On the Mechanism of the Coalescence of Drops at an Oil-Water Interface*

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In regard to the stability of emulsions¹⁾, the following three phenomena should be considered; (1) concentration of the dispersed droplets towards the top or the bottom of the emulsion, on account of a difference in density between the liquids, which is known as "creaming" or "settling", (2) flocculation or clumping of the dispersed droplets to form larger aggregates, without the droplets actually losing their identity, (3) coalescence of droplets to form larger ones and eventually bulk liquid.

Of these phenomena, only the third represents instability in the sense of the reverse process of dispersion. Therefore, the third phenomenon may be the most important clue in order to discuss the stability of emulsions. From this point of view, coalescence of drops at an oil-water interface has been studied. A more reasonable mechanism of the coalescence of drops at the oil-water interface than ever previously accepted is proposed.

Experimental

Materials.—The following surfactants were used as the emulsifier.

Anionic surfactant—Sodium dodecyl sulfate (SDS), (purity, 98.9 %), was offered by the Kaō Sekken Co.

Cationic surfactant—Cetyl-oxymethyl-trimethyl-ammonium chloride (CEA), purity, $\simeq$100 %, was kindly offered by Professor Nirō Murata of our University.

Non-ionic surfactant—Emulgen 120 (polyoxyethylene-lauryl ether), HLB, 15.5; Emulgen 220 (polyoxyethylene-cetyl ether), HLB, 14.0; Emulgen 408 (polyoxyethylene-oleyl ether), HLB, 9.0; Emasol 320 (sorbitan di-stearate), HLB, 2.7; Emasol 410 (sorbitan mono-oleate), HLB, 5.9, were offered by the Kaō Sekken Co.

Cholesterol was a product from Wakō Pure Chemicals Ltd.

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1) C. G. Sumner, "Clayton's the Theory of Emulsions and their Technical Treatment", J. & A. Churchill Ltd., London (1954), p. 198.

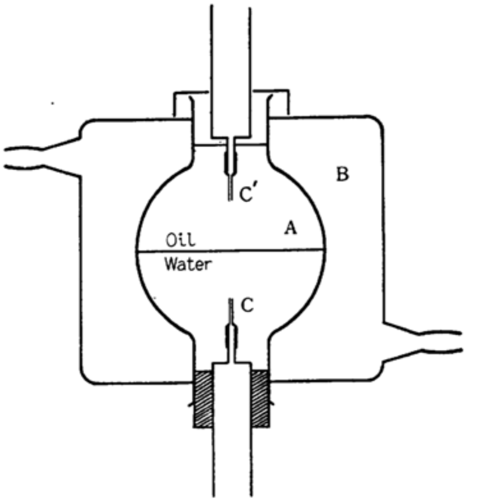

Fig. 1. Apparatus for determining the life-time of drops.

Apparatus and Procedure.—To measure the stability or persistency of water or oil drops at the oil-water interface, an apparatus shown in Fig. 1, similar to that of Cockbain and McRoberts2) was used. It consists of a spherical part A (its diameter, 5 cm.) in which the oil-water interface is made, a thermostatted water jacket B, and tips, C and C' to form oil or water drops respectively. Both C and C' consist of three parts, a syringe (capacity, 2 cc.), a syringe needle with flattened tip, and a micrometer which was modified to push the syringe piston and at the same time to measure the distance travelled by the piston. A drop which was detached from the top of C or C', will ascend or descend in the vessel A and come into contact with a plane oil-water interface and then will coalesce after a certain time. The time of coalescence, life-time of drop, was measured with a stop watch and was taken as the interval in which one drop appears to be in contact with the interface and coalesces. In some cases, the drop did not completely coalesce in a single stage with the bulk liquid phase; partial coalescence occurred leaving a smaller drop, which also partially coalesced after some longer time than in the case of the parent drop, leaving still a smaller drop. In such cases, the time required for the first stage was taken as the life-time of the drop. Each drop was separately formed and its life-time was measured. Drops used for one experiment were 30 to 40.

Results

The life-time of drops at the interface.—The experiment has been made with benzene-water system, in which the surfactant was dissolved in either liquid as an emulsifier. In the given system, the life-times of individual drops were not constant. When N the number of drops whose life-time$\geqq$time t, were plotted in logarithmic scale against t, it was observed that most plots were found to be linear, as shown AB in Fig. 2, in agreement with the results obtained by Cockbain et al.2).

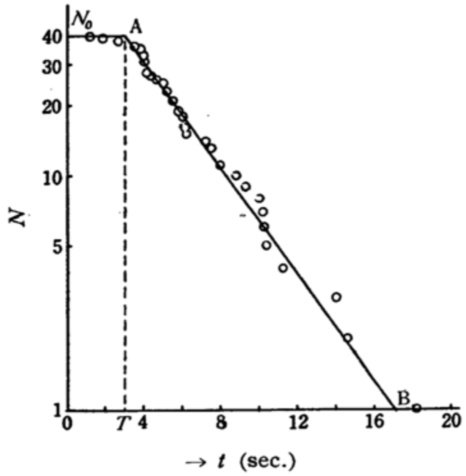

Fig. 2. Typical relationship between N (in logarithmic scale) and t; water phase—pure water, oil phase—2.0 g. cholesterol/100 cc. benzene, drop—pure water drop, temperature—25°C.

Then, the value T was estimated as the time of the intersection (A) of the AB with the straight line drawn parallel to the t axis through N_0, which is the total number of drops experimented. The experimental values are given in Table I. T_O and T_W are the values of T, for oil and water drops respectively.

Behavior of drop at the interface.—Two series of experiments on the behavior of water drop at the oil-water interface were made. First, in order to observe the behavior of the water drop in detail, the drop was colored with various dyes or colored inorganic salts. The experiments were made in the combinations of a drop and an oil-water interface with equal or different interfacial tension to the drop. The behavior of the colored drop is schematically shown in Fig. 3. When a drop comes into contact with an oil-water interface, the interface is deformed and consequently a concave surface is formed around the drop [(I) of Fig. 3]. After a while, coalescence of the drop occurs. If the interfacial tension around the drop (σ_d) is lower than that of the oil-water interface (σ_s), the process of coalescence will proceed as follows.

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2) E. G. Cockbain and T. S. McRoberts, *J. Colloid Sci.*, 8, 440 (1953).

TABLE I

T_W AND T_O OBTAINED WITH BENZENE-WATER SYSTEMS USING VARIOUS SURFACTANTS AS THE EMULSIFIER

Surfactant (dissolved phase)	Concn. of surfactant (g./100 cc.)	Water drop		Oil drop		Temp. (°C)
		Drop volume (cc.)	T_W (sec.)	Drop volume (cc.)	T_O (sec.)	
None	—	0.03	2	0.02	3	20
SDS	1.0	0.003	3	0.004	3×10^2	15
(water)	1.0	0.003	4	0.004	1×10^2	25
	0.1	0.009	1	0.01	2×10	15
	0.1	0.008	1	0.01	2×10	25
	0.01	0.02	1	0.03	5	15
	0.01	0.03	1	0.03	5	25
Emulgen 120	0.02	0.02	3	0.03	2×10	15
(water)	0.02	0.02	1	0.03	1×10	25
Emulgen 220	0.02	0.02	1	0.02	2	15
(water)	0.02	0.02	1	0.02	2	25
Emulgen 408	0.02	0.03	0.5	0.03	3	15
(benzene)	0.02	0.03	0.4	0.03	3	25
Emasol 320	0.02	0.03	0.6	0.03	2	15
(benzene)	0.02	0.04	1	0.04	4	25
Emasol 410	0.02	0.02	2×10	0.02	8	15
(benzene)	0.02	0.02	3	0.02	2	25
Cholesterol	2.0	0.02	3	0.03	2	15
(benzene)	2.0	0.02	3	0.03	1	25
	0.5	0.03	2	0.04	3	15
	0.5	0.03	1	0.04	3	25

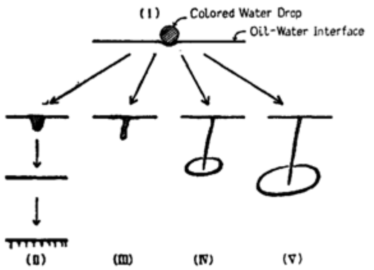

Fig. 3. Schematic presentation of the behavior of water drop at the interface.

Although the interface which is in contact with the drop, is deformed momentarily, the colored liquid can not penetrate into the bulk water phase through the interface. The momentarily deformed portion of the interface is restored to the original flat state and at the same time the colored liquid spreads along the interface, as if it soaked into the interface, and a layer of colored liquid is formed. After the formation of the colored layer, the colored liquid diffuses into the bulk water phase as illustrated in (II) of Fig. 3. If σ_d is approximately equal to σ_s or higher than it, the most part of the colored liquid penetrates into the bulk water phase through the interface, and the rest spreads along the interface as shown in (III) or (IV) of Fig. 3. The rate of penetration of the colored liquid increases with rise of the value, σ_d. The behavior of a colored liquid, having the greater rate of penetration at the moment of coalescence is shown in (IV) and (V) of Fig. 3. The formation of a ring of the colored liquid is observed around the straight penetrating stream of the same colored liquid. The last case (V) illustrated in Fig. 3 is the extreme one of the (IV), where $\sigma_d \gg \sigma_s$, and the spreading of the colored liquid along the oil-water interface is hardly ever observed.

From the above observations, it may be concluded that the main process of the coalescence of a drop at an oil-water interface, is the formation of a defect in the emulsifier layer around the drop at the portion in contact with the interface, and it is followed by the flowing out of the liquid of the drop through the defective portion. If the flowing liquid can make a hole in an oil-water interface owing to the pressure of flowing, the liquid will penetrate into the bulk liquid phase of the same kind. If not, the liquid will spread along the oil-water interface. Here it is supposed that the main factor which may determine the life-time of a drop at an oil-water interface would be the characteristics of the layer of emulsifier around the drop.

The second series of experiments have been carried out in order to investigate the mechanism of the coalescence of a drop from another standpoint. Pure benzene and distilled water or bentonite suspension were used as the oil and the aqueous phase respectively. A drop (volume$\fallingdotseq$0.002 cc.) of 10^{-4} mol./l. solution of CEA was made to flow out from C′ in Fig. 1. When distilled water was used as the aqueous phase, the gradual increase in the life-time of the drop was observed as dropping proceeded, but this regular increase was only until nearly the tenth drop. On the contrary, when bentonite suspension was used as the aqueous phase, the same phenomenon could not be observed.

In these experiments, σ_d is lower than σ_s. Therefore, according to the results obtained with the colored drop mentioned above, it may be concluded that the liquid of the drop spreads along an oil-water interface and thereafter diffuses into the bulk aqueous phase as shown in (II) of Fig. 3. It may be assumed that, compared with the time required for a series of experiments, the diffusion rate of the liquid which forms the drop into the bulk aqueous phase may be slow, so that the marked decrease in the interfacial tension of an oil-water interface may be induced with the successive coalescence of the drop at the interface at least in the initial period of the experiment. The conclusion may be further developed that the lower the interfacial tension of an oil-water interface, the longer the life-time of the drop being in contact with that interface, provided that the interfacial tension around the drop remains constant. The reason why the life-time does not increase as dropping proceeds with bentonite suspension, may be as follows. The cationic surfactant, CEA dissolved in the drop solution may be fixed on the bentonite particles owing to the cationic exchange reaction or adsorption, so that the decrease in the interfacial tension of an oil-water interface may be reduced considerably compared with the above case without bentonite.

Discussion

On the experimental method.—Both Cockbain et al.[2] and Gillespie and Rideal[3] found with benzene-water system that the stability of the drops was markedly increased by putting a cover on A (Fig. 1). The latter authors found that the drops become more stable when the whole apparatus is further surrounded by an air bath whose temperature is approximately the same as that of the water jacket B. These effects were attributed to the elimination of convection currents at the interface. In the present experiments, similar phenomena were also observed when measurements were made under a tightly-fitting cover. However, in the present investigation, where the value of T is simply taken to discuss the observed data and also the singular significant figure is taken to represent the magnitude of the value T, the influence of the above operation on the experimental results can be neglected.

Cockbain et al. observed that the stability of the drops had not been markedly affected by volume in the range 0.0005$\sim$0.01 cc., whereas below 0.0005 cc. the stability had increased rapidly with decreasing volume. On the other hand, Gillespie et al. reported that in the absence of surfactant the stability of the drops had increased with increasing volume in the range 0.014$\sim$0.38 cc. (drop radius; 0.15$\sim$0.45 cm.). In the present experiments, the value of T was not markedly affected by the change of the drop volume as shown in Table I. where singular significant figure was taken to represent the magnitude of the value of T.

In order to obtain a clean oil-water interface in the vessel A, the method by Cockbain et al. was employed. But our experiences showed that it is not necessary to be extremely careful for the cleanliness of the interface to obtain well reproducible values of T. In the present experiments the reproducibility was satisfactory with T in any case.

On the process of the coalescence of a drop.—Cockbain et al. have suggested that the life-times of the drops are determined by two distinct processes, viz., drainage of the continuous phase from the space between the drop and the plane oil-water interface, followed by rupture of the adsorbed film of surfactant. They

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[3] T. Gillespie and E. K. Rideal, *Trans. Faraday Soc.*, **52**, 173 (1956).

concluded that the main factor determining stability is the resistance to wetting of segments of the adsorbed film by the discontinuous phase. But it was not substantiated whether both the films, viz. the film around the drop and that of the plane oil-water interface, must be wetted by the discontinuous phase simultaneously or only one of them.

According to Gillespie et al., the coalescence of a drop at an oil-water interface is very unlikely until the film formed between the drop and the interface has been drained to a certain thickness for which it takes a certain time. The coalescence of a drop will occur owing to the rupture of the film which will be brought about by thermal and possibly mechanical disturbances.

In contrast to the processes proposed by Gillespie et al., the present experiments showed that the main process of the coalescence of a drop at an oil-water interface is the formation of a defect in the emulsifier layer around the drop at the portion in contact with the interface. It is consequently concluded that though the initial process, the drainage of the continuous phase from between the drop and the interface, will occur in the same manner as proposed by them, the final process which includes the main process as mentioned above, will proceed in the following manner.

When a defect has been formed in the emulsifier layer around the drop at the portion in contact with the plane oil-water interface, the local disturbance will be induced at that portion and this will be promoted by thermal or mechanical disturbances such as convection currents etc. Consequently the liquid of the drop will flow out through the defective portion owing to the internal pressure due to the interfacial tension around the drop itself. At the same time, since the interfacial tension of the defective portion becomes higher than that of the other portion of the same drop which is surrounded by the emulsifier layer, the transference of the emulsifier to the defect from the other portion of the drop interface will take place to repair the defect with the new emulsifier layer. In this case, so far as the repairing of the defect with new emulsifier layer has been completed before the arrival of the flowing liquid at the oil-water interface, the coalescence of the drop will not occur. If not, the reformation of emulsifier layer around the drop becomes impossible and the liquid of the drop will flow out through the defective portion progressively and the interface will be exposed to the pressure of the flowing liquid. At this stage if the flowing liquid can make a hole in an oil-water interface owing to the pressure of flow, the liquid will penetrate into the bulk liquid phase of the same kind. If not, the liquid will come into direct contact with the bulk liquid phase of the same kind. As seen from our experimental data using a drop of colored solution, the latter phenomenon can be observed only in the case where σ_d is less than σ_s. Therefore, when the liquid of the drop comes into direct contact with the bulk liquid, it may be considered that the interfacial tension between the former and the latter liquid would be nearly null. In the present case, the interfacial tension between the liquid of the drop and the original continuous phase liquid (σ_d) is lower than that of the oil-water interface (σ_s), so that the liquid of the drop spreads along the oil-water interface and produces the new oil-water interface between the spreading liquid and the original continuous phase liquid, resulting in the disappearance of the original interface.

However, also in the present experiments, it can be still expected that the probability of coalescence will be small until the continuous phase between a drop and an interface has been drained to a certain thickness. Therefore, the values of T may also depend on a factor which is influenced by the rate of drainage of the continuous phase.

On the treatment of the experimental data.—Cockbain et al. have found that after a time t_D (drainage time), $\ln N = -kt + \text{constant}$ holds. The quantity t_D corresponds to T in the present experiments. The constant k (rate constant for the film rupture) will be obtained from the slope of AB in Fig. 2. These authors have discussed the stability of drop using both the values t_D and k. Gillespie et al. have further discussed the probable effect of electric double layer forces, electroviscosity and other factors on the values t_D and k. In the present report, however, an attempt was made to discuss the stability or persistency of drops only referring to the values of T, from the following reasons.

(1) The well-reproducible values of T can be readily obtained, as shown in the above discussion, while the values

of k are readily influenced even by the slight differences in the experimental conditions. Therefore, in order to obtain the significant values of k, the experimental conditions must be more strictly controlled and moreover, according to Gillespie et al., the measurements of the life-time must be made with from 100 to 200 drops.

(2) T denotes, as will be stated later, the time during which most drops can exist without coalescence, while k is a rate constant for the coalescence after time T. Consequently, the stability or persistency of drops may be primarily defined by the value of T and the contribution of k to the same problem is by far less important.

On the life-time of drops.—From the results mentioned above, it is concluded that the values of T are determined by two factors, viz., drainage of the continuous phase from between the drop and the plane oil-water interface, and formation of a defect in the emulsifier layer around the drop.

Now let us consider the latter factor, irrespective of the former one. In the present experiments it was assessed from 30 to 40 drops to obtain the value of T. The number of drops which coalesced within the time T was from 1 to 5 drops. Hence, it may be said that the value of T is the life-time at which the probability of coalescence is about 0.1.

Subsequently, the factors which affect the coalescence of drops will be considered. When a drop comes into contact with an oil-water interface, the interface will be deformed and consequently a concave surface will be formed around the drop as illustrated in (I) of Fig. 3. In this case, it is assumed that the drop remains on the interface at equilibrium position without deformation and the radius of curvature of the concave surface (a) is equal to the radius of the drop (r) itself. The area of the concave surface at the interface which comes into contact with the drop is A. For small drops it may be supposed that this contact portion is a plane surface, since the contact portion itself must be quite small. Then, the following relation is given, since a equals to r

$$\frac{4}{3}\pi dgr^3 \fallingdotseq \frac{2\sigma_s}{a}\cdot A = \frac{2\sigma_s}{r}\cdot A \qquad (1)$$

where d is the difference in the density between the drop and the surrounding medium and g the gravity constant. We see that the contact area A is proportional to r^4.

Next, the probability of the formation of a defect in the emulsifier layer around the drop will be considered. It may be assumed that this probability is constant anywhere around the surface of the drop, since no deformation of the drop is considered. So that the probability of forming the defect at the portion of the drop in contact with the interface will be proportional to A/B, where B is the total surface area of the drop and proportional to r^2. Therefore, the probability of forming a defect at the contact portion of the drop and the interface should be proportional to r^2. However, it may be suggested that the above condition is strictly satisfied only when the diameter of the drop is smaller than 1 mm., which can be deduced from the data obtained by Cockbain et al. or by the present investigation on the effect of the drop volume and also by the calculated values of A using relation (1) with the substitution of appropriate values for σ_s and r.

The experimental results reported in page 239 that if σ_d is smaller than σ_s and at the same time σ_d and the drop volume are constant, the lower the interfacial tension of an oil-water interface, the longer the life-time of the drop being in contact with the interface may be explained as follows.

From the relation (1), it may be expected that the higher the σ_s, the smaller the A; consequently the life-time of a drop would increase. The experimental result is, however, contrary to the above expectation. This inconsistency may be caused by the assumption, viz. $a=r$, and this assumption will not be satisfied under the present experimental conditions. Here it should be expected that a changes with the change of σ_s and consequently a is not equal to r. Therefore, if the value of σ_s is higher, the value of a also becomes greater and consequently variation of the value A with the variation of σ_s will be smaller than that given by the relation (1).

If the area A is constant, the deformation of the drop corresponding to the change of a must be expected. Consequently the strain will be induced on the emulsifier layer of the drop at the contact portion. Under these conditions, the higher the σ_s, the larger the difference between a and r and the larger the strain induced on the emulsifier layer. On the other hand, it is expected that a defect on the emulsifier layer will be more readily formed at the portion on which the strain is induced. As a conclusion, it is expected that when the drop volume and σ_d are constant and σ_d is less than σ_s, the lower the value of σ_s, the longer the life-time of the drop in accordance with the present experimental results.

The above discussion has been presented without the consideration on the drainage process of the continuous phase from between the drop and the plane oil-water interface. However, the time necessary for this drainage process is also included in the values of T, so that it must also be taken into consideration, when the meaning of the value T is strictly discussed. On the other hand, it is hard to say that the values t_D obtained by Cockbain et al. and also probably by Gillespie et al. are determined only by the drainage process. Therefore, the extent of the contribution of the drainage process to the value T, may be estimated from the minimum value of the life-time assessed with a number of drops. Since the life-time of each drop is short in the system without surfactant, the time necessary for the net drainage will be obtained from the data assessed from 100 to 200 drops in each experiment such as in the case carried out by Gillespie et al.

According to Gillespie et al. the time required for drainage process t_D decreases with the decrease in the drop volume. On the other hand, from the results obtained by Cockbain et al. and also by the present authors, it was shown that if the diameter of the drop is about 1 mm. or less, the stability or the life-time increases rapidly with the decrease of the volume. From these results, it is concluded that the time required for drainage with such droplets as in ordinary emulsions whose diameters are in the range of a few μ, will be practically negligible, compared with their whole life-times.

Cockbain et al. have reported that the stability of the drops was not markedly affected by volume in a fairly wide range, whereas below a certain volume the stability increased rapidly with decreasing volume. From the above results, it is concluded that in the range of the volume at which the stability of the drops is nearly constant, the factor increasing the life-time will be compensated by that decreasing it. Therefore, it may be said that one can estimate the life-time of a drop less than 1 mm. in diameter by using the value of T in the present investigation or t_D obtained by Cockbain et al., regarding it as the one which does not include any contribution from the factor of the drainage process. Now, if it can be assumed that the life-time of the drops is determined only by the value of A/B, it may be suggested that when the experiments are made with the drops of 1 μ in diameter under the same condition as the present investigations, the values of T will be about 10^6 times greater than those listed on Table I.

From the discussions mentioned above, the main process of the coalescence of a drop at an oil-water interface may be said to be the formation of a defect in the emulsifier layer around the drop at the portion in contact with the interface. Consequently, the more readily the emulsifier (surfactant) escapes from the oil-water interface around the drop, the more readily the defect on the emulsifier layer will be formed and also the shorter the life-time of the drop will be.

To consider the stability or persistency of the droplets in the ordinary emulsions (droplet diameter=a few μ) referring to that of the drops as discussed above, it must be first examined whether the escaping tendency of the emulsifier from the oil-water interface of the former small droplets is the same as that of the latter. This can be studied by the following Kelvin-Gibbs relation[4,5], where the electric double-layer effect can be neglected;

$$\ln\frac{S_r}{S}=\frac{2\sigma M}{dR\Theta r} \tag{2}$$

where

S_r=escaping tendency of emulsifier molecule from interface of radius r (r is negative for concave interface).

S=escaping tendency from plane interface.

σ=interfacial tension.

M=molecular weight of emulsifier (surfactant).

d=density of emulsifier molecule at the interface.

R=gas constant.

Θ=absolute temperature.

After the examination with relation (2), having substituted the appropriate values into (2), it was found that the variation of S_r/S with r becomes appreciable only when r is less than $10^{-4}\sim10^{-5}$ cm. So that, it

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[4] R. M. Wiley, *J. Colloid Sci.*, 9, 427 (1954).

[5] E. A. Guggenheim, "Thermodynamics, an Advanced Treatment for Chemists and Physicists", Interscience Publishers Inc., New York, (1950), p. 41.

is concluded that the escaping tendency of emulsifier from the interface of the large drops investigated in the present experiments, is practically the same as that of the small droplets with the diameter of a few μ. Referring to effects of the electric double layer on the solubility⁶⁾, the effects of the electric double layer on the escaping tendency of the emulsifier from the oil-water interface may be neglected under the present experimental conditions.

According to the relation (2), the escaping tendency of the emulsifier from the interface to the water or oil phase is independent of the state of the interface, whether it is convex or concave. Therefore it can not be determined by the relation (2) which more stable or persistent, the oil drop or the water drop is. However, if it is assumed that the escaping of the emulsifier molecule into the continuous phase is likely to be hindered by the close juxtaposition of the interfaces, the probability to form a defect will be determined by the escaping tendency of the emulsifier into the aqueous phase or the oil phase, in the case of water drops or oil drops respectively. The difference of the life-time between the aqueous and oil drops, as can be seen in Table I, may clearly be explained with the above assumption.

The type of the emulsion produced with the combination of oil, water and emulsifier will be determined by several factors, including volume ratio of oil to water, characteristics of the emulsifier used and mechanical conditions such as stirring, shaking etc. Therefore, it can not be foretold from the difference of the values T_O and T_W, whether the O/W type emulsions will be produced or W/O type. However, in the system in which the difference in viscosity between oil and water is small such as benzene and water, it may be said that O/W type emulsion is more stable or persistent if T_O is greater than T_W and, W/O type, if T_O is less than T_W, as the emulsions produced using a given emulsifier.

It is not easy to estimate the stability of emulsions according to the values of T. However, it may be said qualitatively that the system having the value of T at least a few times greater than ten seconds must be used in order to obtain the emulsions in which the breaking of emulsions is not observed after a month or more.

Summary

The stability or persistency of drops at an oil-water interface in the presence of emulsifier has been studied. The behavior of drops at an oil-water interface has been observed using colored drops to interpret the process of the coalescence.

A mechanism, which explains the coalescence of drops at an oil-water interface more reasonably, was proposed as follows: the main process of the coalescence of drops at an oil-water interface is the formation of a defect in the emulsifier layer around the drops at the portion in contact with the plane interface.

The stability or persistency of emulsions may be estimated qualitatively by the values of T obtained in the present investigations.

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6) A. E. Alexander and P. Johnson, "Colloid Science", Oxford University Press, London (1949) p. 37.