

Methods for evaluation of emulsion stability at a single drop level

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ABSTRACT

Several techniques are applied to evaluate the emulsion stability at a single drop level. Film Trapping Technique (FTT) allows one to characterise the barrier to coalescence of single, micrometer oil drops with large oil phase, in terms of a critical capillary pressure, P_C^{CR} . It was found that the larger drops coalesce at lower P_C^{CR} , i.e. they are less stable. Centrifugation stability tests with concentrated, protein stabilised emulsions are performed. The emulsion stability in these tests is characterised by a critical osmotic pressure P_{OSM}^{CR} , above which a release of bulk oil, as a result of drop coalescence, is observed. These tests also show that the emulsions containing larger drops are less stable. Furthermore, it is found that the emulsion destabilisation starts at a given critical volume fraction of the oil drops, Φ_{CR} , which is slightly dependent on the mean drop size. A new method is proposed for determination of the function $P_{OSM}(\Phi)$, which allows one to relate the quantity which is easily determined experimentally, P_{OSM}^{CR} , with the quantity which is not easily accessible, Φ_{CR} .

In the present paper we discuss several, recently developed experimental techniques for characterization of emulsion stability. One of them is a modification of the Film Trapping Technique (FTT) which was previously used for measurement of the three-phase contact angle of micrometer particles (1) and for characterization of the entry barrier of oil drops in relation to antifoaming (2). In the present paper, we show that FTT can be used for a characterization of the coalescence stability of single, micrometer-sized oil drops, which are compressed against a large oil phase. Drops of different radius can be studied, which allows one to precisely evaluate the drop size effect on coalescence stability.

The other two techniques are based on centrifugation. In one of the techniques we characterize the stability of batch emulsions in terms of the critical emulsion osmotic pressure, P_{OSM}^{CR} , at which bulk oil layer is released on top of the centrifuged cream (i.e., at which the coalescence process is observed macroscopically). With this technique, we show that the dimensionless P_{OSM}^{CR} and the respective critical volume fraction of oil, Φ_{CR} , do not depend on the mean drop size in a protein stabilized emulsion. The second techniques allows one to determine experimentally the function $P_{OSM}(\Phi)$ and to relate in this way the quantity which is easily determined experimentally, P_{OSM}^{CR} , with the quantity which is not easily accessible, Φ_{CR} .

At the end, we discuss on a theoretical basis the size of the films, which are formed at the top of a centrifuged emulsion and the respective film size effect on the mode of emulsion destruction.

1/ Film Trapping Technique (FTT): coalescence stability of single oil drops.

The principle of the FTT with application to emulsion stability is the following: A vertical glass capillary, partially filled with oil, is held at a small distance above the flat bottom of a glass vessel, Figure 1. The lower edge of the capillary is immersed in the working solution, which contains dispersed oil drops. The capillary is connected to a pressure control system, which allows one to vary and to measure precisely the difference, ΔP_A , between the air pressure in the capillary, P_A , and the atmospheric pressure, P_A^0 . Upon the increase of P_A , the oil-water meniscus in the capillary moves downward against the substrate. When the distance between the oil-water meniscus and the glass substrate becomes smaller than the drop diameter, some of the drops remain entrapped in the formed glass-water-oil layer.

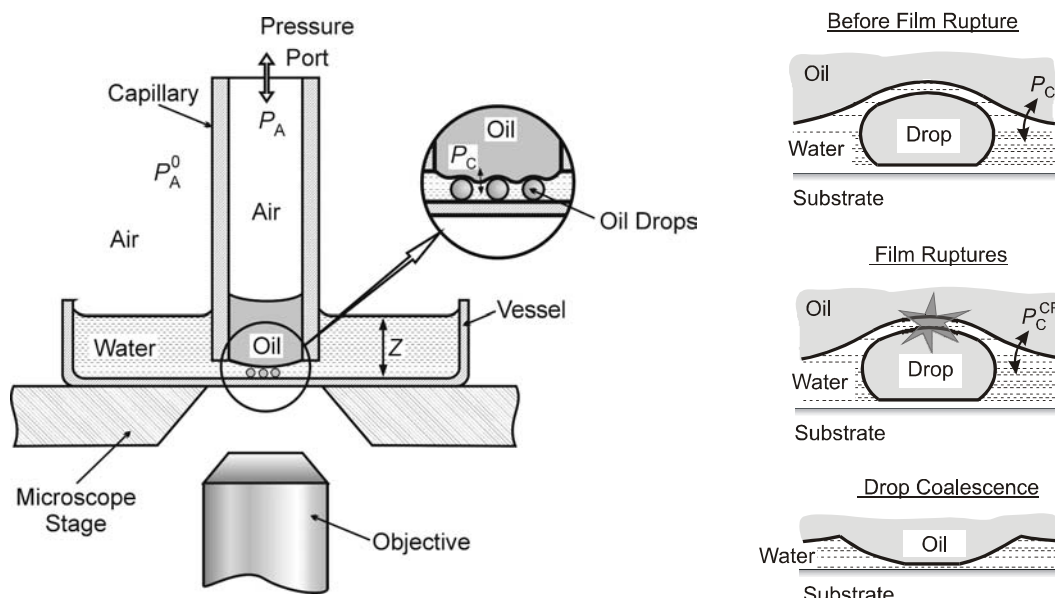


Figure 1. Basic scheme of the film trapping apparatus. Scheme of the droplets trapped between the oil-water and the substrate (see the magnification lens). Consequence stages of the drop entry process.

The pressure P_A is increased until the coalescence of the entrapped oil drops with the upper oil phase is observed. The capillary pressure in the moment of drop coalescence, P_C^{CR} , is called the critical capillary pressure or the coalescence barrier and can be calculated from ΔP_A (3). Higher values of P_C^{CR} correspond to more stable emulsion films and vice versa.

The trapped oil drops and the coalescence process were observed from below with an inverted optical microscope (Carl Zeiss, Jena, Germany), equipped with objective LD Epiplan $\times 20/0.40$. A description of the technical details in the FTT can be found in Refs. 2 and 3.

As an illustration of the applicability of FTT to emulsion systems, we show in Figure 2 the inverse critical capillary pressure for coalescence of oil drops with a large oil-water interface as a function of the drop radius, R_0 . The oil phase was soybean oil, whereas the studied emulsifier was the milk protein β -lactoglobulin (BLG). The results obtained at two different concentrations of BLG show that the larger drops coalesce at lower capillary pressure, P_C^{CR} (i.e. the larger drops are less stable). The results are represented very well by a simple empirical expression, which implies that $1/P_C^{CR}$ is a linear function of R_0 (Figure 2).

One limitation of the FTT method in emulsion systems is the necessary to work at a relatively low emulsifier concentrations. Otherwise, P_C^{CR} becomes very high and cannot be measured. In this aspect, the characterization of emulsion stability by centrifugation has the advantage to be applicable to much higher emulsifier concentrations, viz. to more stable emulsions (3).

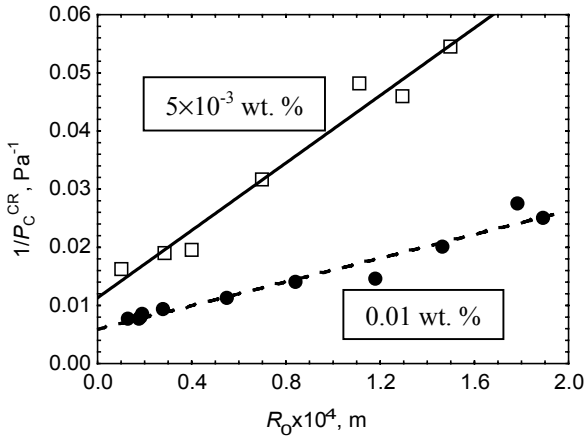


Figure 2. Inverse critical capillary pressure, $1/P_C^{CR}$, as a function of the drop radius, R_0 , as measured by FTT. The aqueous phase contains 0.01 wt. % BLG (full cycles) or 5×10^{-3} wt. % BLG (empty squares), along with 0.15 M NaCl, and 0.1 g/L NaN_3 ; pH = 6.2 (natural).

2/ Evaluation of emulsion stability by centrifugation.

The centrifugation is a relatively simple method and allows one to accumulate a large set of data for a relatively short period of time. For a quantitative characterization of emulsion stability, we use the critical osmotic pressure, P_{OSM}^{CR} , at which an oil layer is released at the top of the emulsion cream during centrifugation, as a result of drop coalescence. P_{OSM}^{CR} is easily calculated from the experimental data, if one assumes that the centrifugation field is homogeneous throughout the emulsion column (3):

$$P_{OSM}^{CR} = \Delta\rho g_k \int_0^{H_k} \Phi(z) dz = \Delta\rho g_k (V_{TOT} - V_R) / A_{TT} \quad [1]$$

Here $\Delta\rho$ is the difference in the mass densities of the oil and water phases; g_k is the centrifugal acceleration; $\Phi(z)$ is the local volume fraction of oil in the cream (z is a co-ordinate parallel to the centrifugal field, see Figure 3); V_{TOT} is the total volume of oil in the emulsion; V_R is the volume of released oil on top of the cream; A_{TT} is the cross-sectional area of the test tube.

We applied the centrifugation method for characterization of the emulsion stability as a function of the mean drop size for emulsions stabilized by whey protein concentrate (WPC). A series of four emulsions was prepared with different mean drop diameters (varying between 16 and 30 μm), at practically the same density of the protein adsorption layers on drop surface, $\Gamma \approx 1.9 \text{ mg/m}^2$. The obtained results are presented in Figure 4 in terms of the dimensionless critical osmotic pressure (4,5):

$$\tilde{P}_{OSM}^{CR} = P_{OSM}^{CR} (R_{32} / \gamma_{OW}) \quad [2]$$

where γ_{OW} is the interfacial tension and R_{32} is the volume-surface mean radius of the drops in the studied emulsions. As one can see from Figure 4, \tilde{P}_{OSM}^{CR} does not depend on the mean drop size – this result is discussed at the beginning of section 3 below. Let us note, however, that the actual (dimensional) critical pressure, P_{OSM}^{CR} , decreases with the mean drop size (see Eq. 2), which is another result showing that the emulsions containing larger drops are less stable. Figure 4 and Eq. 2 imply that the dependence of $1/P_{OSM}^{CR}$ on R_{32} is linear.

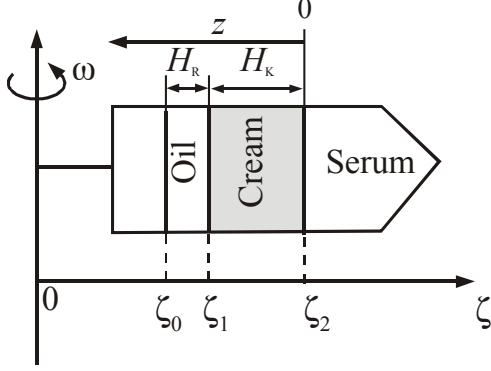


Figure 3. Equilibrium configuration of an emulsion column in a centrifugal field: H_k is the equilibrium height of the cream, whereas H_r is the height of the layer of released oil (as a result of drop coalescence in the uppermost layer of the cream).

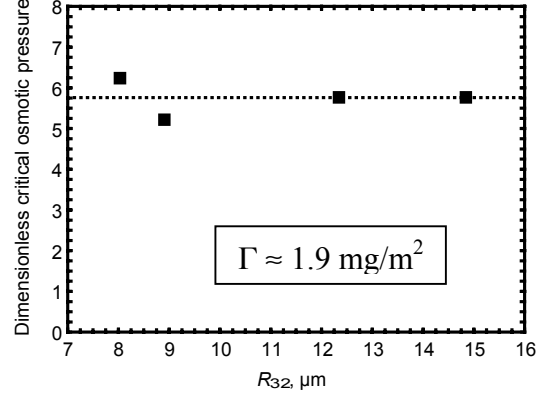


Figure 4. Dimensionless critical osmotic pressure, \tilde{P}_{OSM}^{CR} , as a function of the surface-volume radius, R_{32} at constant protein adsorption $\Gamma = 1.9 \text{ mg/m}^2$ for WPC-containing emulsions.

3/ Determination of the dependence $P_{OSM}(\Phi)$ by centrifugation

As discussed by Princen, the dimensionless osmotic pressure, \tilde{P}_{OSM} , is a function of the drop volume fraction, Φ , and should not depend significantly on R_{32} . Under this assumption, one can interpret the result from Figure 4 as an indication for the existence of a critical oil volume fraction, Φ_{CR} , which is independent of the mean drop size, and above which the emulsion becomes unstable. In principle, one can determine Φ_{CR} from \tilde{P}_{OSM}^{CR} if the dependence $\tilde{P}_{OSM}(\Phi)$ is known.

The experimental data about the dependence $\tilde{P}_{OSM}(\Phi)$ are very scarce in the literature, due to technical difficulties encountered in the methods used so far (4,5). That is why, we have developed (6) a new procedure for determination of the dependence $\tilde{P}_{OSM}(\Phi)$ by centrifugation. The procedure relies on measuring the equilibrium height of the emulsion cream in the centrifugal test tube, H_k , as a function of the centrifugal acceleration, g_k (the acceleration being below the critical one leading to drop coalescence). The following rigorous expression was derived in Ref. 6 for the volume fraction of the oil drops at the top of the cream, $\Phi(z = H_k)$:

$$\Phi(\tilde{H}_k) = \left(\tilde{H}_k + \frac{d \tilde{H}_k}{d \ln k} \right)^{-1} \quad [3]$$

where $\tilde{H}_k = H_k / H_{TOT}$ is the dimensionless cream height and k is the dimensionless centrifugal acceleration, $k = g_k/g$. On the other hand, in the absence of coalescence, the dimensionless osmotic pressure at the top of the cream during centrifugation is

$$\tilde{P}_{OSM} = \Delta \rho g_k (V_{TOT} / A_{TT}) (R_{32} / \gamma_{OW}) \quad [4]$$

and can be easily calculated from the experimental data. In this way, we find a relation between \tilde{P}_{OSM} and Φ , which can be used to construct the dependence $\tilde{P}_{\text{OSM}}(\Phi)$.

In our experiments, we determined $H_k(k)$ by observation of emulsions during their centrifugation in transparent glass tubes. A binocular lens (Zeiss), stroboscope illumination (Kruss SITE 11), digital CCD camera (Kappa CF 8/1 DX) and video-recorder (Panasonic NV-HD680) were used for these observations. The position of the boundary between the emulsion cream and the underlying serum (aqueous phase deprived of oil drops) was precisely determined from the video-records, by using a capture PC-board and an image analysis software. The position of the upper boundary cream-air did not depend on the acceleration, g_k (due to the incompressibility of oil and water), and its position was determined immediately after stopping the centrifuge at the end of the experiment. The distance between the upper and lower boundaries of the cream at given g_k is equal to H_k .

To illustrate the feasibility of the method, we studied two emulsions with different mean drop-size, see Table 1. In Figure 5 we plot the experimental data $\tilde{H}_k(\ln k)$ for three parallel samples of emulsion No 2. As seen from the plot, the reproducibility of the data is rather good. From these data, the volume fraction of the oil at the top of the cream was found by using Eq. 3. The respective dimensionless osmotic pressure was calculated from Eq. 4. The final results for the dependence $\tilde{P}_{\text{OSM}}(\Phi)$ for the studied emulsions are presented in Figure 6, along with the empirical dependence obtained by Princen (5) (the solid curve) and the theoretical curve for a face-centered close packed (fcc-packed) array of monodisperse emulsion drops (7) (the dashed curve). One sees that the experimental points for the two emulsions follow relatively well the curves from Refs. 5 and 7. A larger set of experimental data with the respective discussion of the results is presented in Ref. 6.

Table 1. Studied emulsions: R_{32} is volume-surface radius, σ is width of drop-size distribution, γ_{ow} is interfacial tension and $\Delta\rho$ is difference in the mass densities of the oil and water phases.

Sample	Emulsifier	Oil phase	R_{32} μm	σ μm	γ_{ow} mN/m	$\Delta\rho \times 10^{-3}$ kg/m ³
Emulsion 1	1 wt. % SDS	Hexadecane	6.9	2.9	9.0	0.23
Emulsion 2	2 wt. % SDS	Soybean oil	33	22.5	3.2	0.08

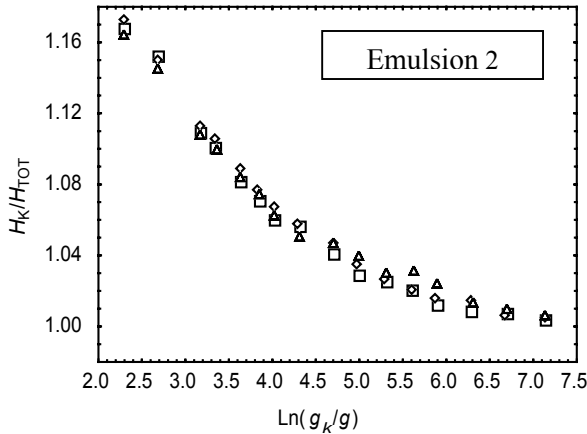


Figure 5. Dimensionless cream height, as a function of the dimensionless centrifugal acceleration for 3 samples of emulsion 2.

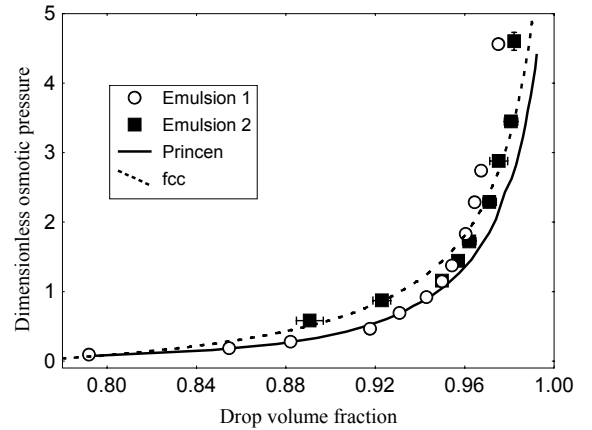


Figure 6. Dimensionless osmotic pressure, \tilde{P}_{OSM} as a function of the oil volume fraction at the top of the cream.

4/ Theoretical analysis of the size of liquid films at the interface between an emulsion and a large phase (solid wall or oil macrophase).

As explained in sections 1 and 2, the critical pressure for film rupture depends on drop size. In fact, what matters for the coalescence stability is the size (area) of the emulsion films rather than the drop-size itself. The larger films are less stable, because the probability for formation of an unstable spot (nucleus of film rupture) increases with the film area.

Two different in size films appear at the top of an emulsion column, even when the emulsion drops are perfectly monodisperse: (1) films formed between the drops located in the uppermost layer of the emulsion and the large interface, and (2) films formed between two drops of similar size, see Figure 7. A simple force balance shows that the film of type 1 must be larger in area than the film of type 2 at mechanical equilibrium. To illustrate this effect, we consider the following idealized cases: Two-dimensional emulsion (i.e., an emulsion of cylindrical drops oriented in parallel to the interface) in contact with solid wall, Figure 7A; Three-dimensional (3D) emulsion of monodisperse drops in fcc-arrangement, in contact with solid wall or with oil homophase.

The two-dimensional (2D) emulsion is considered first, because the physical interpretation in this simpler case is very transparent. The 3D fcc-emulsion is more representative for the real emulsions. The use of other particular arrangements would lead to similar final equations with slightly different numerical coefficients.

4.1. Two-dimensional (2D) emulsion in contact with solid wall, Figure 7A.

The mechanical equilibrium of a drop in the uppermost layer 1 requires that the repulsive force between the drop and the solid wall, F_W , must be counterbalanced by the vertical projections of the two forces, F_D , exerted in the contacts of this drop with its two neighbors from the second layer

$$F_W = 2F_D \cos \theta \quad [5]$$

where $\theta = \pi/6$ is the angle between the direction of F_D and the vertical co-ordinate, z . On the other hand, the forces F_W and F_D are equal to the respective product of the film area, A_K , and the repulsive disjoining pressure stabilizing the liquid film, Π_K , that is $F_K = \Pi_K A_K$ ($K = W$ or D for the drop-wall and for the drop-drop film, respectively). In the case of solid surface and monodisperse drops, all films in the idealized system are flat and the disjoining pressure in mechanical equilibrium is exactly equal to the capillary pressure between the drops and the surrounding them aqueous phase, $P_{CAP} \equiv P_D - P_W = \Pi_K$. Therefore, Eq. 5 can be represented in the form:

$$A_W / A_D = 2 \cos(\pi/6) \approx 1.732 \quad \text{2D emulsion; solid wall} \quad [6]$$

which shows that the area of the film between the drop and the solid wall is almost twice larger than the area of the film between two equally sized drops of the same size. This difference is mainly due to the fact that the force, F_W , at *one film of type drop-wall* must be counterbalanced by the forces created by *two contacts of drop-drop type*.

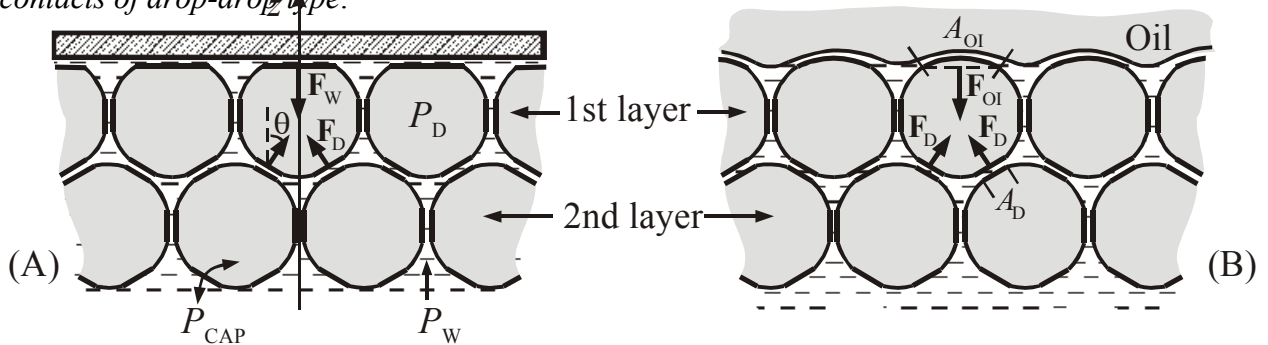


Figure 7. Schematic presentation of the upper layers of a 2D foam in contact with: (A) solid wall, and (B) with large oil phase.

4.2. Three-dimensional (3D) emulsion in contact with a solid wall.

Similar consideration can be made for a 3D-emulsion. The balance of the forces acting on a drop in the uppermost layer of the emulsion can be written in the form

$$F_w = mF_D \cos \theta \quad [7]$$

where m is the number of neighbors of the chosen drop, which are located in the second layer, whereas θ is again the angle between the direction of the forces and the vertical axis. Both m and θ depend on the particular arrangement of the drops and in the case of fcc-packing $m=3$ and $\cos\theta=(2/3)^{1/2} \approx 0.816$. Introducing these values and $F_K=\Pi_K A_K$ in Eq. 7, one obtains

$$A_w / A_D = 3\sqrt{2/3} \approx 2.449 \quad \text{3D fcc-emulsion; solid wall} \quad [8]$$

The difference between the areas of the two types of film is even larger in this case (as compared to 2D emulsions), because the force created by one drop-wall contact is counterbalanced by forces created by three drop-drop contacts. Note that Eqs. 6 and 8 present only the ratio of the film areas. The actual film size is determined also by two other parameters: the drop volume, V_D , and the drop volume fraction, Φ .

4.3. Three-dimensional (3D) emulsion in contact with an oil phase.

The mechanical balance in the case of an emulsion in contact with a large oil phase is more complex, because the films formed between the drops in the uppermost layer and the large phase are curved, Figure 7B. This case is considered elsewhere (6) and here we present only the final result for a 3D fcc-packed emulsion:

$$A_{OI} / A_D = m \cos(\theta)(2 - f_{OI}) \approx 2.449(2 - f_{OI}) \quad \text{3D fcc-emulsion; oil macrophase} \quad [9]$$

where the subscript "OI" indicates the contact of the emulsion with oil interface; A_{OI} is the projected area (in a plane parallel to the macroscopic interface) of the film formed between the drop and the oil phase; f_{OI} is the fraction of the oil-water interface occupied by films. Note that for a given type of drop packing, f_{OI} depends only on the drop volume fraction, Φ , and presents an analogue of the function $f(\Phi)$, introduced by Princen (5,7) for emulsion in contact with solid wall.

For slightly deformed drops (not very high volume fractions), the numerical value of $f_{OI} \ll 1$, and one obtains $(A_{OI} / A_D) \approx 4.9$. For high volume fractions, $\Phi \rightarrow 1$, the interfacial fraction occupied by films $f_{OI} \rightarrow 1$, and Eq. 9 predicts that the ratio of the film areas approaches the value for the contact of an emulsion with a solid wall, cf. Eqs. 8 and 9.

This consideration shows that, with respect to film size, the films formed between the oil drops and the large oil layer should be less stable than the films between two drops. Indeed, experiments with protein stabilized emulsions showed that the coalescence between the oil drops in the uppermost layer of the cream with the bulk oil layer on top of the cream is more pronounced than the coalescence between the drops within the cream (3). Further analysis of the stability of the films is presented in Ref. 6.

5/ Conclusions

- ◆ Both FTT and centrifugation can be used to characterize the effect of drop size on the coalescence stability of emulsions. The results show that emulsions containing larger drops are less stable under equivalent other conditions.
- ◆ Results from centrifugation experiments with protein stabilized emulsions show that the coalescence starts at a certain, critical volume fraction of the oil drops, which is independent of the drop size.
- ◆ A new experimental procedure is proposed, which allows one to determine the dependence of the osmotic pressure of an emulsion on the drop volume fraction, $P_{OSM}(\Phi)$.
- ◆ A theoretical analysis shows that two different in area liquid films are formed in the uppermost layer of an emulsion column of monodisperse drops. This result has implications for the mode of emulsion destabilization, drop-drop or drop-homophase coalescence (3).

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