition process is discussed in Subsection 3.2.

One can distinguish two regions in Fig. 4: (I) above pH 7.5, where the surface electric potentials of both oil drops and bare glass particles are negative, and consequently the glass plate repels the oil droplets; (II) below pH < 7.5, where the glass and the oil drops bear surface charges of opposite sign, and the glass substrate attracts the oil drops. Figure 3 shows that the most pronounced oil deposition really occurs in region (II), where the positive charge of the drops is the largest. Note, however, that the boundary between the regions with and without pronounced oil deposition in Fig. 3 is at ca. pH 6, rather than at pH 7.5. The most probable explanation of this observation is that in the real oil-drop deposition experiments the negative surface charge of the glass can be reduced (and even inverted) owing to adsorption of Aminoxide (see the next subsection). This effect makes the surface potential of glass closer to that of the oil drops and has the tendency to inhibit the oil deposition on the glass.

3.2. Effect of Aminoxide Concentration on Oil Deposition

Experimental results for the deposition of oil drops as a function of the Aminoxide concentration, c_{AO} , are presented in Fig. 5 for fixed pH 6.3 in the absence of added NaCl. One sees that the increase of c_{AO} leads to a significant decrease of the deposited amount of soybean oil. These results indicate that a modification of the surface charge of the glass plate takes place owing to the adsorption of Aminoxide. Indeed, one can expect that the adsorption of surfactant on the glass becomes faster at higher c_{AO} , which gives rise to a modification of the glass surface during the period of the oil deposition experiment.

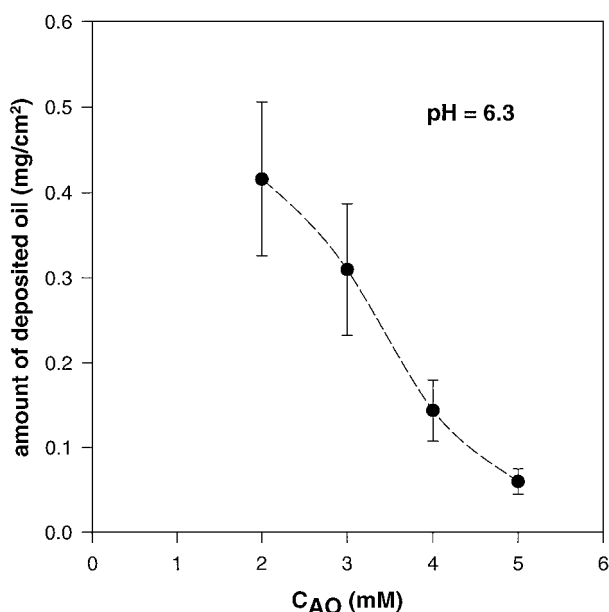


FIG. 5. Experimental data for the deposited soybean oil on a glass plate as a function of Aminoxide concentration, c_{AO} , at pH 6.3.

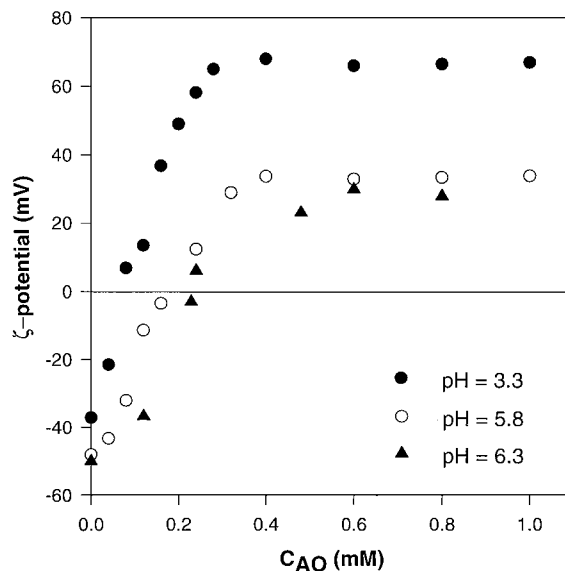


FIG. 6. Plot of the measured ζ -potential of glass particles vs the concentration of the amphoteric surfactant Aminoxide, c_{AO} , for three different values of pH.

To check the latter hypothesis we measured the ζ -potentials of glass particles at various surfactant concentrations at pH 3.3, 5.8, and 6.3. Figure 6 shows the experimental results. The results for $c_{AO} = 0$ correspond to bare glass particles (without AO in the aqueous phase). The increase of c_{AO} first reduces the negative potential of the glass particles and then leads to their positive charging (Fig. 6).

For low Aminoxide concentrations the glass surface is still negative. In this concentration range the adsorption of Aminoxide can be attributed predominantly to electrostatic attraction between the Aminoxide cations and the negatively charged glass surface; see Fig. 7a. Thus the negative charge of the glass is reduced and then completely neutralized; the latter situation corresponds to the intersection points of the experimental curves with the line $\zeta = 0$ in Fig. 6. Note that in this range of Aminoxide concentration the reduction of the negative charge is accompanied by an increasing hydrophobization of the glass surface.

At higher Aminoxide concentrations, one may expect that surfactant molecules adsorb predominantly over the hydrophobic tails of the already bound surfactant ions, as sketched in Fig. 7b. This leads to a hydrophilization of the glass surface and to a further increase of its ζ -potential, which levels off at a positive value for the higher c_{AO} (Fig. 6); the latter fact evidences saturation of the surfactant adsorption on the glass. The limiting value of ζ for high c_{AO} increases with the rise of acidity. This could be expected, because the fraction of the cationic Aminoxide increases with the acidity; see Eq. [3] and Ref. (9). The latter effect can explain also the fact that the value of c_{AO} , corresponding to $\zeta = 0$, decreases with the decrease of pH (Fig. 6).

The identity of the ζ -potentials of the 300-nm glass particles (Fig. 6) and of the glass plates used in the oil deposition

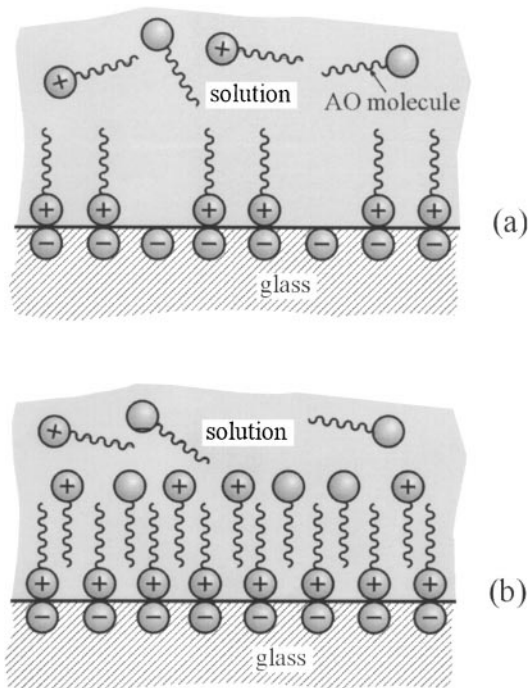


FIG. 7. Formation of (a) an adsorption monolayer and (b) a bilayer from the surfactant AminoXide on a negatively charged glass surface in contact with the surfactant solution; note that AminoXide is present in both cationic and electroneutral (zwitterionic) forms.

experiments deserves a special discussion. The glass particles have been first dispersed in water for many days, and then they have been kept in the surfactant solution for many hours. Hence, we expect that an equilibrium surfactant adsorption layer has been formed on the particle surfaces, and that the values of the ζ -potential in Fig. 6 are the equilibrium ones. On the other hand, the glass plates are in contact with the surfactant solution only during the oil deposition experiment (typically 1.5 min). Independent ellipsometric experiments (to be reported in a subsequent paper) show that an equilibrium adsorption layer of surfactant (AminoXide) on a SiO_2 substrate is formed within 5 s. Hence, we can expect that our glass plates are covered with an equilibrium AminoXide adsorption layer during the stage of their dipping in the solution, which takes about 40 s. The only difference between the glass plates and the particles could stem from the different procedures for pretreatment. Indeed, the thermal treatment (drying) of the plates before their use may lead to a chemical modification of their surfaces, viz. two ionizable surface $-\text{OH}$ groups can release a water molecule and combine to form a nonionizable $-\text{O}-$ group (6). This would lead to a decrease of the negative surface charge of the glass plates in water as compared to the glass particles. Therefore, one may anticipate that the adsorption of the positively charged AminoXide on the glass plates (and their ζ -potential) is lower than that on the glass particles in the surfactant solution. In other words, the ζ -potential of the glass plates is expected to be intermediate between that of the bare glass particles and that of the particles

covered with equilibrium surfactant adsorption monolayer. The observed pronounced correlation between the deposition efficiency and the potential of the bare glass surface indicates that a dense adsorption layer has not been formed on the surface of the plates. Hence, the measured equilibrium ζ -potentials of glass particles can serve as a basis for qualitative conclusions, but they cannot give quantitative information about the real surface potential of the glass plates.

The electrophoretically measured ζ -potentials of the oil drops should be expected to be the same as in the oil deposition experiments, insofar as in both types of experiments (electrophoretic measurements and oil deposition) the drops have been in contact with the surfactant solution for at least several hours before the measurement; this guarantees the formation of a dense adsorption monolayer at the oil–water interface.

3.3. Effect of Electrolyte on Oil Drop Deposition

Additional information about the importance of the electrostatic interaction for the oil drop deposition can be obtained by examining the effect of added electrolyte on the amount of deposited oil. If the electrostatic interaction really plays an important role, one should expect a strong dependence of the oil deposition on the ionic strength of the aqueous phase. The effect of added NaCl was investigated at fixed values of the other experimental parameters, viz. AminoXide concentration $c_{\text{AO}} = 2 \text{ mM}$ and pH 6.3. The results are shown in Fig. 8. One sees that the rise of salt concentration enhances the oil deposition. In the presence of 10 mM NaCl the amount of deposited oil is about seven times higher than in the absence of NaCl.

As seen in Fig. 6, under these conditions ($c_{\text{AO}} = 2 \text{ mM}$, pH 6.3) the glass surface is positively charged. The oil drops are also positively charged (Fig. 4). Then, one can conclude that for pH 6.3

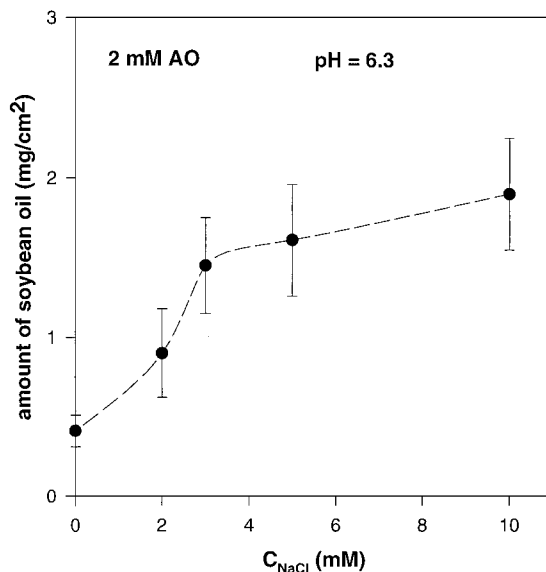


FIG. 8. The measured amount of deposited oil plotted against the concentration of NaCl at fixed pH 6.3 in the presence of 2 mM AminoXide.

the addition of electrolyte suppresses the electrostatic repulsion between the oil drops and the glass surface, and decreases the thickness, h , of the water film intervening between an oil drop and the glass substrate; for this reason the deposition of oil drops becomes easier—see the discussion after Eq. [4].

3.4. Emulsions Stabilized by an Anionic–Amphoteric Mixture

In detergency the amphoteric surfactants are most frequently used in mixtures with anionic surfactants. For that reason we carried out oil deposition experiments using emulsions stabilized by a mixture of AO and SDP3S at constant total surfactant concentration, $c_t = 1$ mM, with 1 mM added NaCl. The molar fraction of the two surfactants was varied from 0 to 1.

Experimental data for the oil deposition in mixed AO–SDP3S solutions are plotted in Fig. 9 vs the molar fraction of Aminoxide (X_{AO}) at fixed pH 3.0. The quantity of deposited soybean oil in the presence of SDP3S only ($X_{AO} = 0$) does not depend on pH and is very small. Note that in this case both the glass surface and the oil drops are negatively charged. For $0 < X_{AO} < 0.4$ the oil deposition is rather low. However, at $X_{AO} > 0.4$ a significant increase in the oil deposition with the rise of X_{AO} is observed. The curve in the inset of Fig. 9 presents the same data but scaled with the lowest value of the measured deposition, that at $X_{AO} = 0$; this curve shows that the oil deposition increases more than 100 times with the increase of X_{AO} .

We performed oil deposition experiments also at pH 6.3 (data not shown in Fig. 9); qualitatively the experimental results ex-

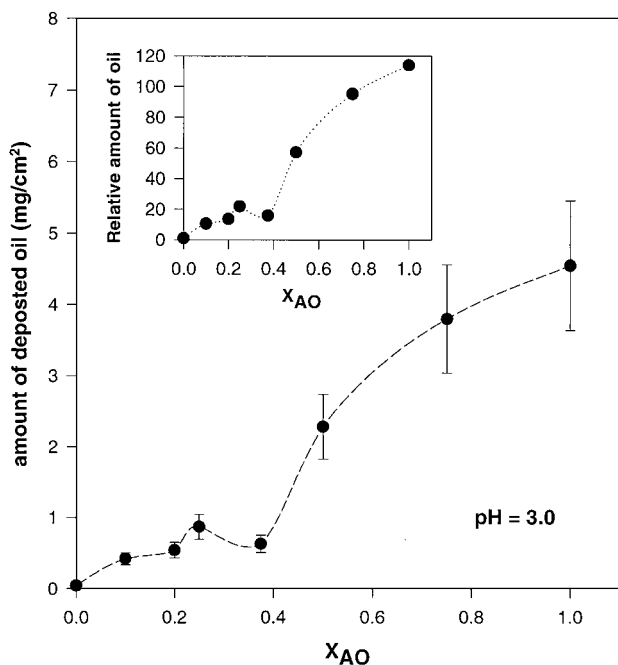


FIG. 9. The amount of deposited soybean oil plotted against the molar fraction of Aminoxide, X_{AO} . The experiments are carried out at pH 3.0 and total surfactant concentration $c_t = 1$ mM in the presence of 1 mM added NaCl. The inset shows the amount of deposited oil scaled by its value at $X_{AO} = 0$ (SDP3S only).

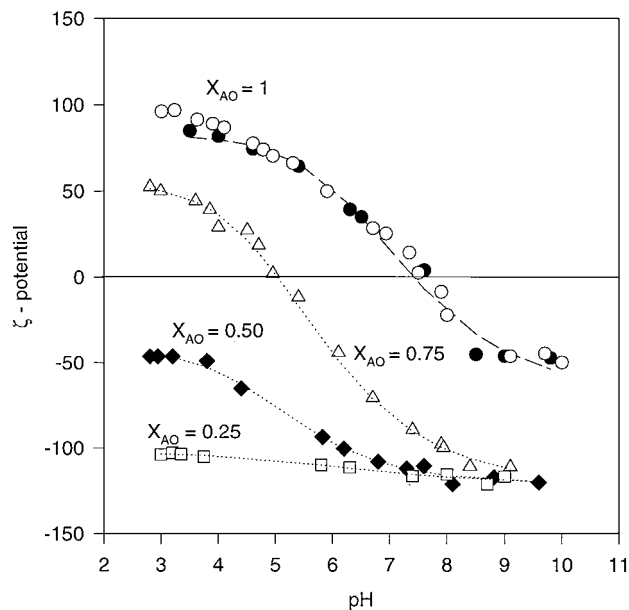


FIG. 10. Measured ζ -potential of soybean-oil drops vs pH of the aqueous phase, which contains 1 mM NaCl. Each curve corresponds to a given molar fraction, X_{AO} , of Aminoxide in its mixture with SDP3S at fixed total surfactant concentration, $c_t = 1$ mM.

hibit a similar behavior, but quantitatively the effect of the variation of X_{AO} is weaker: the difference between the two end points ($X_{AO} = 0$ and 1) is about 20 times.

Experimental results for the ζ -potential of soybean-oil drops in mixed AO–SDP3S solutions vs pH are plotted in Fig. 10. All samples contain 1 mM NaCl and surfactant mixture of total concentration $c_t = 1$ mM, as in the oil deposition experiments. Each curve corresponds to a fixed molar fraction of Aminoxide: $X_{AO} = 0.25, 0.50, 0.75$, and 1.00. The experimental points for $X_{AO} = 1.00$ are the same as in Fig. 4 and are given for comparison. The oil drops in the presence of SDP3S only (not shown in Fig. 10) are negatively charged in the whole studied pH range; their negative ζ -potential increases slightly in magnitude, from -110 mV at pH 3.0 to -125 mV at pH 9.5. Comparison of the different curves in Fig. 10 shows a strong influence of the added anionic surfactant (SDP3S) on the charge of the emulsion droplets. As could be expected, SDP3S makes the surface charge of the drop more negative (closer to that of the glass substrate), which is in qualitative agreement with the observed reduction of the oil-drop deposition in the presence of SDP3S; see Fig. 9. In particular, the anionic SDP3S is expected to make a complex with the amphoteric Aminoxide, especially in the adsorption layer (8). The positive values of the ζ -potential for the curves with $X_{AO} > 0.5$ (Fig. 10) are due to an excess of Aminoxide cations, which are not bound in complexes with the SDP3S.

Figure 11 presents the results for the amount of deposited oil from Fig. 9 plotted as a function of the corresponding values of the ζ -potential from Fig. 10 at pH 3. The ζ -potential increases with about 240 mV (from about -140 up to $+100$ mV) in the studied composition range, $0 \leq X_{AO} \leq 1$. Remarkably, the oil

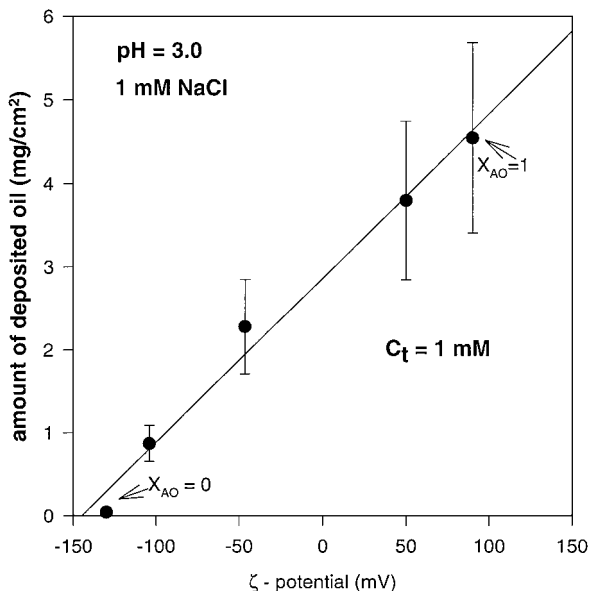


FIG. 11. Plot of the data from Fig. 9 for soybean-oil deposition on a glass substrate vs the data from Fig. 10 for the ζ -potential of oil drops independently measured for the same X_{AO} at pH 3.0.

deposition increases almost linearly with the increase of the ζ -potential. This indicates that the surface electric potential (the double-layer force) is one of the major factors governing the oil drop deposition on a glass substrate. However, for the time being we are not able to give a quantitative interpretation of the linear dependence in Fig. 11 since a hydrodynamic theory of the oil drop deposition is still missing; see the next section.

4. DISCUSSION: HYDRODYNAMIC FACTORS

The experimental results reported and discussed in the previous section show an important effect of the electrostatic (double-layer) interaction on the oil deposition. In particular, the oil deposition is much enhanced when the oil drops and the glass substrate are oppositely charged (the drops positive, the glass negative) and *attract* each other. On the other hand, if the two surfaces have electric charge of the same sign, the resulting electrostatic *repulsion* suppresses the oil drop deposition.

Our preliminary experiments (see Fig. 1a and Section 2.1) show that oil drops resting below a glass surface do not exhibit significant deposition on the glass plate. Hence, the combined action of buoyancy force and electrostatic surface force is not enough to cause deposition of the oil drops. Therefore, the effect of the receding meniscus, sketched in Fig. 1b, has a primary importance for the oil deposition our experiments. In other words, the real process of oil drop deposition is governed by an interplay of hydrodynamic and electrostatic effects.

In our experiments (and in many practical processes) the solid surface and the air–water meniscus are moving with respect to each other. If an oil drop is confined into the wedge between the receding meniscus and the solid wall, it will be pressed by the

meniscus against the wall and could undergo some deformation, as schematically depicted in Fig. 12a. The meniscus will push the drop downward. However, the *viscous* friction force, F_v , due to the dissipation of energy in the narrow gap of thickness h between the drop and the wall (Fig. 12a), will decelerate the motion of the drop. Note that our experiments are carried out at relatively high surfactant concentration, at which the oil–water interface is tangentially immobilized by the formed dense adsorption monolayer of surfactant; see, e.g., Refs. (12, 13). In such a case F_v can be estimated as the viscous friction force due to the shear flow in the gap between two plane-parallel solid plates (14),

$$F_v = A\eta u/h, \quad [4]$$

where A is the area of the plane-parallel plates, η is the viscosity of water, and u is the relative rate of motion of the two surfaces separated by a gap of width h . Equation [4] shows that if h is larger, say due to the presence of *long-range* electrostatic repulsion between the oil drop and the solid substrate, then F_v will be smaller and not be able to cause a significant deceleration of the oil drop. The latter will be then carried along with the receding meniscus without any deposition on the solid surface (Fig. 12a).

On the other hand, if the gap width h is small enough, which could be due to the presence of electrostatic *attraction* or *short-range repulsion* between the oil drop and the solid surface, then in view of Eq. [4] F_v could become sufficiently large to decelerate the motion of the drop, which will be then overtaken by the receding meniscus (Fig. 12b) and will be further entrapped in the residual aqueous wetting film. As already mentioned, irrespectively of whether the residual wetting film is stable or unstable, the entrapped drop will be firmly pressed against the solid substrate by capillary forces, and it will finally stick to the substrate after the drainage and/or evaporation of the water. In

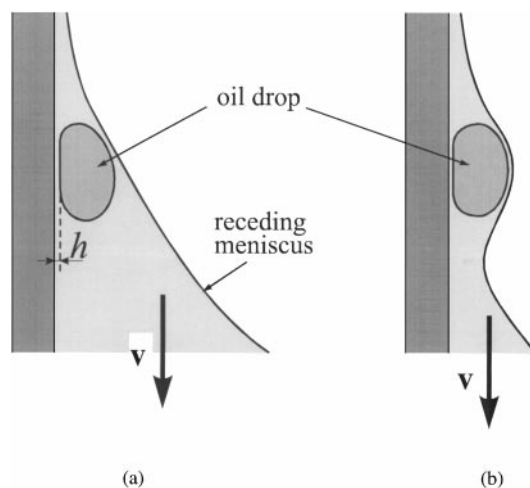


FIG. 12. Schematic representation of an oil drop (a) pressed against a vertical solid plate by a receding meniscus and (b) entrapped in the residual wetting film left after the meniscus; v is the velocity of the receding meniscus with respect to the solid plate; h is the thickness of the water film between the drop and plate.

the framework of this mechanism the increase of the deposited oil with the rise of NaCl concentration (Fig. 8) can be interpreted as a result of the decrease in the film thickness h by the added electrolyte.

The above qualitative explanation of the mechanism of oil drop deposition takes into account the action of both hydrodynamic and electrostatic factors. However, its development into a quantitative theoretical model is rather difficult. The difficulties in the hydrodynamic description could arise from (i) the complicated geometry of the system, (ii) the movable boundaries of the phases, including deformation of the oil drop and meniscus surfaces, and (iii) the possibility that the drop could be involved in both translational and rotational motions depending on the distance h and the drop deformation; see, e.g., Ref. (13). As a first step toward the development of a theoretical model, one could consider the simpler case, in which the droplets remain spherical (nondeformed) when overtaken by the receding meniscus. For such droplets it was recently established (15) that the critical value of h (critical thickness of film rupture) can be up to 100–200 nm for oil drops of micrometer size, if attractive interaction between the film surfaces is present. The latter finding may lead to a modification of the model of oil deposition. In any case, we believe that the dependence of the oil deposition on the rate of pulling of the plate should be investigated *experimentally* prior to the development of any hydrodynamic model. This can be a subject of a subsequent study.

When a wetting film is left after a receding meniscus, there is another dynamic factor which could facilitate the oil drop deposition, viz. the evaporation of water from the residual wetting film. In such a case, the evaporation-driven flux of water from the meniscus-zone toward the wetting film carries along the dispersed colloidal particles (the oil drops) toward the three-phase contact line, where their attachment to the substrate takes place. This effect has been used to form two-dimensional arrays from colloidal particles on both horizontal (16, 17) and vertical (18, 19) solid substrates. The velocity of the receding of the contact line in the latter experimental works, which is determined by the rate of water evaporation, is typically between 1 and 10 $\mu\text{m/s}$; this is much smaller than the velocity of plate pulling-up (630 $\mu\text{m/s}$) in the experiments reported here. For that reason we believe that in our present experiments the influence of evaporation is not significant for the capturing of the oil drops by the receding meniscus. On the other hand, the drops, already captured in the residual wetting film, could be separated from the glass substrate by an aqueous film; the evaporation of water will lead to thinning and eventual rupture of the latter film, which will bring about a firm attachment of the oil drops to the substrate.

5. CONCLUSIONS

Our observations show that the drops of an oil-in-water emulsion cannot be deposited on a glass plate by the buoyancy force; however, the drops of the same emulsion can be deposited when pressed against the substrate by a receding meniscus. We exam-

ined this effect experimentally by using an experimental setup which allows one to pull up a vertical glass plate out of an oil-in-water emulsion at a given controlled speed; see Fig. 2.

First of all we investigated the oil deposition from emulsions, stabilized by an amphoteric surfactant (AO), as a function of pH. The results show that the deposition rises with the decrease of pH (Fig. 3). By ζ -potential measurements, we established that the oil drops are positively charged at lower pH, whereas the glass bears a negative charge (Fig. 4). The enhanced oil deposition at low pH correlates with the domain in which the emulsion drops and the solid substrate bear opposite electric charges.

The oil deposition decreases with the rise of the concentration of the amphoteric surfactant AO (Fig. 5). The ζ -potential measurements with glass particles reveal that AO adsorbs not only on the oil drops but also on the glass surface, and it can invert the sign of its charge from negative to positive; see Figs. 6 and 7. Then the reduction of the oil deposition with the rise of the AO concentration can be attributed to a transition from attractive to repulsive interaction between the oil drops and the glass substrate. The addition of NaCl reduces the double-layer repulsion and enhances the oil drop deposition (Fig. 8).

We studied also the oil deposition from emulsions stabilized by a mixture of amphoteric and anionic surfactants (AO and SDP3S). The anionic surfactant brings negative surface charge to the oil droplets and suppresses the oil deposition; see Figs. 9–11. With the increase of the molar fraction of AO in the mixture, the ζ -potential is converted from negative to positive and the oil deposition grows almost linearly with the ζ -potential; see Fig. 11.

Our experimental results imply that the oil drop deposition by a receding meniscus is governed by an interplay of hydrodynamic and electrostatic factors. A possible qualitative explanation is the following. If the thickness h of the aqueous film (between the oil drop and the solid substrate) is large due to the presence of long-range electrostatic repulsion, then the friction force exerted on the drop is small and the drop will be dragged along by the receding meniscus; see Eq. [4] and Fig. 12a. On the other hand, if h is small enough due to the presence of electrostatic attraction or short-range repulsion, then the friction between drop and substrate could become sufficiently strong to decelerate the motion of the drop; the latter will then be overtaken by the receding meniscus (Fig. 12b) and will be entrapped in the residual aqueous wetting film left behind the receding meniscus.

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