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Effect of Age on Ultracentrifugal Stability of Liquid Petrolatum–Water Emulsions

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Abstract ☐ The effect of aging over 135 days on the rate of separation of oil from 50% liquid petrolatum–50% water emulsions with both 0.2 and 0.4% sodium dodecyl sulfate (based on the water) was determined in an ultracentrifuge at 25° and 39,460 r.p.m. The concentration of sodium dodecyl sulfate in the equilibrium aqueous phase was also determined. The stability of the emulsion with 0.2% sodium dodecyl sulfate decreased for the first 25 days and thereafter increased with time, with a qualitative change in the mode of loss of oil after 135 days. There was no change in the stability of the emulsion with 0.4% sodium dodecyl sulfate over the same time period. The results with the 0.2% sodium dodecyl sulfate emulsion can be rationalized in terms of an initial increase in drop size with an accompanying desorption of sodium dodecyl sulfate and a decrease in stability, followed by coverage of a greater fraction of the remaining oil–water interface by adsorbed sodium dodecyl sulfate from the more concentrated solution of sodium dodecyl sulfate resulting from the initial desorption.

Keyphrases ☐ Liquid petrolatum–water emulsions—effect of age on stability, ultracentrifugation ☐ Stability of liquid petrolatum–water emulsions—age effect ☐ Emulsions, liquid petrolatum–water—effect of age on stability, ultracentrifugation ☐ Ultracentrifugation—determination of stability of liquid petrolatum–water emulsions

Since the stability of emulsions is of great importance in the pharmaceutical, food, and cosmetic industries, studies elucidating the mechanism of the demulsification process or seeking an accelerated test for determining stability are very useful. In a recent review, Garrett (1) referred to numerous attempts that have been made to characterize emulsions in terms of their drop size or interfacial area, particularly in terms of the change in these quantities with time, as well as by means of the rate of separation in an ultracentrifuge of bulk oil from freshly prepared emulsions. While there have been many studies of drop size and surface area as a function of time (2–10), only limited informa-

tion is available as to the effect of the age of the emulsion on the rate at which oil separates. Merrill (11) found that the amount of oil separated from a relatively unstable butyl phthalate–water–sodium laurate emulsion in a basket centrifuge seemed to vary linearly with time, and the rate *increased* from 0.03 to 0.33 ml./min. over 4 days. Garrett (12) reported a small *decrease* in the rate of separation of oil from a toluene–water–polyoxyethylene stearate emulsion in an ultracentrifuge after 11 days of aging. The present authors (13) found that the ultracentrifugal rate of separation of oil from a liquid petrolatum[1]–water–sodium dodecyl sulfate (I) emulsion increased by about one-third after the emulsion stood undisturbed for 18 days.

The present paper reports data on the rate of separation of oil at 25° in an ultracentrifuge at 39,460 r.p.m. from 50% liquid petrolatum–50% water–I emulsions with the same drop size distribution but containing either 0.2 or 0.4% I on the basis of the aqueous phase after different times of standing up to 135 days. From previous work (8, 14, 15) it was known that initially in such an emulsion with 0.2% I, the oil–water interface would not be completely covered by adsorbed I; whereas at 0.4% initial concentration of I in the aqueous phase, adsorption at the interface would have already reached the saturation limit. The observed differences in the effect of age on the ultracentrifugal stability in the two cases can be explained in terms of this difference between the two systems. However, caution must be exercised in extrapolating the conclusions based on ultracentrifugal data to free-standing emulsions, since the latter consist of spherical

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[1] Nujol.

Table I—Adsorption of I at the Oil–Water Interface in 50% Liquid Petrolatum–50% Water Emulsions (Sample M 062769)

Initial Concentration of I, wt.% in Aqueous Phase	Equilibrium Concentration of I, mmoles/l. (C)	Amount of I Adsorbed, moles/ml. Oil (x/m)	Fraction of Saturation Adsorption
0.20	3.16	3.80×10^{-6}	0.60
0.25	4.41	4.28	0.68
0.30	5.80	4.54	0.72
0.35	7.18	5.00	0.80
0.40	8.83	5.06	0.81
0.45	10.40	5.22	0.83

drops suspended at considerable distances from each other in a continuous medium; in the ultracentrifuge the oil drops are deformed into space-filling globules separated only by very thin films of the aqueous medium, more nearly analogous to a foam (14, 15).

EXPERIMENTAL

Materials and Methods—The same sample of liquid petrolatum (refined mineral oil) was used as in the previous work (13). The sodium dodecyl sulfate (I), Sample P1, also was described previously (13) and was a purified preparation free of inorganic salts and containing not more than 0.05% lauryl alcohol. Distilled water[2] was used without further purification.

Emulsions were prepared and characterized by the methods of Vold and Groot (8, 14). To obtain systems of the same drop size distribution and interfacial area but with varying concentrations of I, four batches of 150 ml. liquid petrolatum and 120 ml. 0.2% I solution were each stirred at 5000 r.p.m. in a counter-rotating mixer[3], passed eight times through a mechanized hand homogenizer[4], and combined into a single stock emulsion. After standing overnight, two 360-ml. portions of this stock emulsion were withdrawn, and 40 ml. of I solution of appropriate concentration was added gently to each so as to obtain 400-ml. samples with a 50:50 oil–water volume ratio and I concentrations of 0.2 and 0.4% on the basis of the aqueous phase. These were then allowed to age undisturbed, and samples were withdrawn periodically for ultracentrifugation and determination of the concentration of I in the equilibrium aqueous phase.

To characterize the degree of fineness of the emulsion quantitatively, the specific interfacial area was determined. This was done as described before (8) by determining the adsorption isotherm for I at the oil–water interface. Forty-five-milliliter samples of the fresh stock emulsion were gently blended with 5 ml. of I solutions of appropriate concentration to give 50% liquid petrolatum–50% water emulsions with concentrations of I between 0.20 and 0.45% on the basis of the aqueous phase, all of the same drop size distribution. After waiting a day for establishment of equilibrium, 40-ml. samples were centrifuged 30 min. at 5000 r.p.m. in a high-speed angle centrifuge[5]. This was sufficient to separate a nearly clear aqueous layer with no visible separation of oil. The aqueous layer was then analyzed for I by titration with cetylpyridinium chloride (8), and the amount adsorbed was calculated from the change from the initial concentration.

All of the emulsion samples were ultracentrifuged at 25° at 39,460 r.p.m. The technique of ultracentrifugation and the treatment of the raw data were the same as in previous work (8, 13).

RESULTS

Adsorption of I at the Oil–Water Interface—The extent of adsorption of I at the oil–water interface in the emulsion used in this work is given in Table I as a function of the concentration of I in the aqueous phase. When plotted according to the linear form of the
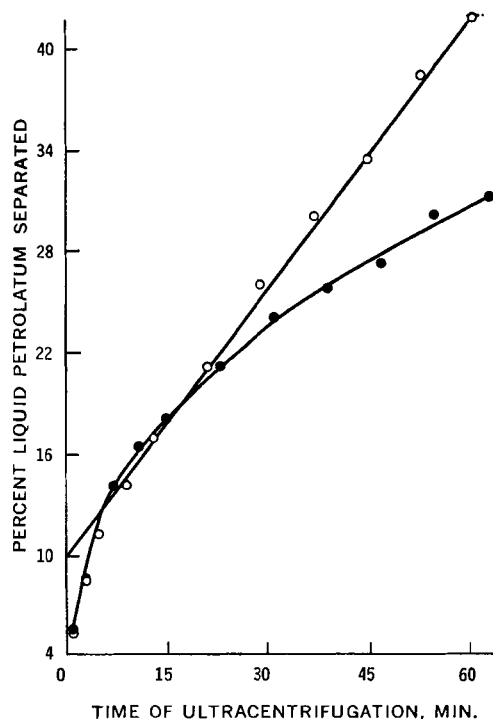
Figure 1—*Ultracentrifugal separation of oil from fresh and aged 50% liquid petrolatum–50% water–0.2% I emulsions. Key: O, after 1 day; and ●, after 135 days.*

Langmuir equation:

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{C}{a} \qquad (\text{Eq. 1})$$

a good straight line is obtained which permits evaluation of a, the extrapolated monolayer capacity, and b, the adsorption energy parameter, from the slope and the intercept. Dividing the actual quantity adsorbed at any solution concentration by the amount required hypothetically for formation of a close-packed monolayer (the monolayer capacity) gives the values in the last column for the fraction of saturation adsorption.

The data show, in accord with previous results (8), increasing adsorption with more complete coverage of the interface by adsorbed film until the CMC is reached (8.1 mmoles/l.) and essential constancy thereafter. They also demonstrate that in the case of emulsions prepared with an initial concentration of 0.4% I on the basis of the aqueous phase, the amount of I adsorbed at the interface has already reached its maximum value and will be independent of any further increase in concentration. It is tempting to speculate that this corresponds to complete coverage of the interface with adsorbed I, since it was also noted in earlier work (8, 14) that saturation was reached at values somewhat less than those corresponding to the monolayer capacity as calculated from the Langmuir equation. This peculiarity may be due to difficulties with the extrapolation of the Langmuir equation since, although it represents the present data very accurately, it is based on site adsorption of neutral molecules whereas the present case deals with charged species at a mobile interface.

From the observed saturation adsorption, taking 54 Å^2 as the area of the adsorbed I molecule in the close-packed film (16), the specific interfacial area of the emulsion used in the present studies (Sample M 062769) is $2.04 \times 10^4 \, \text{cm.}^2/\text{ml. oil}$.

Effect of Age on Ultracentrifugal Stability of 0.2% I Emulsions—Table II presents the data on the effect of age on the rate of separation of oil from emulsions stabilized with 0.2% I and on the equilibrium concentration of I in the aqueous phase in these emulsions. As is seen in Fig. 1, with freshly prepared emulsions the percent oil separated increases linearly with time after an initially more rapid increase, corresponding to a constant rate of separation given by the slope of the line. The extrapolated amount separated at zero time, corresponding to initially poorly emulsified oil or to rapid

Table II—Effect of Aging on the Ultracentrifugal Stability of a 50% Liquid Petrolatum–50% Water–0.2% I Emulsion (Sample M 062769)

Age, days	Rate of Separation of Oil, % Oil/min.	Extrapolated Percent Oil at Zero Time	Equilibrium Concentration of I, mmoles/l.
1	0.50	11.2	3.16
9	0.58	9.4	3.16
16	0.62	13.7	3.28
25	0.66	11.6	3.31
42	0.52	7.5	3.57
72	0.47	6.6	—[b]
135	0.31[a]	13.0	—[b]

[a] Rate measured at 25 min. of ultracentrifugation. [b] Samples lost before analyses were made.

Figure 2—*Effect of age on the ultracentrifugal rate of separation of oil from 50% liquid petrolatum–50% water emulsions stabilized with 0.2 or 0.4% I. Key: O, 50% liquid petrolatum–50% water–0.2% I; and ●, 50% liquid petrolatum–50% water–0.4% I.*

separation resulting from formation of unprotected new interface on starting centrifugation (15), is obtained from the intercept of the line with the zero-time axis. Obviously, from the results shown in Table II, there is no correlation between this quantity and the age of the emulsion.

Similar behavior was found at ages up to 72 days. However, after 135 days the rate of separation of oil decreased with increasing time of centrifugation (Fig. 1) following a curve well represented by the empirical equation (13):

$$\frac{t}{\% \text{ oil}_{\text{sep.}}} = \frac{1}{b \cdot \% \text{ oil}_{\text{max.}}} + \frac{t}{\% \text{ oil}_{\text{max.}}} \quad \text{(Eq. 2)}$$

where $\% \text{ oil}_{\text{sep.}}$ is the amount separated at time t, b is a constant, and $\% \text{ oil}_{\text{max.}}$ is the extrapolated maximum amount separable at the given speed. Values of b and $\% \text{ oil}_{\text{max.}}$ are simply obtained from the slope and intercept of the straight-line plot of $t/\% \text{ oil}_{\text{sep.}}$ *versus* t. This qualitative change in behavior strongly suggests that as aging occurs, a different step becomes rate determining in the complicated series of processes resulting ultimately in separation of oil.

From the linear plot of the data for the 135-day-old emulsion, the calculated value of $\% \text{ oil}_{\text{max.}}$ is 40.3%, which is markedly less than the actual amount of liquid petrolatum separated in a 6-hr. run on a fresh emulsion (91.5%). The rate of separation of liquid petrolatum from this emulsion, calculated from the slope of the tangent to the curve at the particular time, is, respectively, 0.31, 0.20, and 0.18% oil/min. after 25, 50, and 75 min. of ultracentrifugation. Even the fastest of these rates is substantially slower than the rate of separation of oil from the emulsion aged 72 days (0.47% oil/min.).

The rate of separation of oil is plotted as a function of the age of the emulsion in Fig. 2. It is evident that the rate first increases with age up to 25 days and then decreases with further aging.

Table II shows that as the emulsion ages, the concentration of I in the aqueous phase increases. This implies that the average drop size is increasing with time, with a resultant decrease in the total area of oil–water interface and consequent desorption of I. However, the accuracy of the present analytical data is not sufficient to permit quantitative comparison of changes in equilibrium concentration of I in the aqueous phase with changes in the rate of separation of oil. Moreover, the possibility cannot be excluded that separation of oil may be occurring exclusively at the bulk oil–emulsion interface, with desorbed I percolating down to the underlying aqueous layer.

Effect of Age on Ultracentrifugal Stability of 0.4% I Emulsions—The effect of age on the stability of emulsions stabilized with 0.4% I and on the concentration of I remaining in the equilibrium aqueous phase is given in Table III. In all cases the amount of oil separated varied linearly with time after the first few minutes, corresponding to a constant rate independent of time of centrifugation. Since both the rate of separation of oil and the composition of the equilibrium liquid remained constant over the whole period, it appears that there was no change in the physical nature of the emulsion over the 135-day period.

Unlike previous results with emulsions of similar composition (8), in most cases the present emulsions underwent a short induction period before any oil separated in the ultracentrifuge; *i.e.*, the linear plot of amount of oil separated *versus* time of ultracentrifugation extrapolated to a negative intercept at zero time. Similar results
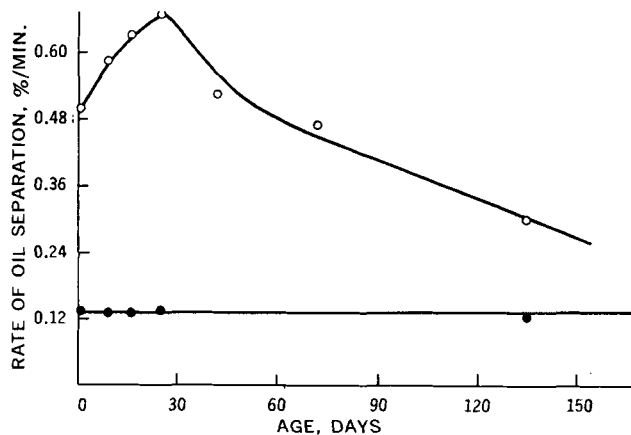
have been found frequently with other relatively stable emulsions (17).

DISCUSSION

These results are of importance primarily because of the greater confidence they engender in using the general theories of emulsion stability to interpret the actual behavior of specific systems. The chief points to be explained are the initial decrease in stability followed by an increase in stability with time in the case of 50% liquid petrolatum–50% water emulsions stabilized with 0.2% I on the basis of the aqueous phase; the contrast with the behavior of the same composition stabilized with 0.4% I where the stability remained unchanged with age; and the qualitative change in shape of the percent oil separated–time of ultracentrifugation curve occurring some time after the 0.2% I emulsions had aged for 42 days. The results are explicable in terms of the hypothesis that in the case of emulsions of this type, the stability varies inversely as the drop size, and that the rate of separation of oil in the ultracentrifuge is directly proportional to the area of the oil–water interface not covered by an adsorbed film of emulsifier. This area of bare surface can be obtained from the fraction of saturation adsorption and its dependence on the concentration of I in the solution.

In the system with 0.2% I, it is clear from Table I that there is a considerable bare oil–water interface. On aging, it can be assumed that some coalescence is occurring, with resultant formation of larger drops and a consequent desorption of I because of the reduction in the total area of the oil–water interface. If it is correct that larger drops result in an intrinsically less stable emulsion (1, 15, 18), this would account qualitatively for the observed initial increase in rate of oil separation with increasing age of the emulsion. The observed decrease in ultracentrifugal stability with decreasing specific interfacial area (15) supports this conclusion, as does Garrett's (1) hypothesis that perhaps only emulsions with drop sizes below some maximum allowable value will be stable.

However, as this process continues, the concentration of I in the aqueous lamellae between the remaining drops increases. This

Table III—Effect of Aging on the Ultracentrifugal Stability of a 50% Liquid Petrolatum–50% Water–0.4% I Emulsion (Sample M 062769)

Age, days	Rate of Separation of Oil, % Oil/min.	Extrapolated Percent Oil at Zero Time	Equilibrium Concentration of I, mmoles/l.
1	0.135	−1.2	8.83
9	0.132	−0.8	8.77
16	0.130	−1.0	8.77
25	0.134	−1.5	8.79
135	0.120	0.3	—[a]

[a] Sample lost before analyses were made.

would necessarily cause an increase in the amount of I adsorbed on their surface and a consequent decrease in the fraction of the total oil–water interface not covered by adsorbed emulsifier (Table I). Since it has already been shown that there is an inverse linear relation between the rate of separation of oil and the fractional saturation of the interface with adsorbed I (14), this increased adsorption of I would result in a decreased rate of separation of oil. Recent experiments (13) on the effect of lauryl alcohol on the stability of these emulsions confirmed that the rate of oil separation depends simply on the fraction of the surface not covered by adsorbed film.

Therefore, it appears that for the first month the effect of the gradual increase in drop size is predominant, resulting in a decrease in stability with age, but that subsequently the effect of readsorption of I due to its slowly increasing concentration in the aqueous phase becomes dominant, with a resultant increase in stability on further aging. The analytical data on the equilibrium concentration of I in the aqueous phase afford further qualitative support for this interpretation, since the value increases progressively with time. However, one might have expected a more continuous rate of increase and a larger change in magnitude in view of the substantial change in rate of separation of oil. Possibly there may have been some difficulty in establishing equilibrium conditions, which require transport of I in both directions between the bulk aqueous phase and the interlamellar aqueous layers separating the deformed oil drops in a centrifuged emulsion.

The absence of change in stability of the emulsion with initial 0.4% I would be predicted by this same reasoning. Here the adsorption data (Table I) show that the oil–water interface is already as saturated with adsorbed I as it will ever become, despite a further increase in concentration of I in the solution. The constancy of the concentration of I in the aqueous phase independent of time (Table III) shows that there has been no net change in interfacial area with time, with the inference that the drop size distribution has remained unaltered. Hence, since neither drop size nor fractional saturation of the interface with adsorbed I has changed with time, it would be expected that the ultracentrifugal stability would remain constant. This is exactly what happens (Fig. 2 and Table III).

The qualitative change in the time dependence of the rate of separation of oil in the 135-day-old 0.2% I system as contrasted with the younger emulsions is not yet fully understood. Constancy of rate, as found with the fresher emulsions, suggests that initially the rate-determining step during centrifugation of such emulsions may be the rate at which coalescence occurs at the interface between the creamed emulsion and bulk oil (12, 15); whereas in older emulsions the rate of coalescence, if any, between "drops" within the bulk of the creamed emulsion may have an effect. However, there is not yet any unambiguous direct evidence bearing on this point.

Formerly, the rate of separation of oil from the oldest emulsion conformed to the equation:

$$\frac{\% \text{ oil}_{sep.}}{\% \text{ oil}_{max.}} = \frac{bt}{1 + bt} \qquad \text{(Eq. 3)}$$

as already stated. If bt is sufficiently less than unity, this reduces to:

$$\frac{\% \text{ oil}_{sep.}}{\% \text{ oil}_{max.}} = bt \qquad \text{(Eq. 4)}$$

or, more simply, $\% \text{ oil}_{sep.} = Kt$, which is the linear relationship actually found with the younger emulsions. Since the value of t is not particularly small, the value of the empirical constant, b, must be extremely small to achieve this result.

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