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# Differences in Ultracentrifugal Stability of Various Oil-in-Water Emulsions*

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**Synopsis**—Studies of Nujol–water and olive OIL–WATER EMULSIONS stabilized with sodium dodecyl sulfate, cetyl pyridinium chloride, Tween 20, or Triton X-100 show that generally the rate of separation of oil in an ultracentrifuge decreases with time of CENTRIFUGATION, approaching zero at sufficiently long times. The marked differences in behavior of these systems suggest that the chemical nature of the oil and of the SURFACTANT, and the molecular geometrical compatibility, may be more important than such general characteristics as VISCOSITY and INTERFACIAL TENSION.

## INTRODUCTION

A large and discordant literature exists with respect to the stability of emulsions but only in relatively recent times, with the application of the ultracentrifuge to these systems, has it become possible to make quantitative measurements in reasonable time. Much of this work has recently been summarized by Garrett (1, 2). The present work was undertaken (a) to investigate the ultracentrifugal behavior of emulsions with a greater variety of oils and emulsifying agents than had been

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studied previously, (b) to establish and compare different criteria for quantitative comparison of the stability of the different emulsions, (c) to assess the relative importance of physical and chemical factors in determining the stability of emulsions prepared with different oils and different stabilizing agents, and (d) to obtain further information leading to identification of the rate-determining step or steps in the demulsification process and the locus of coalescence in ultracentrifugal demulsification.

There is much disagreement in the literature concerning the effect of the nature of the oil and the nature of the surfactant on the stability of the emulsions formed. Garrett (1) reports that in many experiments the nature of the oil has no effect except for oils of high polarity, as was also found by King and Mukherjee (3), although King (4) later recognizes its probable importance. Similarly, although the importance of proper choice of surfactant for attainment of desired emulsion properties is clearly recognized (5), there are also reports of quantitative experiments (6) showing no difference in stability between, for example, sodium oleate and various nonionic surfactants, as determined by size distribution measurements on emulsions subjected to ultracentrifugal stress. Possibly, much of the confusion concerning the stability of emulsions is due to the multiplicity of meanings given to the term (7), particularly to the failure to distinguish clearly between creaming and coalescence, together with insufficient sensitivity of some methods (8)—such as surface area—to detect subtle changes occurring in the emulsions. In addition, different methods of characterization may well be measuring entirely different properties of the emulsion, or the emulsions may be in a quite different physical state in the various experiments. Particularly, in ultracentrifuge experiments, the emulsion is present as a flocculated system resembling a foam (9) and not as a system of free drops, so that presumably only factors involving the rate of coalescence are determined, with little or no effect due to those governing the rate of flocculation. Hence, great caution is necessary in extrapolating the conclusions from such experiments to free-standing emulsions.

In the present work, Nujol and olive oil were used as examples of polar and nonpolar oils. Sodium dodecyl sulfate, cetyl pyridinium chloride, Triton X-100®,* and Tween 20®† served as emulsifiers, representing positively and negatively charged ionic surfactants and two types of nonionics. It was hoped to determine whether observable differences in sta-

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bility could be explained in terms of physical characteristics (e.g., viscosity, interfacial tension, drop size distribution, etc.) or whether less quantitative concepts (e.g., the chemical nature and the geometric fit between the oil and the surfactant molecules) were of greater importance, the latter having been emphasized by Schulman *et al.* (10). Since not only the quantity and rate of separation of oil from the emulsion but also the qualitative nature of the time dependence of the rate of separation of oil were found to change markedly with both the nature of the oil and the nature of the surfactant, it seems apparent that chemical and geometrical factors must be considered in addition to the nonspecific physical factors.

## EXPERIMENTAL

### *Materials*

The sodium dodecyl sulfate (SDS) was a pure sample used in another investigation (11) and estimated to contain not more than 0.05% lauryl alcohol as an impurity. Cetyl pyridinium chloride (CPC)* was used as received and was found to be 98% active by titration (8) against pure SDS. Triton X-100 (Lot 2788) was used directly as furnished and is reported to be 100% polyoxyethylene p-t octyl phenyl ether with 9 to 10 ethylene oxide groups. Tween 20 was also used directly as furnished and is reported to be polyoxyethylene (20) sorbitan monolaurate, HLB number 16.7.

### *Preparation of Emulsions*

Emulsions were generally prepared as in previous work (8) by first stirring 150 ml of oil and 120 ml of 0.2% aqueous solution of the surfactant for 5 min at 5000 rpm in a Brookfield counter-rotating mixer, followed by eight passes through a motorized Cenco hand homogenizer. After standing overnight, 45-ml aliquots were taken and gently blended with 5-ml solutions of surfactant of appropriate concentration to give 50 ml of emulsion containing a 50–50 volume ratio of oil and water and any desired concentration of surfactant. By this method, it was possible to prepare a set of emulsions of the same drop size distribution but of varying initial concentration of surfactant in the aqueous phase. In the case of emulsions stabilized with Tween 20 and Triton X-100, 0.15% solutions of the surfactant were used in the initial preparation, and 0.1% solutions in the case of CPC, since 0.2% solutions of the latter gave such stable emulsions that oil did not separate at a sufficiently rapid rate in the

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* Matheson, Coleman & Bell, East Rutherford, N. J.

ultracentrifuge. Where larger quantities of emulsion were required, two batches of 270 ml each were prepared separately as described above, and blended together before addition of the final portions of aqueous surfactant solution.

### *Ultracentrifugation Technique and Treatment of Data*

Unless otherwise indicated, all the emulsions were centrifuged in a Beckman Model E ultracentrifuge at 39,460 rpm at 25°C. The technique of ultracentrifugation and the treatment of the data to deduce the volume of separated oil from the experimental observations were the same as used previously (8, 11). Generally, determinations were made at least in duplicate to establish the reproducibility of the behavior observed.

## RESULTS

In previous ultracentrifugal studies of Nujol–water emulsions stabilized with SDS (8, 9, 11, 12), the rate at which oil separated was found to be constant independent of time except for a transitory more rapid separation at the beginning of the experiment. It now appears that this behavior is the exception rather than the rule, since most of the systems studied in the present work showed a decreasing rate of separation of oil with increasing time of centrifugation approaching zero as a limit. Such behavior is also found with Nujol–water emulsions themselves, provided centrifugation is carried out for much longer periods of time, i.e., resulting in reduction of the residual emulsified oil to smaller fractions of the original amount present (Fig. 1).

Figure 1 shows the per cent of oil separated from a 50% Nujol–50% water–0.2% SDS emulsion as a function of time of centrifugation at 39,460 rpm at 25°C over a period of 7 hours. The curve has been divided into four regions. In region I at the beginning of centrifugation, the rate of oil separation is relatively much faster and changes rapidly with time. In region II, the rate is constant, i.e., a linear relation between amount separated and time of centrifugation. In region III, this relation is no longer linear, but the rate of separation decreases progressively with increasing time of centrifugation. With some systems, including Nujol–water–SDS emulsions, this behavior is accurately represented by an empirical equation (11).

$$\frac{t}{\%\ \text{oil}_{\text{sep}}} = \frac{1}{b\cdot\%\ \text{oil}_{\text{max}}} + \frac{t}{\%\ \text{oil}_{\text{max}}}$$

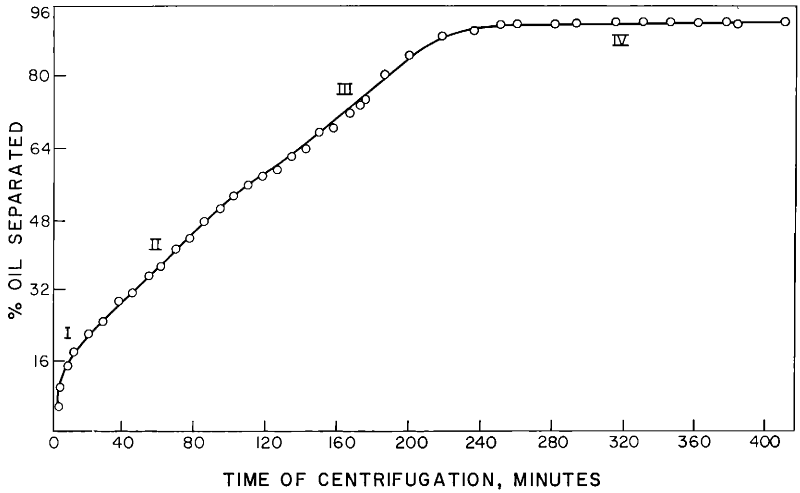

*Figure 1.* Separation of oil from 50% Nujol–50% water–0.2% sodium dodecyl sulfate emulsion (M 060669). Regions shown: I, initial rapid separation of oil; II, rate of oil separation independent of time; III, rate of oil separation decreasing with time, III-A if (as with Nujol) conforms to empirical eq 1, otherwise III-B; IV, rate of oil separation is zero independent of time

In such cases, it will be referred to as region III-A. In other systems, no simple analytical function could be found, and in such cases the region of decreasing rate of oil separation with increasing time is called III-B. In region IV, there is no further separation of oil, the rate having become zero, although a certain fraction of the original oil still is present in the emulsified state. Unfortunately, it is not possible to deduce the composition (or oil–water volume ratio) of the residual emulsion unambiguously from the per cent oil separated, as this will depend on whether the separation of oil occurs exclusively at the interface between bulk oil and emulsion or whether it occurs also throughout the body of the emulsion (12).

In more stable systems, whether due to the intrinsic character of the oils and surfactants or simply to use of a higher concentration of emulsifier, there was frequently an induction period of 5 to 20 min after ultracentrifugation was started before any free oil appeared. In such cases, the total curve of per cent oil separated *vs.* time of centrifugation usually was made up of regions I, III-B, and IV as described above, with no linear portion and no fit to the empirical equation developed to describe the rate of separation of oil in region III-A.

Figure 2 shows the quantity of oil separated as a function of time of centrifugation at 39,460 rpm at 25°C for 50% oil–50% water–0.2% sur-

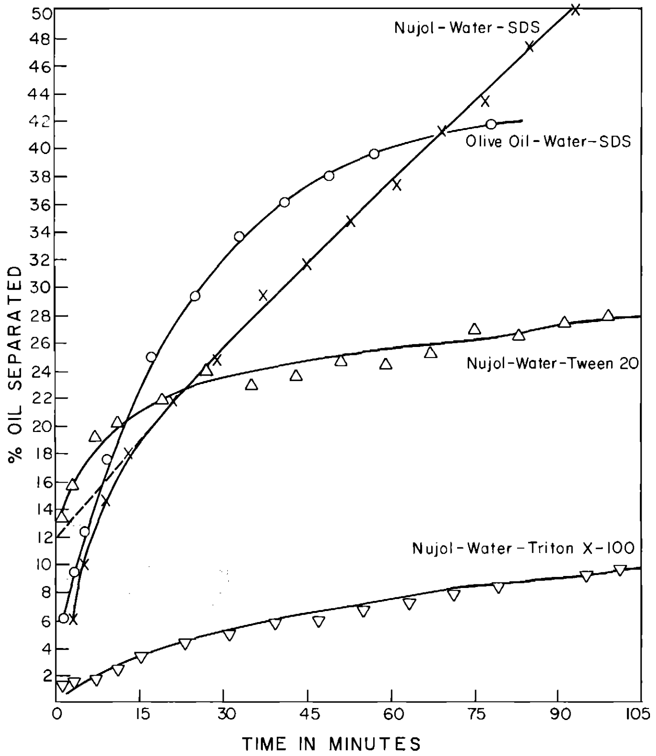

*Figure 2.* Separation of oil at 39,460 rpm from 50% oil–50% water–0.2% surfactant emulsions. Nujol-SDS emulsions M 111968; olive oil–SDS emulsions M 060669; Nujol–Tween 20 emulsions A 091069; Nujol–Triton X-100 emulsions A 090969

factant Nujol–water emulsions with SDS, Tween 20, and Triton X-100, and olive oil with SDS. Experiments with emulsions stabilized with Tween and Triton were carried out for 10 min and 85 min longer than the results shown in the figure with no change from the smooth curve found for shorter periods. For the most significant comparison of the behavior of the different systems, it would have been desirable to have equal drop size distribution in all, and to make comparisons at constant equilibrium rather than initial concentration of surfactant, or better yet at constant fraction of the oil–water interface covered by adsorbed emulsifier in all cases.

To accomplish this, it would be necessary to have adsorption isotherms for each of the surfactants, in order to make appropriate adjustments of the initial concentrations so as to obtain the same equilibrium concentration in the different cases, and to change the extent of mechanical processing during emulsification so as to obtain emulsions of equal

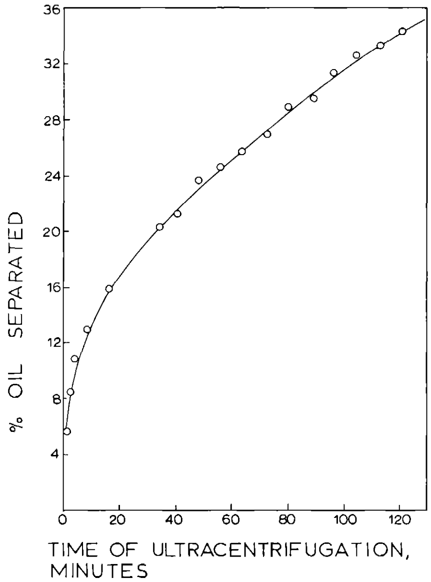

*Figure 3.* Separation of oil from 50% Nujol–50% water–0.1% cetyl pyridinium chloride emulsion (A 112669)

specific interfacial area and hence of equal average drop size (8, 12). However, although a good chemical method is available for determination of SDS, permitting determination of the amount adsorbed by difference between the initial and equilibrium concentrations in the aqueous phase, no satisfactory methods were found for determination of Triton X-100 or Tween 20 in the equilibrium aqueous phase separable from the emulsions. Absorbance methods for Triton failed because of inability to obtain totally transparent equilibrium solutions from the emulsions free of turbidity due to residual traces of unseparated oil, while neither surface tension lowering (13) nor chemical methods (14, 15) based on the formation and estimation of a cobaltothiocyanate complex could be made to give accurate results for the concentration of Tween 20 (16). Nevertheless, the differences in behavior between the different systems are so extreme that it is easily possible to draw significant conclusions from the results with equal initial concentrations of the surfactants.

Figure 3 presents the results obtained with 50% Nujol–50% water–0.1% CPC emulsions. The curve obtained is very similar to that obtained with many of the other emulsifying agents at higher concentrations, and shows a decrease in rate of separation of oil with increasing time of centrifugation not conforming to the empirical equation (III-B).

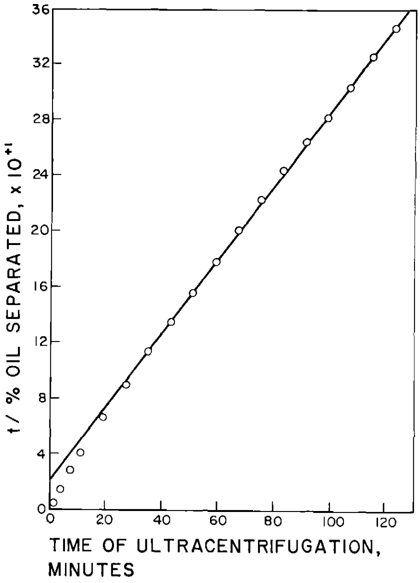

*Figure 4.* Separation of oil from 50% Nujol–50% water–0.15% Tween 20 emulsion (A 091069) plotted according to empirical eq 1

Emulsions prepared with 0.2% CPC were so stable as to be amenable to ultracentrifugal study only with difficulty, since even after 2 hours at 39,460 rpm only 8% of the Nujol had separated.

Figure 4 illustrates that the rate of separation of oil from 50% Nujol–50% water–0.15% Tween emulsions in the ultracentrifuge at 25°C at 39,460 rpm is well represented by the empirical equation. A similar result was obtained with 50% olive oil–50% water–0.2% SDS emulsions (11).

It is useful to summarize briefly the different types of behavior found with each system with respect to rate of separation of oil. In the case of 50% Nujol–50% water–SDS emulsions at all concentrations of SDS, the curve of per cent oil separated *vs.* time of ultracentrifugation usually showed only regions I and II, although with very long periods regions III-A and IV were also found. Generally, there is no induction period even at high concentrations of SDS. However, an induction period of about 12 min was found in some of the present emulsions prepared with 0.4% SDS by direct mixing of the SDS solution and the oil instead of by mixing the oil with a 0.2% SDS solution followed by blending in sufficient concentrated SDS solution to give an overall final initial concentration of 0.4% in the aqueous phase, as in the standard method of preparation. This difference in behavior may be due to the smaller drop size presumably achieved by direct emulsification in the presence of the higher concentration of surfactant.

50% Nujol–50% water–Tween 20 emulsions containing initially 0.15 to 0.35% Tween 20 on the basis of the aqueous phase separated oil in the ultracentrifuge following curves showing regions I and III-A. Above 0.35%, where oil separates only very slowly, the empirical equation was no longer obeyed and the curve consisted of regions I and III-B.

With 50% Nujol–50% water emulsions stabilized with Triton X-100 at 0.1% Triton on the basis of the aqueous phase, the curve of oil separated *vs.* time of ultracentrifugation consisted of regions I and III-A. At higher concentrations (0.15 to 0.4%), only regions I and III-B were observed.

Nujol–water emulsions stabilized with 0.1% CPC gave a curve (Fig. 3) showing only regions I and III-B, resembling in type of behavior those stabilized with 0.2% Triton X-100.

50% olive oil–50% water–0.2% SDS emulsions gave curves of oil separated *vs.* time showing regions I and III-A. However, when such emulsions were prepared by direct mixing with 0.4% SDS there was an induction period before any oil separated, and then it separated according to I and III-B.

To facilitate quantitative comparison of the behavior of the different systems, the per cent oil separated after various times and the parameters of the empirical equation (extrapolated maximum % oil separable and *b*) where applicable are given in Table I. Table II presents the ob-

Table I

Dependence of Per Cent Oil Separated from 50% Oil-Water Emulsions on Oil and Emulsifier

| | Oil Separated After *t* Min (%) | | | | |
|---|---|---|---|---|---|
| Emulsion | 25 | 75 | 100 | $\text{Oil}_{\text{max}}$ (%) | $b \times 10^2$, $\text{min}^{-1}$ |
| Nujol–water–0.2% SDS[a] | 23.6 | 42.8 | 52.4 | 91.6 | ... |
| Nujol–water–0.2% Tween 20[b] | 21.9 | 26.1 | 27.6 | 29.5 | 13 |
| Nujol–water–0.2% Triton X-100[c] | 4.2 | 8.1 | 9.5 | ... | ... |
| Olive oil–water–0.2% SDS[d] | 29.3 | 41.6 | ... | 52.1 | 5.5 |
| Nujol–water–0.1% CPC[e] | 17.5 | 27.4 | 31.5 | ... | ... |

[a] Emulsions M 111968.
[b] Emulsions A 091069.
[c] Emulsions A 090969.
[d] Emulsions M 060669.
[e] Emulsions A 112669.

served rate of separation of oil after varying periods of centrifugation and Table III after separation of various constant fractions of the oil present.

Table II

Rate of Oil Separation from 50% Oil-Water Emulsions

| Emulsion | % Oil/Min After *t* Minutes | | | |
|---|---|---|---|---|
| | 25 | 50 | 75 | 100 |
| Nujol–water–0.2% SDS[a] | 0.53 | 0.53 | 0.53 | 0.53 |
| Nujol–water–0.2% Tween 20[b] | 0.21 | 0.068 | 0.033 | 0.020 |
| Nujol–water–0.2% Triton X-100[c] | 0.09 | 0.07 | 0.047 | 0.030 |
| Olive oil–water–0.2% SDS[d] | 0.51 | 0.20 | 0.11 | 0.07 |
| Nujol–water–0.1% CPC[e] | 0.24 | 0.17 | 0.16 | 0.15 |

[a] Emulsions M 111968.
[b] Emulsions A 091069.
[c] Emulsions A 090969.
[d] Emulsions M 060669.
[e] Emulsions A 112669.

Table III

Rate of Oil Separation from 50% Oil-Water Emulsions
(Per Cent/Minute)

| Emulsion | Amount of Oil Separated (%) | | |
|---|---|---|---|
| | 10 | 20 | 30 |
| Nujol–water–0.2% SDS[a] | . . . | 0.53 | 0.53 |
| Nujol–water–0.15% Tween 20[b] | 3.0 | 1.2 | 0.24 |
| Nujol–water–0.12% Triton X-100[c] | 0.13 | 0.01 | . . . |

[a] Emulsions M 111968;
[b] Emulsions A 091069.
[c] Emulsions M 111969 TR.

## Discussion

As is evident from the experimental results, in most cases the rate of separation of oil decreased with time of ultracentrifugation, in many cases following the empirical equation developed to describe the behavior of olive oil–water–SDS emulsions (11). According to this relation,

$$\frac{t}{\%\ \mathrm{oil}_{\mathrm{sep}}} = \frac{1}{b \cdot \%\ \mathrm{oil}_{\mathrm{max}}} + \frac{t}{\%\ \mathrm{oil}_{\mathrm{max}}} \qquad (1)$$

where $\%\ \text{oil}_{\text{sep}}$ is the per cent of the initial emulsified oil present as free bulk oil after time $t$, $\%\ \text{oil}_{\text{max}}$ is the maximum amount separable at the given speed of centrifugation, and $b$ is an arbitrary constant.

Where this equation fits the data, which can be easily ascertained by plotting $t/\%\ \text{oil}_{\text{sep}}$ against $t$ and checking whether a linear relation is obtained, it provides a very convenient means for calculating the rate of oil separation after any given time of centrifugation or after separation of any given fraction of the initially emulsified oil. The derivative of eq 1 is

$$\frac{d(\%\ \text{oil}_{\text{sep}})}{dt} = \frac{\%\ \text{oil}_{\text{max}} \cdot b}{(1 + bt)^2} \tag{2}$$

which permits easy calculation of the rate at any time $t$. By algebraic manipulation, it can also be shown that

$$\frac{d(\%\ \text{oil}_{\text{sep}})}{dt} = \frac{b(\%\ \text{oil}_{\text{max}} - \%\ \text{oil}_{\text{sep}})^2}{\%\ \text{oil}_{\text{max}}} \tag{3}$$

Eq 3 permits ready calculation of the instantaneous rate of oil separation after separation of any given fraction, such as 10% or 30%.

Provided $b$ is sufficiently small, eq 1 reduces to the equation of a straight line, since

$$\%\ \text{oil}_{\text{sep}} = \frac{Kt}{1 + bt} \tag{4}$$

This could account for the linear relation between per cent oil separated and time found with so many Nujol–water–SDS emulsions, but requires that $b$ have a very low value in such systems since the values of $t$ in region II—the linear portions of the curves—can be rather large (90 to 120 min).

### *Mechanistic Implications of the Results*

It is reasonable to conclude from the very great differences in stability shown by the emulsions of Fig. 2 that specific factors involving the chemical nature and molecular geometry of both the oils and the surfactants are of dominant importance in determining the stability of emulsions. All the emulsions had the same oil–water volume ratio, the same initial concentration of surfactant, and were made by the same preparative technique. Nevertheless, dependent on the nature of the oil (polar *vs.* nonpolar), and, more particularly, the nature of the surfactant, there are very great differences in rate of separation of oil and in total fraction separated, probably greater than could be ascribed to differences in relative adsorbability of the surfactants with resultant differences in the extent of surface coverage of the oil–water interface in the different cases.

One of the questions to which an unambiguous answer still cannot be given is whether the differences in the rates at which free oil appears in the different emulsions are due to differences in intrinsic probability of coalescence or in rate of drainage of residual water from between the deformed oil drops. Another is whether the separation of oil is occurring throughout the body of the emulsion or solely at the interface between flocculated emulsion and separated oil. The available evidence is not conclusive (2, 12, 17) on either of these points.

However, in all cases, as oil separates the total area of oil–water interface decreases, with release of previously adsorbed surfactant to the aqueous lamellae separating the deformed oil drops. Whether this is transported rapidly to the underlying bulk aqueous phase, thus increasing its concentration throughout, or, more likely, some is readsorbed directly from the lamellae at the residual oil–water interface, the net result would be to increase the coverage of the residual oil–water interface with adsorbed surfactant, at least until surface saturation was attained, thereby decreasing the subsequent rate of separation of oil (9). This may well account for the tendency of the rate of separation of oil to decrease with increasing time of centrifugation, approaching zero as a limit, and for the fact that the empirical equation (eq 1) found to describe the behavior of many systems reduces to approximately zero rate of separation of oil at long times of centrifugation.

It is useful to identify as many as possible of the processes which must occur during coalescence before free bulk oil appears in the system, since comparison of theoretically calculated rates for such steps with the overall rate of appearance of oil may succeed in establishing which is the rate-determining step in the sequence, or of transition from one to another rate-determining process as demulsification proceeds. Possible rate-determining processes include drainage of solution from the aqueous lamellae to the underlying bulk aqueous phase; rupture of the adsorbed surfactant film surrounding the oil globules, presumably dependent on film yield value or viscosity or elasticity; desorption of surfactants from the oil–water interface; readsorption of surfactants at the oil–water interface; diffusion of desorbed surfactant from the site of coalescence through the aqueous lamellae; electrostatic effects on the forces of attraction and repulsion between oil globules, affecting the equilibrium distances and the rate of approach; and transport of larger oil "drops" through the flocculated emulsion layer to the site of coalescence to form visible bulk oil. Even where absolute rates are uncertain, the relative effect of changes in such operating variables as speed of ultracentrifugation, temperature, concentration of surfactant, concentration of added electrolyte, phase volume ratio, drop size as influenced by method of preparation, etc., on possible rate-determining steps can be calculated and compared with its observed effect on the macroscopic rate of oil separation. Earlier studies of this type (9, 17) suggest that interfacial film properties may be more important than the rate of drainage of the residual aqueous phase.

Since the flocculated emulsions in the ultracentrifuge resemble foams in their physical structure, it is interesting to test the applicability of foam drainage equations to the present data. Ross (18) considers the following three equations for expressing the rate of drainage of water from foam, and applies them to the reported stability of the emulsions of King *et al.* (3, 4) equating the volume of oil remaining in the emulsion after a specified length of time with the amount of water remaining in a foam after drainage.

$$V_d = V_o(1 - e^{-kt}) \tag{5}$$

$$\frac{V_o - V_d}{V_o} = \frac{1}{(bt + 1)^{1/2}} \tag{6}$$

$$kt = \log \frac{1 + \left(\dfrac{100V_d}{V_o}\right)^{1/2}}{1 - \left(\dfrac{100V_d}{V_o}\right)^{1/2}} \tag{7}$$

where $V$ is the volume of oil remaining in the emulsion after time $t$, $V_o$ is the initial volume of oil in the emulsion, $V_d$ is the volume of oil separated from the emulsion, and $b$ and $k$ are experimental constants. The problem has also been treated in some detail by Bikerman (19).

Ross (18) reports that the behavior of the emulsions described by King (4) is represented over wide limits by eq 6, whereas the behavior of the less stable emulsions reported by King and Mukherjee (3) is described by eq 7. None of these equations describe properly the separation of oil from the present emulsions. This may be taken as further evidence that in all likelihood the rate of drainage of residual water from the flocculated emulsion in the ultracentrifuge is not the rate-determining step governing the rate of demulsification as measured by the appearance of bulk oil.

### *Quantitative Comparison of Emulsion Stability*

It would be of great practical value if an accelerated test could be devised for quantitative comparison of the stability of emulsion systems to aid in rapid screening of the effect of changes in emulsification procedures, concentration of surfactants, phase volume ratio, type of emulsifier, etc., without the need for tedious observation of shelf stability. Ultracentrifugal methods may be useful in this connection, although they suffer from two major handicaps and ultimately must be checked by more conventional methods in any case. The first of these, already discussed, is the difference in the physical state of the emulsion in the ultracentrifuge as contrasted with standing undisturbed in the natural state. The second is the problem of selection of the most meaningful centrifugal criterion for purposes of comparison.

The more important of these parameters in terms of which the emulsions can be compared quantitatively are: (a) the amount of oil which has separated after $t$ minutes of centrifugation; (b) the limiting amount of oil which will separate at infinite time, either from an experimental determination or as the extrapolated $\%$ $\text{oil}_{\text{max}}$ of the empirical eq 1; (c) the value of the constant $b$ in the empirical equation, the larger values corresponding to less stable emulsions; (d) the rate of separation of oil after $t$ minutes of centrifugation; and (e) the rate of separation of oil after a given constant fraction of that initially present has separated. Illustrative values of these parameters for some of the variety of emulsions studied in this work are given in Tables I, II, and III. In addition, use might be made of the quantity of oil separated rapidly at the beginning of centrifugation (extrapolated per cent oil separated at zero time), the length of the induction period in cases where such is present, or the calculated value of the rate constant for the process of oil separation in cases where the data fit one of the standard kinetic equations, as may be the case with the Nujol–water–SDS emulsion data.

Criteria based on the quantity of oil separated may be of practical interest but are perhaps of less theoretical value since the value includes rather large and variable quantities of oil separated under nonequilibrium conditions at the beginning of centrifugation. Moreover, because of differences in the steady-state rate of separation of oil, the order of stability found will depend on the time chosen at which to make comparisons. This is apparent from the tabulation in Table IV based on the data given in Table I. The results with cetyl pyridinium chloride are not included in Table IV because at the same concentration of surfac-

Table IV

Order of Stability Based on Quantity of Oil Separated

| | % Oil Separated After | | $Oil_{max}$ (%) |
|---|---|---|---|
| | 25 min | 75 min | |
| Most stable | Nujol–Triton X-100 | Nujol–Triton X-100 | Nujol–Tween 20 |
| ↓ | Nujol–Tween 20 | Nujol–Tween 20 | Olive oil–SDS |
| | Nujol–SDS | Olive oil–SDS | Nujol–SDS |
| Least stable | Olive oil–SDS | Nujol–SDS | |

tant as used with the other emulsifiers it was so stable as not to give reliable quantitative data.

At the concentrations used, Triton X-100 gave the emulsion separating the least oil whether results are compared after long or short periods of centrifugation. The inversion in order of stability of olive oil–SDS and Nujol–SDS emulsions compared after 25 and 75 min of centrifugation arises because the olive oil emulsions separate oil faster than the Nujol emulsions initially but then the rate decreases markedly with time (i.e., as the per cent of oil separated increases), whereas Nujol emulsions separate less oil initially but continue to separate it at a constant steady-state rate over the period of these experiments.

The maximum amount of oil separated at 39,460 rpm (% $oil_{max}$) was determined experimentally for Nujol–SDS emulsions (Fig. 1) and by extrapolation of the empirical equation (eq 1) in the case of Nujol–Tween 20 and olive oil–SDS emulsions. No value can be reported for Nujol–Triton X-100 or Nujol–CPC emulsions since, in these cases, ultracentrifugation was not carried out for a sufficiently long time to reach a limiting oil separation experimentally nor did the data conform to the empirical equation which would have made calculation of an extrapolated value possible. It is worth noting here in Table I that the differences between the presumed maximum amounts of oil separable from the emulsions with different stabilizers are very large, as contrasted with the smaller differences found at shorter time intervals and the near-identity of Nujol–Tween 20 and Nujol–SDS after 25 min, or of olive oil–SDS and Nujol–SDS after 75 min.

Much the same difficulty is found if rates of oil separation are used as the criterion of emulsion stability, as summarized in Table V derived from the data of Table II. These values were obtained simply as the slope of the straight line of oil separated *vs.* time (region II of Fig. 1) in the case of Nujol–SDS emulsions. For Nujol–Tween 20 and olive oil–SDS emulsions, they were easily calculated by eq 2, since the data con-

Table V

Order of Stability Based on Instantaneous Rate of Separation of Oil

| | Rate of Separation in % Oil Per Minute After | | |
|---|---|---|---|
| | 25 min | 75 min | 100 min |
| Most stable | Nujol–Triton X-100 | Nujol–Tween 20 | Nujol–Tween 20 |
| ↓ | Nujol–Tween 20 | Nujol–Triton X-100 | Nujol–Triton X-100 |
| | Nujol-SDS | Olive oil–SDS | Olive oil–SDS |
| Least stable | Olive oil-SDS | Nujol-SDS | Nujol-SDS |

formed to the empirical eq 1. For Nujol–Triton X-100 and Nujol–CPC emulsions, they were obtained from the slopes of the graphically determined tangents to the curves of per cent oil separated *vs.* time at the indicated times of centrifugation.

The inversions in apparent order of effectiveness of the different emulsifying agents with time is due to the differences in shape of the curves of amount of oil separated *vs.* time. Thus, per cent oil separated per minute remains constant for Nujol–water–SDS emulsions but decreases more rapidly with time for emulsions stabilized with Tween 20 than with Triton X-100, thus showing Triton as the better emulsifying agent when the results are compared after relatively short periods of ultracentrifugation and Tween as superior when results are compared at longer periods. It is worth noting that since the amount of oil separated seems to tend to a constant limit ultimately with all emulsions studied that the rates of oil separation must tend toward zero, and that differences between them will therefore become progressively smaller as results are compared at longer and longer times of centrifugation.

The criterion of rate of oil separation after separation of the same fraction of the oil in different systems is more difficult to apply, as seen in Table III. If too low a fraction is chosen as the basis of comparison, difficulty arises with the less stable emulsions because a steady-state rate subsequent to the initial spurt on starting centrifugation may not yet have been reached. If too high a fraction is used, the more stable emulsions may not separate that much when prepared with the same concentration of surfactant used with the less stable emulsions. Possibly, it would be worth exploring the utility as a criterion of stability of determination of the value of the percent oil separated at the point where the rate of further separation has dropped to some arbitrary low number, greater stability corresponding to reaching a near zero rate of separation after separation of the lesser amount of the oil present.

In conclusion, there appears to be no single universally applicable criterion for the quantitative characterization of the rate of demulsification, unless it were to be an actual specific reaction rate constant for the process, a parameter which cannot be unambiguously obtained from the present data without additional assumptions. It is therefore necessary to choose rather empirically that parameter which seems most likely to provide useful data for the particular application.

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