Effect of Oily Additives on Foamability and Foam Stability.

2. Entry Barriers

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In the preceding paper of this series we studied the effect of several oils of different chemical structure on the foaming properties of sodium dodecylbenzenesulfonate solutions. A straightforward correlation was found between the foam stability and the so-called “entry barrier”, which prevents the emergence of pre-emulsified oil drops on the solution surface. In the present article we perform a systematic experimental study of the entry barriers for several oils by means of the recently developed film trapping technique. The latter consists of trapping oil drops in wetting films on a solid substrate, followed by a controlled increase of the capillary pressure of the meniscus that compresses the drops against the substrate. At a certain critical capillary pressure, \(P_{CCR}\), the asymmetric oil—water—air films rupture and the drops enter the water—air interface. This event is observed microscopically, and \(P_{CCR}\) is determined as a function of various parameters (type of oil, surfactant concentration, drop size, and others). The entry barrier increases with the surfactant concentration, especially in the range where the surfactant micelles are expected to stabilize the asymmetric films. The results obtained with a series of alkanes (from octane to hexadecane) show that the entry barrier increases with the alkane chain length. Furthermore, it is shown that the presence of a spread oil (even as an ultrathin, molecular layer) on the surface of the foam film might lead to a significant change of the magnitude of the entry barrier. For decane and dodecane, the layer of spread oil reduces the entry barrier, whereas for hexadecane the effect is the opposite. As far as we know, such a role of oil spreading in the antifoaming action of oils has not been reported so far. Since the stability of thin liquid films is usually discussed in the literature in terms of the disjoining pressure, we estimate from the experimental data the critical disjoining pressure, \(P_{CCR}\), at which the asymmetric oil—water—air film ruptures and the drop entry occurs. The estimates show that the curvature of the asymmetric film is very important in the overall consideration of the mechanical equilibrium in the system and there is a big difference between the numerical values of \(P_{CCR}\) and \(P_{CCR}\) unlike the case of planar films where \(P_{CCR} = P_{CCR}\). Additionally, we find that \(P_{CCR}\) is a weak function of the oil drop size and of the asymmetric film radius, while \(P_{CCR}\) scales as \((\text{film radius})^{-1}\) for all of the studied systems. These results are discussed with respect to the possible mechanisms of film rupture. Concerning the foam stability, \(P_{CCR}\) is a more convenient quantity for description of the entry barriers, because its magnitude correlates with the foam height, whereas the magnitude of \(P_{CCR}\) does not.

1. Introduction

In the first paper of this series we studied how several oils of different chemical structure affected the foam stability and the foamability of sodium dodecylbenzenesulfonate solutions. The results from the foam tests demonstrated a straightforward correlation between the foam stability and the entry barrier, which prevents the emergence of pre-emulsified oil drops on the solution surface. In the present article we perform a systematic experimental study of the entry barriers for several oils by means of the recently developed film trapping technique. The latter consists of trapping oil drops in wetting films on a solid substrate, followed by a controlled increase of the capillary pressure of the meniscus that compresses the drops against the substrate. At a certain critical capillary pressure, \(P_{CCR}\), the asymmetric oil—water—air films rupture and the drops enter the water—air interface. This event is observed microscopically, and \(P_{CCR}\) is determined as a function of various parameters (type of oil, surfactant concentration, drop size, and others). The entry barrier increases with the surfactant concentration, especially in the range where the surfactant micelles are expected to stabilize the asymmetric films. The results obtained with a series of alkanes (from octane to hexadecane) show that the entry barrier increases with the alkane chain length. Furthermore, it is shown that the presence of a spread oil (even as an ultrathin, molecular layer) on the surface of the foam film might lead to a significant change of the magnitude of the entry barrier. For decane and dodecane, the layer of spread oil reduces the entry barrier, whereas for hexadecane the effect is the opposite. As far as we know, such a role of oil spreading in the antifoaming action of oils has not been reported so far. Since the stability of thin liquid films is usually discussed in the literature in terms of the disjoining pressure, we estimate from the experimental data the critical disjoining pressure, \(P_{CCR}\), at which the asymmetric oil—water—air film ruptures and the drop entry occurs. The estimates show that the curvature of the asymmetric film is very important in the overall consideration of the mechanical equilibrium in the system and there is a big difference between the numerical values of \(P_{CCR}\) and \(P_{CCR}\) unlike the case of planar films where \(P_{CCR} = P_{CCR}\). Additionally, we find that \(P_{CCR}\) is a weak function of the oil drop size and of the asymmetric film radius, while \(P_{CCR}\) scales as \((\text{film radius})^{-1}\) for all of the studied systems. These results are discussed with respect to the possible mechanisms of film rupture. Concerning the foam stability, \(P_{CCR}\) is a more convenient quantity for description of the entry barriers, because its magnitude correlates with the foam height, whereas the magnitude of \(P_{CCR}\) does not.

Similar results were obtained recently with other surfactant—oil couples, and a quantitative relation between the final foam height and the entry barrier was established. The primary reason for this correlation is that any mechanism of foam destruction by emulsified oil should include the stage of formation and rupture of asymmetric oil—water—air films. As noticed long ago by Kruglyakov and Kulinkarni et al., these asym-

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2 Garrett, P. R. J. Colloid Interface Sci. 1980, 76, 587.
metric films might be stabilized by various surface forces (electrostatic, van der Waals, etc.), which suppress the drop entry and impede the antifoam action of oil. Furthermore, if the asymmetric film is stable, the introduction of oil into the foaming solution might lead to a foam-breaking effect (i.e., to more voluminous and stable foam) due to (i) reduced dynamic surface tension of the solutions, and (ii) decelerated water drainage, as a result of the Plateau border obstruction by oil drops. Hence the oil drop entry is a key stage in the overall process of foam destruction by oils.

Several different parameters have been suggested in the literature to quantify the entry barriers for oil drops. Lobo and Wasan suggested to use the energy of interaction per unit area in the asymmetric oil-water-air film, \( f \), as a criterion of its stability

\[
f = - \int_{h=\infty}^{h_0} \Pi_{AS} \, dh
\]

where \( \Pi_{AS}(h) \) is the disjoining pressure, while \( h_0 \) is the equilibrium thickness of the asymmetric film at a certain capillary pressure (which has to be specified). In a parallel study, Bergeron et al. suggested the so-called generalized entry coefficient

\[
E_g = - \int_0^{\Pi_{AS}(h_0)} h \, d\Pi_{AS}
\]

where the lower limit of the integral corresponds to \( \Pi_{AS}(h=\infty) = 0 \). As shown by Bergeron et al., the classical entry coefficient, \( E \), can be obtained as a particular case of \( E_g \) in the limit \( h_0 \to 0 \). One can deduce from eqs 1 and 2 that \( f \) and \( E_g \) are interrelated:

\[
f(h_0) + E_g(h_0) = -h_0 \Pi_{AS}(h_0).
\]

The determination of the values of \( f \) and \( E_g \), and their comparison with the antifoam efficiency of different oils is a difficult task, because one needs to know the disjoining pressure isotherms, \( \Pi_{AS}(h) \). The most thorough analysis of this type was carried out by Bergeron et al., who measured the disjoining pressure isotherms of planar foam and asymmetric oil-water-air films for several surfactant-oil couples. They found a good correlation between the stability of the asymmetric films and the stability of foams in porous media, in the presence of oil. Furthermore, Bergeron et al. showed that the destabilizing effect of oil is indeed caused by a lower stability of the asymmetric oil-water-air films as compared to the stability of the foam air-water-air film.

In the same study, another possible quantity as a measure of the asymmetric film stability was also discussed, namely, the critical capillary pressure leading to rupture of the asymmetric film. A similar idea had been used before to explain the collapse of foams in porous media in the absence of oil—as shown by Aronson et al., the measured value of the foam collapse pressure (which acts as to suck liquid from the foam) was close to the rupture pressure of a single foam film, as determined by the porous plate method. Indeed, the critical capillary pressure seems to be the most adequate measure of the film stability in such systems, because the capillary pressure is the actual external variable that compresses the film surfaces toward each other, against the repulsive surface forces (disjoining pressure) stabilizing the film.

The quoted authors studied planar films, where the imposed capillary pressure in equilibrium is exactly equal to the disjoining pressure; that is, the concept of the critical capillary pressure, \( P_{CR} \), is equivalent to the concept of the critical disjoining pressure, \( \Pi_{CR} \). Bergeron showed with foam films that, in some systems, the measured \( \Pi_{CR} \) corresponded to an actual maximum of the calculated DLVO-curve representing \( \Pi(h) \), whereas \( \Pi_{CR} \) was well below the maximum of the calculated \( \Pi(h) \) curves in other systems (for a possible explanation see Discussion in ref 22).

Recently, another experimental tool became available for quantifying the entry barriers of oil drops. Hadjiiski et al. developed the so-called film trapping technique (FTT), which consists of trapping oil drops in a wetting film, formed from surfactant solution on a solid substrate, and a subsequent measurement of the critical capillary pressure that leads to drop entry on the fluid surface of the wetting film (see below for details). It is worthwhile noting several important features of the FTT: First, the FTT allows an independent variation of the radius of the asymmetric oil-water-air film and of the applied capillary pressure in a relatively wide range. Therefore, the dependence of \( P_{CR} \) and \( \Pi_{AS} \) on the size of the asymmetric film can be investigated. The obtained results indicate a strong dependence of \( \Pi_{AS} \) on the size of the asymmetric films (see below), which means that the critical pressures for microscopic and macroscopic films might be very different. Second, experiments with real antifoam drops of micrometer size can be carried out, giving a quantitative measure of the entry barrier that can be used to explain the foam stability.

Third, the asymmetric films formed in both the FTT and the real foams are strongly curved (radius of curvature on the order of micrometers), which means that the imposed capillary pressure is not equal to the disjoining pressure that stabilizes the film. Hence an additional analysis is required to interpret the experimental data (measured in terms of \( P_{CR} \)) from the viewpoint of the surface forces stabilizing the asymmetric film (expressed by \( \Pi_{AS} \)).

This analysis gives also information about the shape of the trapped drops, which are typically strongly deformed under the compressing force created by the water-air-meniscus. Fourth, the method can be applied to different types of films (asymmetric oil-water-air, emulsion and foam films), so that a comparison of their stability for a given surfactant-oil system is possible. Last but not least, FTT requires relatively simple
and cheap equipment, and after accumulating some experience one can rapidly obtain a large set of data. These features make the method an interesting complement and/or alternative to the classical porous plate method, from both fundamental and practical viewpoints.

In the present article we make a systematic experimental study of the entry barriers for several oils of different chemical structure by means of the FTT. Along with the practical question about the comparison of the entry barriers and their importance for the foam stability, we address also several other issues. The results prove that the presence of a spread oil (even as an ultrathin, molecular layer) on the surface of the foam film might lead to a significant change of the entry barrier. The critical disjoining pressure, \( \Pi_{AS}^{\infty} \), is estimated from the experimental data, and the curvature of the asymmetric films is found to be very important for the overall consideration of the mechanical equilibrium. It is shown that \( \Pi_{AS}^{\infty} \) scales as (film radius) \(^{-1} \) for all of the studied systems—an observation that calls for explanation and that poses a number of interesting questions concerning the mechanism of film rupture. Let us note here that the major aim of the present work is to clarify some of the factors affecting the entry barrier, rather than to understand and explain the mechanism of film rupture. The latter task requires additional experimental and theoretical efforts.

2. Experimental Details

2.1. Materials. Sodium dodecylbenzenesulfonate, SDBS (product of Aldrich), is used as a main surfactant. The working solutions contain also 12 mM NaCl and 0.15 vol % of emulsified oil. The following oils are studied: n-octane, n-C\(_8\); n-decane, n-C\(_{10}\); n-dodecane, n-C\(_{12}\); n-hexadecane, n-C\(_{16}\); n-heptadecane, n-C\(_{17}\); n-octadecane, n-C\(_{18}\); 2-butyloctanol, 2BO; isohexyl-neopen- tanoate, IHP; silicone oil SH200 of dynamic viscosity 5 mPa s. SO. The n-alkanes are products of Sigma Co. Details about the other chemicals are given in ref 1. Hexadecane is refined by passing it through a glass column filled with chromatographic adsorbent (Florisil). The other chemicals are used as received. The solutions are prepared with deionized water from Milli-Q Organex system (Millipore). The oily additives are emulsified in the surfactant solutions by intensivestirring on a magnetic stirrer for 12 h.

2.2. Methods and Procedures. 2.2.1. Film Trapping Technique (FTT). The critical capillary pressure leading to rupture of the asymmetric air–water–oil film and to subsequent oil drop entry is measured by the FTT \(^{24,25} \) (Figure 1). A vertical glass capillary, a few millimeters in radius, is positioned at a small distance above the flat bottom of a glass vessel. The lower end of the capillary is immersed in the working solution, which contains dispersed emulsion drops. The capillary is connected to a pressure control system, which allows one to vary and to measure the difference, \( \Delta P_A \), between the air pressure in the capillary, \( P_A \), and the ambient atmospheric pressure, \( P_0 \). The data acquisition equipment includes a pressure transducer (Omega Engineering, Inc., Stamford, U.S.A.) and a digital multimeter Metex M-4660A (Metex Instruments) connected to a PC. The specifications of the used pressure sensors are presented in Table 1.

When \( P_A \) increases, the air–water meniscus in the capillary is pushed against the glass substrate and a wetting film is formed, which traps some of the oil drops (Figure 1B). These drops remain sandwiched between the air–water meniscus and the glass substrate. The capillary pressure of the air–water meniscus around the trapped drops is \( P_C = P_A - P_W \), where \( P_W \) is the pressure in the liquid around the drops, which can be determined from the liquid level in the external part of the vessel (outside the capillary). The height of water there is \( Z + Z_c \), where \( Z \) is the distance between the flat air–water interface and the lower capillary end, whereas \( Z_c \) is the distance between the substrate and the capillary end (Figure 1B). Thus the pressure at the bottom of the liquid is \( P_C = P_A - \rho_W g (Z + Z_c) \), where \( \rho_W \) is the water mass density and \( g \) is the acceleration of gravity. If one neglects the

\[
P_C = \Delta P_A - \rho_W g Z
\]

The depth of the liquid, \( Z \), is measured during the submergence of the capillary in the solution (before starting the actual experiments) by a micrometer translator having an accuracy of \( \pm 5 \mu m \), which corresponds to precision of \( \pm 0.05 \) Pa in the determination of the hydrostatic pressure (the last term in eq 3).

\[
\text{Pressure Control and Measuring Systems}
\]

\[
\text{Microscope Objective}
\]

Figure 1. Scheme of the experimental setup and the basic principle of operation of the film trapping technique (FTT). (A) A vertical capillary, partially immersed in surfactant solution containing oil drops, is held close above the bottom of the experimental vessel. (B) The air pressure inside the capillary, \( P_A \), is increased, and the water–air meniscus in the capillary is pressed against the glass substrate. Some of the oil drops remain trapped in the wetting glass–water–air film and are compressed by the meniscus. At a given critical capillary pressure (see section 2.2 for details) the asymmetric film formed between the oil drop and the solution surface ruptures and a drop entry event is observed by an optical microscope. (C) Another modification called “gentle FTT” is used for measuring very low entry barriers (below 20 Pa); a flat meniscus is formed, which allows the trapping of drops at virtually zero capillary pressure.

<table>
<thead>
<tr>
<th>Model and Main Characteristics of the Used Pressure Sensors</th>
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<td>pressure transducer model *</td>
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<tr>
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<tr>
<td>PX274-01DI</td>
</tr>
<tr>
<td>PX163-005BDSV</td>
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<tr>
<td>PX142-001D5V</td>
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* Omega Engineering, Inc., Stamford, U.S.A.
During the experiment, one increases the pressure in the capillary, $P_0$, by very small increments. After each step of pressure increase, one waits for liquid drainage from the wetting film region and for reaching a mechanical equilibrium. The changes of the meniscus shape around the trapped drops (caused by the liquid drainage) are observed by optical microscopy in reflected monochromatic light of wavelength $\lambda \approx 546 \text{ nm}$; a characteristic interfacial meniscus shape can be seen, which reflects the dynamic processes occurring in the wetting film region. The equatorial diameter of the trapped drops, $2R_0$, is measured microscopically (in white transmitted light) with an accuracy of $\pm 0.8 \mu \text{m}$. A Carl Zeiss Jena inverted microscope, equipped with objective LD Epiplan, 20/0.40, digital CCD camera (Kappa CF 8/1 DX), and VCR (Panasonic NV--HD 680), is used for these observations.

2.2.1. Critical Micelle Concentration (cmc) of SDDBS. The cmc obtained from the surface tension isotherm, around the cmc, which is an indication that the main surfactant is not contaminated by surface active impurities. The cmc obtained from the surface tension isotherm of the SDDBS in the presence of 12 mM NaCl shows no minimum (cmc) of SDDBS.

The experiments, in which the effect of the spread layer is to be studied with water-soluble and volatile oils (octane, decane, 2B0, IHPN), are difficult and require a more complex procedure. When the oil drops are trapped in a wetting film, whose surface is cleaned from oil by the TTP, a significant oil evaporation through the asymmetric oil--water--air film occurs (evidenced by the rapid decrease of the drop size), because the air in the capillary is not saturated with oil vapor. The evaporation of the oil drops is certainly not caused by solubilization in the surfactant micelles, because the surfactant solutions are pre-equilibrated with oil and because no drop size reduction is observed before trapping the drops in the wetting film. Since the process of oil evaporation is very fast, the trapped oil drops disappear (evaporate) before the capillary pressure in the FTT equipment is increased up to the critical values, corresponding to drop entry. Hence it is impossible to measure the entry barrier with clean solution surface for these oils, because the air phase should be almost saturated with oil vapors to reduce the rate of oil evaporation, which inevitably leads to the formation of a spread oil layer. That is why, we employed another procedure to study the effect of the spread layer on the entry barrier for the volatile oils. First, we measure the entry barrier for a solution saturated with oil, so that no drop evaporation takes place. In a separate experiment, which starts with saturated solution surface, we increase the capillary pressure up to a value just below the critical one. Afterward, maintaining the capillary pressure constant, we connect the air in the capillary with a much bigger volume of air (“buffer” of the same mechanical pressure), which is free from oil. As a result, the oil vapors diffuse into the buffer and the air in the capillary becomes undersaturated with oil. Thus an evaporation from the spread layer is induced, which is evidenced by the observed shrinking of the oil drops. In this moment, the capillary pressure is increased further, and a comparison of the entry barrier under these conditions (nonsaturated, evaporating oil layer) with the barrier in the presence of saturated oil layer becomes possible.

All experiments are carried out at the ambient room temperature ($T = 25 \pm 2^\circ \text{C}$). The experiments are performed at 27 °C, to be well above its melting point (24 °C). The water evaporation inside the capillary is avoided, because the atmosphere above the wetting film is kept always saturated with aqueous vapors.

### 2.2.2. Drop Entry Measurements in the Presence of Spread Oil Layer

One series of experiments is directed to reveal the effect of the oil layer, spread over the water--air interface, on the height of the drop entry barrier. For this purpose parallel experiments in the presence and in the absence of spread oil are performed.

Fluids that are not very much soluble in the surfactant solution, like dodecane and hexadecane, a clean surface (free of spread oil) is created by pouring the studied emulsions into the surface of the wetting film at a given, critical capillary pressure, $P_{0,C}$. The moment of drop entry, which is accompanied with a significant local change in the shape of the air--water interface, is clearly seen in both reflected and transmitted light. Therefore, the equipment allows one to measure $P_{0,C}$ as a function of the solution composition and drop radius. As mentioned above, for brevity we refer to $P_{0,C}$ as the barrier to drop entry. Larger $P_{0,C}$ corresponds to higher barriers (more difficult drop entry) and vice versa.

The experimental setup described above allows one to measure the entry barriers higher than ca. 20 Pa. This limit is determined by the capillary pressure of the meniscus formed in the capillary before trapping the drops. Since the liquid wets the inner surface of the capillary, a spherical meniscus is formed of capillary pressure $P_c \approx 20 \text{ mN/m}$, which is the surface tension of the solution and $R_{C} \approx 3 \text{ mm}$ is the capillary radius. Therefore, the equipment allows one to measure $P_{0,C}$ up to a value just below the critical one. Afterward, maintaining the capillary pressure constant, we connect the air in the capillary with a much bigger volume of air (“buffer” of the same mechanical pressure), which is free from oil. As a result, the oil vapors diffuse into the buffer and the air in the capillary becomes undersaturated with oil. Thus an evaporation from the spread layer is induced, which is evidenced by the observed shrinking of the oil drops. In this moment, the capillary pressure is increased further, and a comparison of the entry barrier under these conditions (nonsaturated, evaporating oil layer) with the barrier in the presence of saturated oil layer becomes possible.

### 3. Experimental Results and Discussion

#### 3.1. Effect of SDDBS Concentration on the Drop Entry Barrier

3.1.1. Critical Micelle Concentration (cmc) of SDDBS. The surface tension isotherm of the surfactant solution is measured by the Wilhelmy plate method, whereas the surface tension of the oil is measured by DuNoüy ring technique on Kruss K10T digital tensiometer. The value $0.15 \pm 0.05 \text{ mN/m}$ measured with aqueous sodium dodecyl benzene sulfonate (SDDBS) solution at $T = 25 \pm 2^\circ \text{C}$, is in a reasonable agreement with the value $0.1 \pm 0.05 \text{ mN/m}$ measured at $T = 25 \pm 1^\circ \text{C}$ by other authors.

The cme obtained from the surface tension isotherm, $0.25 \pm 0.1 \text{ mN/m}$, is in a reasonable agreement with the value $0.25 \pm 0.1 \text{ mN/m}$ measured by electrical conductivity (conductivity meter model 30, Denver Instrument Co., Arvada, CO). In the following discussions we use the measured value, $c_{\text{mc}} = 0.2 \text{ mN/m}$.

3.1.2. Dependence of $P_{0,C}$ on the Surfactant Concentration. This series of experiments is performed with drops of hexadecane, and the obtained results are shown in Figure 2. The working emulsion is poured in the experimental vessel by using the TTP to avoid the presence of the experimentally determined value of the surfactant concentration.
of oil on the solution surface. The surfactant concentration, C_s, is varied between 0.16 and 12.8 mM (from 0.8 to 64 times cmc), while the salt concentration is fixed at 12 mM NaCl. To eliminate a possible effect of the drop size on the entry barrier, the average values obtained with drops of equatorial diameter, 2R_e, confined between 5 and 6 μm are plotted in Figure 2. At least three independent experimental runs are carried out at a given value of C_s, with two to three entry events observed in each run. The reproducibility of the data is very good, typically ±5%.

The results shown in Figure 2 indicate a complex dependence of P_CR on the surfactant concentration: At concentrations below 0.16 mM (0.8 × cmc), the entry barrier is too low to be measured by the usual experimental procedure. The main problem is that one observes numerous lenses of hexadecane covering the solution surface even after the TTP is used for loading the experimental cell. Therefore, one may expect that the surfactant adsorption and the entry barrier increase above the cmc for ionic surfactants.

3.2. Drop Entry Barriers for Different Oils. All experiments described in sections 3.2 and 3.3 are performed with spread oil layer on the solution surface. The fraction of the SDDBS micelles, Φ, including the contribution of the counterion atmosphere, is about 6% at the kink point (9 mM):

\[
\Phi = \frac{4}{3} \pi R_e^3 \rho_M
\]

\[
R_e = \left( \frac{d_M}{2} + \kappa^{-1} \right)
\]

ρ_M is the number concentration of micelles, κ⁻¹ = 2.6 nm is the Debye screening length, and d_M is the actual diameter of the micelles (aggregation number n_M = 50 and d_M = 5 nm were adopted for this estimate). From the values of ρ_M and Φ, one can estimate the height of the last maximum (corresponding to one layer of micelles trapped in the film) in the oscillatory component of the disjoining pressure, by using the formulas from ref 30. The estimate shows that this maximum is about 73 Pa, which is not far away from the measured values of P_CR ≈ 160 Pa (note that the electrostatic and van der Waals forces also contribute to the height of this maximum in the real film).

More difficult for explanation is the increase of P_CR in the intermediate concentration range, between 2.5 and 45 × cmc, because the micelles are not expected to play a significant role there. Most probably, the increase of P_CR is due to a gradual increase of the density of the surfactant adsorption layers on the oil—water and air—water interfaces. Indeed, the ionic strength of the ionic surfactant solutions increases above the cmc, due to the counterions dissociated from the micelles.30,31 On the other side, the adsorption layers are denser at higher ionic strength, because the electrostatic repulsion between the ionized surfactant molecules is screened.36 As a result, one may expect that the surfactant adsorption and the entry barrier increase above the cmc for ionic surfactants.

The solid squares represent the experimental data for 26 drops of similar size, while the error bars show the standard deviation. Two curves are shown in Figure 3: The solid squares present the experimental data for 26 drops (5.0 ± 2.8 μm mean diameter) in the presence of a thin spread layer of oil on the solution surface. The empty squares present the experimental data for 27 drops (7.6 ± 2.8 μm mean diameter) in the absence of a spread oil—air emulsions are poured by the TTP in these experiments. The barrier measured in the experiments with the spread oil layer is 48 ± 5 Pa, which is two times lower than the barrier for the surface free of oil (96 ± 5 Pa). Such a systematic change of the entry barrier in the presence of spread oil is detected with other systems as well and will be discussed in more detail in the next section. All experiments discussed hereafter in this section are performed with spread oil layer on the solution surface.

rather high with saturated surface reveal that the entry barrier is measured with silicone oil (P$_{CCR}$). The experiments with drops of alkane: for octane P$\_CCR$ = 30 ± 2 Pa, for decane P$\_CCR$ = 35 ± 5 Pa, for dodecane P$\_CCR$ = 48 ± 5 Pa, and for hexadecane P$\_CCR$ = 400 ± 10 Pa. The latter value is much higher than the value reported in the previous section, P$\_CCR$ = 80 ± 5 Pa, in the absence of a spread hexadecane layer (for discussion see section 3.3). Such a significant increase of the entry barrier with the alkane chain length is certainly important for the antifoam action of these oils, and systematic foam tests are planned soon to check quantitatively this relation. The mean entry barrier for IHNP drops (Figure 4) is P$\_CCR$ = 75 ± 7 Pa, obtained as an average from 195 drops of diameter 6.6 ± 3.2 μm. For 2BO the barrier P$\_CCR$ = 44 ± 2 Pa (in this case 8 drops of diameter 6.4 ± 3.7 μm are observed). The experiments with drops of n-dodecanol with saturated surface reveal that the entry barrier is rather high—above 1500 Pa. Similarly, a very high entry barrier is measured with silicone oil (P$\_CCR$ > 3 000 Pa). Note that these values correlate rather well with the results from the foam stability tests reported in ref 1.

The mean values of the drop entry barrier, P$\_CCR$, measured for the different oils are summarized in Table 2. The results demonstrate that the entry barrier for n-alkane drops increases with the molecular mass of the alkane: for octane P$\_CCR$ = 30 ± 2 Pa, for decane P$\_CCR$ = 35 ± 5 Pa, for dodecane P$\_CCR$ = 48 ± 5 Pa, and for hexadecane P$\_CCR$ = 400 ± 10 Pa. The latter value is much higher than the value reported in the previous section, P$\_CCR$ = 80 ± 5 Pa, in the absence of a spread hexadecane layer (for discussion see section 3.3). Such a significant increase of the entry barrier with the alkane chain length is certainly important for the antifoam action of these oils, and systematic foam tests are planned soon to check quantitatively this relation. The mean entry barrier for IHNP drops (Figure 4) is P$\_CCR$ = 75 ± 7 Pa, obtained as an average from 195 drops of diameter 6.6 ± 3.2 μm. For 2BO the barrier P$\_CCR$ = 44 ± 2 Pa (in this case 8 drops of diameter 6.4 ± 3.7 μm are observed). The experiments with drops of n-dodecanol with saturated surface reveal that the entry barrier is rather high—above 1500 Pa. Similarly, a very high entry barrier is measured with silicone oil (P$\_CCR$ > 3 000 Pa). Note that these values correlate rather well with the results from the foam stability tests reported in ref 1.

The question about the actual reasons for the different entry barriers of the studied oils is very important, but the information available so far is rather insufficient to answer it. That is why we restrict our comment only to the list (probably nonexhaustive) of different factors that could affect significantly the entry barriers: (1) the density and the other properties of the surfactant and/or of spread oil layers at the water–air interface;6 (2) the formation of mixed oil–surfactant and/or of spread oil layers at the water–air film;7–9 (3) change of the micellar aggregation number due to oil solubilization;37 (4) change in the micelle–micelle and micelle–surface interactions in the presence of solubilized oil.38 All of these factors are rather specific for the different oils, and further systematic studies are needed to reveal their importance for the studied phenomenon.

3.3. Effect of the Spread Oil Layer on the Entry Barrier. As mentioned in section 3.2, the experiments with dodecanol demonstrate a significant effect of the spread oil layer on the entry barrier of the drops—it is two times lower in the presence of spread dodecanol. A similar effect of the spread oil was measured also for decane; the


barrier obtained in the presence of spread layer was 35 ± 5 Pa, whereas the capillary pressure can be increased up to 70 Pa without drop entry to take place for a solution surface that is free of oil (the trapped drops evaporated without entry, as explained in section 2.2.2). Therefore the barrier for decane with a clean surface is at least two times higher than the barrier for the surface covered by a spread layer. On the contrary, the formation of a mixed adsorption layer SDBS–hexadecane led to about a five times higher barrier (section 3.2) as compared to the barrier measured with solution surface free of hexadecane (section 3.1). Therefore, the presence of oils on the solution surface might significantly affect the magnitude of the entry barriers. It is rather possible that the high entry barrier observed with n-C_{12}OH is similar to the formation of a dense mixed adsorption layer on the solution surface.\(^{(39,40)}\)

The observed increase of the entry barrier with the molecular mass of the alkanes (from octane to hexadecane) might be also related to the structure of the formed spread or mixed layers on the solution surface. As shown by Aveyard, Binks and co-workers,\(^{(27-29)}\) mixed adsorption layers are formed typically by long-chain alkanes (C\(_{12}\)), which do not spread in the form of a monomolecular layer on the surface. On the contrary, the short-chain alkanes often either form a thin monomolecular layer or spread as a thick (duplex) film. It is worthwhile noting that the interaction of an oil drop with a solution surface covered by a thick oil layer would resemble the interaction of the drop with its own homophase (i.e., an oil–water–oil film of emulsion type will be formed), but a systematic comparison of the stability of the asymmetric oil–water–air and the emulsion oil–water–oil films is still missing.

Let us note at the end of this section that the observed change of the entry barrier in the presence of spread oil has an important implication for the antifoaming action of the oils. However, as discussed in refs 1, 3, 5, 6, 41, and many others, different factors are often more important and no straightforward correlation between the spreading behavior and the antifoam activity is observed.

### 4. Dependence of the Critical Disjoining Pressure for Film Rupture on the Film Size

The results presented in Figures 3 and 4 show that the critical capillary pressure, \(P_{cr}^{cr}\), is a very weak function of the size of the asymmetrical oil–water–air film. Additional analysis is needed, however, to understand how the critical disjoining pressure, \(\Pi_{AS}^{cr}\), depends on the film size. In this section we investigate this dependence and discuss it from the viewpoint of the mechanism of rupture of the thin asymmetric films.

#### 4.1. Estimation of the Critical Disjoining Pressure for Curved Asymmetric Films

**4.1.1. Disjoining Pressure for Spherical Films**

The disjoining pressure, \(\Pi_{AS}\), accounts for the interactions between the two film surfaces (van der Waals, electrostatic, steric, etc.) and is conventionally defined as the surface force per unit area (a more general and rigorous definition was given through the components of the pressure tensor).\(^{(42,43)}\) Positive disjoining pressure corresponds to a repulsive surface force (i.e., to film stabilization) and vice versa. In the case of planar films, the condition for mechanical equilibrium requires that the capillary sucking pressure must be exactly counterbalanced by the disjoining pressure.\(^{(42-45)}\) However, the thin films in our experiments are curved and the condition for mechanical equilibrium is more complex, because it includes the capillary pressure jumps across the curved film surfaces. The relevant theoretical approach to this configuration was developed by Ivanov and Kralchevsky,\(^{(24,26,44)}\) who showed that the disjoining pressure is related to the capillary pressure across the water–air interface, \(P_c = P_A - P_W\), by the expression

\[
\Pi_{AS} = P_F - P_W = (P_F - P_A) + (P_A - P_W) = \frac{2\sigma_{AW}}{R_f} + P_c \quad (5)
\]

where \(P_F\) is the pressure in the asymmetric oil–water–air film and \(R_f\) is its radius of curvature (Figures 5 and 6). The aqueous phase, from which the asymmetric film is formed, is chosen as a referent phase for the definition of the disjoining pressure as usual.\(^{(26,44)}\)

For micrometer-sized drops, \(R_f\) is on the order of the drop size and \(2\sigma_{AW}/R_F > 10^5\) Pa. In most of our systems \(P_c \approx 10^2\) Pa and can be neglected in eq 5. Thus only the radius of film curvature, \(R_f\), would be sufficient to calculate \(\Pi_{AS}\), because \(\sigma_{AW}\) is a known quantity (the slight change

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\(^{(41)}\) Garrett, P. R.; Davis, J.; Rendall, H. M. Colloids Surf., A 1994, 85, 159.


of the surface tension of the film due to the surface forces is neglected in eq 5, because it is a higher order effect). Note, however, that \( R_F \) depends on the drop deformation, which in turn is determined by the applied capillary pressure, \( P_C \). For large drops or bubbles, one can measure directly the radius of film curvature, \( R_F \), by using the microscopic method of differential interferometry,\(^{46}\) but this method cannot be used for small, micrometer sized drops. That is why we apply below an indirect method to estimate the magnitude of \( \Pi_{AS} \) from the accessible experimental data and to study how the critical disjoining pressure for drop entry, \( \Pi_{AS}^{cr} \), depends on the size of the asymmetric film.

**4.1.2. Main Assumption.** From the experiment we know the capillary pressure \( P_C \), the equatorial drop radius \( R_S \), and the interfacial tensions, \( \sigma_{AW} \) and \( \sigma_{OW} \). To make the problem tractable and to estimate \( \Pi_{AS} \), we make the assumption that the contact angles between the films and the adjacent menisci (see Figure 5) are known and have some small (fictitious) values: \( \psi_S \), angle of the oil—water—glass film; \( \psi_S \), angle of the wetting glass—water—air film; \( \alpha \), angle of the curved asymmetric film. Since these angles are of the type liquid film—meniscus, they are typically below \( 5^\circ \). The numerical calculations revealed that the estimated disjoining pressure, \( \Pi_{AS} \), is virtually insensitive to the chosen values of the contact angles in the range 0—5°. Therefore, for clarifying the effect of the film size on the value of \( \Pi_{AS}^{cr} \), one may choose any value between 0 and 5° for these angles. Once the angles are chosen, one can calculate \( \Pi_{AS} \) from the experimental data as explained below. In most computations, we will use for simplicity \( \psi_S = \psi_S = \alpha = 0 \). The influence of this assumption on the calculated values of \( \Pi_{AS} \) is checked a posteriori (see below).

**4.1.3. Derivation of the Basic Equations.** The shapes of the water—air and oil—water interfaces are described by solutions of the Laplace equation of capillarity, which can be presented in the following form for axially symmetrical system:\(^{47,48}\)

\[
\frac{1}{r} \frac{d}{dr} \left( r \sin \phi \right) = 2 k_i, \quad k_i = \frac{P_C}{2 \sigma_i} \tag{6}
\]

\[
\frac{dz}{dr} = \pm \tan \phi = \pm \frac{\sin \phi_i}{1 - \sin^2 \phi_i}^{1/2} \tag{7}
\]

Here \( \phi \) is the running slope angle of the interface and \( P_C \) is the capillary pressure. The index \( i \) denotes the following interfaces: \( i = 1 \) for the oil—water interface, \( P_{C1} = \sigma_{oil} - \sigma_{ow} \); \( i = 2 \) for the air—water interface, \( P_{C2} = \sigma_{oc} = \sigma_{ow} \).

Let us consider the shape of the drop interface described by eqs 6 and 7 for \( i = 1 \). The integration of eq 6 from the equatorial radius \( R_E \) to a given value of the running coordinate \( r \) leads to

\[
\sin \phi_1(r) = \frac{1}{r} \left[ k_1 (r^2 - R_E^2) + R_E \right] \tag{8}
\]

Substituting \( \phi_1(R_S) = \psi_S \) in eq 8, one derives an expression for the contact radius, \( R_S \), of the drop with the substrate

\[
R_S = \frac{\sin \psi_S + (\sin^2 \psi_S - 4k_1 R_E (1 - k_1 R_E))^{1/2}}{2k_1} \tag{9}
\]

\[k_1 R_E > 1 \]

Similarly, one can express the angle \( \psi_C \), which is complementary to the slope angle of the drop generatrix at the contact line of the asymmetric film, \( \phi_i(R_C) \)

\[
\psi_C = \pi - \phi_2(R_C) = \arcsin \frac{k_1}{R_C} (R_C^2 - R_E^2) + R_E \frac{R_E}{R_C} \tag{10}
\]

The angles \( \psi_C \) and \( \theta_C \) (Figure 5) can be expressed through \( \psi_C \) in the following way

\[
\psi_C = \psi_C - \alpha \tag{11}
\]

\[
\theta_C = \arctan \left( \frac{\alpha_{AW} \sin \psi_C + \sigma_{OW} \sin \psi_C}{\sigma_{AW} \cos \psi_C + \sigma_{OW} \cos \psi_C} \right) \tag{12}
\]

The last equation is a corollary of the horizontal and vertical balances of the interfacial tensions acting on the contact line\(^{46,49} \) of the asymmetric film, with neglected effect of the line tension\(^{50} \)

\[
\sigma_{AW} \cos \psi_C + \sigma_{OW} \cos \psi_C = \gamma \cos \theta_C \tag{13}
\]

\[
\sigma_{AW} \sin \psi_C + \sigma_{OW} \sin \psi_C = \gamma \sin \theta_C
\]

Here \( \gamma \) is the membrane tension\(^{26} \) of the asymmetric film. From the geometric relation

\[
R_F = R_C \sin \theta_C \tag{13}
\]

one obtains the radius of the film curvature, \( R_F \). Therefore, if one knows the capillary pressure at the oil—water interface, \( P_{C1} \), and the contact radius, \( R_C \), which are still unknown at that stage, the disjoining pressure, \( \Pi_{AS} \), can be calculated by means of eqs 5, 12, and 13.

An equation for calculating \( R_C \) can be derived from the balance of the vertically resolved forces acting on the trapped drop (the horizontal force balance is trivial, because the system is axially symmetric). Since the drop size is very small, one can neglect the variations of the hydrostatic pressure around the drop surface and assume that \( P_W \) is constant. Therefore, \( P_W \) does not contribute to the vertical force balance. The drop contacts with the substrate through the oil—water—glass film and with the air phase through the asymmetric oil—water—air film (see Figure 6). The condition for mechanical equilibrium in these two thin films implies that the respective disjoining pressures, arising from the interaction between the film surfaces, are exerted on the surface of the drop. Therefore, the vertical force balance includes the contributions of the disjoining pressures acting in the oil—water—air film, \( \Pi_{AS} \), and in the film formed between the drop and the substrate, \( \Pi_{ES} \) (multiplied by the respective projected film areas). Since the aqueous film between the drop and the substrate is planar, \( \Pi_{ES} \) must be equal to the capillary pressure \( P_{C1} \).

Along with the contribution of the disjoining pressures, the force balance includes the contributions of the linear


forces acting on the contact lines of the films, due to so-called "transversal line tensions". The vertical projection of the force created by the transversal tension at the contact line of the oil—water—air film is $2\pi R_C \cos \theta_C$, where $r_C$ is the corresponding transversal tension

$$\tau_C = \sigma_{OW} \sin(\psi_C - \theta_C)$$

The linear excess force acting on the contact line of the film with the glass substrate is $2\pi R_S$, where $r_S$ is

$$\tau_S = \sigma_{OW} \sin \psi_S$$

Thus one obtains the following balance of forces acting on the drop surface

$$\pi R_C^2 \Pi_{AS} - 2\pi R_C \sigma_{OW} \cos \theta_C \sin(\psi_C - \theta_C) = \pi R_S^2 \Pi_{C1} - 2\pi R_S \sigma_{OW} \sin \psi_S$$

The left-hand side of eq 14 presents the force acting in the region of the asymmetric oil—water—air film: the first term accounts for the disjoining pressure in the film, while the second term accounts for the transversal tension acting on the contact line. The right-hand side of eq 14 presents the corresponding terms for the film intervening between the drop and the substrate.

Finally, we should define a procedure for determination of the capillary pressure at the oil—water interface, $P_{C1}$. The procedure is based on the necessary geometrical condition for matching the generatrix of the air—water meniscus with the drop surface and with the substrate at the specified contact angles, $\psi_C$ and $\psi_S$. The shape of the water—air meniscus can be obtained by integration of eqs 6 and 7 (i = 2, $P_C$ is known from the experiment) with boundary conditions at the contact line of the asymmetric film

$$\phi_2(r) = -\psi_C, \quad r = R_C, \quad z = Z_C$$

This meniscus has to intersect the plane of the substrate at the following angle

$$\phi_2(r) = -\psi_S, \quad r = R_S, \quad z = -Z_S$$

Explicit expressions for $z_C = z(R_C)$ and $z_S = z(R_S)$ can be found from the solutions of the Laplace equation of capillarity (eq 6 and 7) for the drop surface (i = 1)

$$z(r) = \pm \left[ R_E - \frac{1}{k_1} \right] F(\Lambda, q) - R_E E(\Lambda, q)$$

$$R_1 \leq r \leq R_E, \quad k_1 R_E > 1$$

where $R_1$, $q$, and $\Lambda(r)$ are defined as

$$R_1 = \left| \frac{1 - k_1 R_E}{k_1} \right|$$

$$q = \left( 1 - \frac{R_1^{21/2}}{R_E^{2}} \right)^{1/2}$$

$$\sin \Lambda = q^{-1} \left( 1 - \frac{r^2}{R_E^2} \right)^{1/2}$$

Note that $k_1$ depends on $P_{C1}$ (eq 6), which allows one to use eqs 15—17 for determination of $P_{C1}$ (see the following subsection).

**4.1.4. Numerical Iterative Procedure for Calculation of $\Pi_{AS}$**

On the basis of the above analysis, one can calculate the disjoining pressure of the asymmetric film, $\Pi_{AS}$, by means of an iterative procedure whose block scheme is shown in Figure 7. One starts with an initial guess for the two independent unknowns—the capillary pressure of the drop, $P_{C1}$, and the contact radius of the asymmetric film, $R_C$ (see Figure 5). From eq 9 one calculates a value for the contact radius drop substrate, $R_S$. Then, from eqs 10—12 one calculates the angles $\psi_C$, $\psi_S$, and $\theta_C$ and by eqs 13 and 5, the radius of film curvature, $R_F$, and the disjoining pressure, $\Pi_{AS}$, respectively. One

$$F(\Lambda, q) = \int_{0}^{\Lambda} \frac{d\xi}{(1 - q^2 \sin^2 \xi)^{1/2}}$$

$$E(\Lambda, q) = \int_{0}^{\Lambda} (1 - q^2 \sin^2 \xi)^{1/2} d\xi$$

Figure 8. Dependence of the critical disjoining pressure, \( \Pi_{AS}^{CR} \), on the inverse radius of the asymmetric film, \( R_{EFF}^{-1} = (a R_{F})^{-1/2} \). \( R_{F} \) is the actual area of the asymmetric film, and \( a R_{F} \) is the area of the film corresponding to the arc AA' in Figure 5. The calculations are made for 3.2 mM SDDBS, 12 mM NaCl, and hexadecane drops (clean water – air surface). The solid line represents the calculations with \( \alpha = \theta_S = 0^\circ \), whereas the dashed line corresponds to \( \alpha = \theta_S = 5^\circ \). The angle of the wetting glass–water–air film in both cases is \( \theta_S = 0 \) since direct microscope observations show that in all experiments this angle is virtually zero.

The observed dependence \( \Pi_{AS}^{CR} \) on \( R_{EFF} \) is by no means a trivial fact. The isotherm \( \Pi_{AS}(h) \) is not expected to depend on either the film size or the film curvature, because the film thickness \( h \) is much smaller than both \( R_{EFF} \) and \( R_F \). Therefore, if the film rupture were accomplished by surmounting the maximum in the isotherm \( \Pi_{AS}(h) \), then the rupture event for a given system would be expected to occur always at \( \Pi_{AS}^{CR} = \Pi_{AS}^{MAX} \), independently of the drop size.

One possible explanation of the observed dependence might be related to the relatively small size of the asymmetric films. As shown previously for micrometer-sized liquid films, the interaction force and energy across the film might be comparable in magnitude with the interaction across the meniscus region surrounding the film. If such is the case, the film destabilization will depend on the overall force of interaction between the drop and the water–air interface, including the meniscus region; i.e., \( \Pi_{AS}^{CR} \) should not necessarily coincide with \( \Pi_{AS}^{MAX} \) and might depend on the film size. Another possible explanation of the experimental results is that the film rupture in our systems occurs by passing below the barrier \( \Pi_{AS}^{MAX} \) (Figure 9), similar to other results obtained with planar foams by Bergeron. Such a possibility is offered by different theoretical models of film rupture, in which the formation of unstable spots in large liquid films by various mechanisms is considered. However, all these models are developed for planar films and cannot be directly applied without a careful analysis of the role of film curvature in the film rupture process. For soluble oils (octane, decane, dodecane, 2BO, etc.) it was recently shown that the asymmetric oil–water–air films can be below 1°. As evidenced from the comparison of the solid and dashed lines in Figure 8, the variation of the contact angles does not affect significantly the magnitude of the calculated \( \Pi_{AS}^{CR} \) or its linear dependence on \( R_{EFF} \).

**4.2. Numerical Results.** In Figure 8, the calculated dependence of \( \Pi_{AS}^{CR} \) as a function of the inverse film radius for 3.2 mM SDDBS, 12 mM NaCl, and hexadecane drops (clean water–air surface) is shown by a solid line. The contact angles are taken as equal to zero, \( \theta_S = \theta_F = 0^\circ \). Since the asymmetric film is curved, there are different possible definitions of its size. For this plot we have chosen the “effective” film radius to be equal to the radius of a planar film, which has the same area as the real asymmetric film

\[
R_{EFF} = (A_F / \pi)^{1/2}
\]

where \( A_F \) is the actual area of the asymmetric film. As seen from Figure 8, \( \Pi_{AS}^{CR} \) is a linear function of \( R_{EFF} \). It is worth noting that such a linear dependence is observed also if \( \Pi_{AS}^{CR} \) is plotted against \( 1/R_C \) or \( 1/R_F \); i.e., this is not a particular property of \( R_{EFF} \). The dashed line shows the same plot but for different contact angles, \( \theta_S = \theta_F = 5^\circ \). The angle of the wetting glass–water–air film in both cases is taken as \( \theta_S = 0^\circ \) because the direct microscope observations show that in all experiments this angle is virtually zero.

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destabilized by a transfer of oil molecules across the film. Since the conditions in our experiments are not entirely compatible with some of the assumptions made in the respective theoretical model, it is impossible to make a direct comparison of the theoretical predictions with our experimental results. Further experimental and theoretical work is intended to reveal the actual mechanism of film rupture in our systems, to modify some of the existing models or to develop a new model of this process, and to explain the observed dependence \( \Pi_{AS}^{CR}(\Gamma_{EFF}) \).

5. Conclusions

A systematic experimental study of the entry barriers for several oils of different chemical structure in SDSDBS solutions is performed by means of the film trapping technique. First, the critical capillary pressure, \( P_{CCR} \), which leads to rupture of the asymmetric oil–water–air film and to drop entry at the water–air interface, is measured (for brevity, \( P_{CCR} \) is denoted as “the entry barrier” throughout the paper). Second, the critical disjoining pressure in the moment of film rupture, \( \Pi_{AS}^{CR} \), is estimated from the experimental data. The obtained results and conclusions can be summarized in the following way:

The entry barrier increases with the surfactant concentration. Close to the cmc, the increase of the entry barrier is relatively slow, whereas at about 9 mM (45 x cmc, effective volume fraction of the micelles \( \approx 6\% \)) the increase becomes much steeper. The latter observation implies that the micelles play a significant role in the film stabilization above a certain threshold surfactant concentration.

The presence of a spread oil layer on the surface of the solution was shown to reduce significantly the entry barrier for decane and dodecane. Remarkably, the presence of hexadecane on the solution surface (which makes a mixed adsorption layer with the SDSDBS) leads to a 5-fold increase of the entry barrier with important consequences for the antifoam activity of this oil.1 The explanation of this effect is certainly connected to the incorporation of oil molecules into the surfactant adsorption layer. However, without a more detailed picture of the mechanisms of asymmetric film rupture and drop entry, it is impossible to specify what are the properties of the mixed adsorption layer that play a major role (Gibbs elasticity, surface charge density, etc.). As far as we know, such a role of oil spreading in the antifoaming action of the oils has not been reported so far.

The entry barriers for a series of \( n \)-alkanes are measured in the presence of a spread oil layer. The barriers increase with the molecular mass of the alkane. Again, additional studies are needed to clarify the main factors, which govern this trend.

The calculations show that for micrometer-sized oil drops, like those in the real oil-containing antifoams, there is a big difference between the numerical values of \( P_{CCR} \) and \( \Pi_{AS}^{CR} \) (unlike the case of planar films where \( P_{CCR} = \Pi_{AS}^{CR} \)). The reason is that the radius of curvature of the asymmetric oil–water–air film is very small and the capillary pressure jumps across the film surfaces are very large and cannot be neglected. Therefore, one should separately consider the dependence of \( \Pi_{AS}^{CR} \) and \( P_{CCR} \) on the size of the asymmetric film.

The experiments show that \( P_{CCR} \) is a weak function of the oil drop size and of the asymmetric film radius, while \( \Pi_{AS}^{CR} \) scales as \((\text{film radius})^{-1}\) for all of the studied systems. The strong dependence of \( \Pi_{AS}^{CR} \) on the film radius shows that the rupture of the asymmetric film does not occur simply by surmounting the barrier in the \( \Pi_{AS}(h) \) curve, because the latter is expected to be independent of the film radius in the studied size range. Some possible explanations of this experimental fact are discussed.

When discussing the foam stability, \( P_{CCR} \) is a more convenient quantity for description of the entry barriers, because its magnitude correlates with the foam height, whereas the magnitude of \( \Pi_{AS}^{CR} \) does not.

Let us conclude that the film trapping technique is a powerful and versatile tool for quantifying the entry barriers of oil drops. The obtained new experimental results have posed several interesting questions concerning the general mechanism of film stability, which call for further experimental and theoretical work on this subject.

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