

Physical Degradation of Emulsions Via the Molecular Diffusion Route and the Possible Prevention Thereof

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The quantitative aspects of the rate of growth of the large particles and the rate of dissolution of the small particles in emulsions were theoretically examined for the case in which the process is diffusion controlled in the external phase. It was found that even if the miscibility of the dispersed phase is as low as about 1×10^{-7} Gm. per ml. the size distribution of micron size emulsion particles may change appreciably in 1 year. Furthermore, according to this mechanism the emulsion stability is approximately proportional to the particle volume. It is proposed that such unstable emulsions may be stabilized with respect to this process by the addition of small amounts of a third component which must distribute preferentially in the dispersed phase. Sedimentation experiments carried out with carbon tetrachloride emulsions in water with and without hexadecane and Nujol as additives support the theory.

WHEN one speaks of the instability of emulsions he most frequently has in mind the processes of creaming or sedimentation followed by coalescence, or the last process alone. Little thought, even at the qualitative level, has been given to examining the possible importance of molecular diffusion as a pathway in the degradation of emulsions.

This report presents a quantitative theoretical study of the various factors governing the degradation rate of emulsions when the process is strictly molecular diffusion controlled, i.e., when the coalescence rate is negligible. In Figs. 1A and 1B we illustrate the two processes of coalescence and molecular diffusion degradation, respectively. Coalescence then is the formation of a droplet from two smaller droplets, the significant step occurring when the two droplets get close enough to allow a contact of the droplet phases. Now in a molecular diffusion process two droplets may form a single droplet if conditions are such that one droplet is allowed to grow while the other dissolves. Hence, in

the molecular diffusion process, the droplet phases are not required to come into contact.

We can qualitatively visualize situations in which one mechanism will be more important than the other. For example an emulsion "stabilized" with respect to droplet contact by means of either a charge inducing agent or by means of a suitable protective colloid may yet yield to the mechanism of molecular diffusion degradation. On the other hand, an emulsion in which the internal phase is sufficiently immiscible in the external phase can only degrade by the droplet contact route.

THEORY

Case I. Simple Case of a Mixture of Two Sizes.—The differential equations for the rate of change of an arbitrary distribution of emulsion particle sizes cannot be solved by usual methods. For this reason it would be profitable to examine a specific simple case first so that a complete understanding of the situation in at least this one case might be obtained. We could then examine a more realistic case.

Consider an emulsion in which one finds particles of two sizes only. Let a_A and a_B be the radii of these particles and n_A and n_B their respective number concentrations. At time $t = 0$, let $a_A = a_{A0}$ and $A_B = a_{B0}$, with $a_{A0} < a_{B0}$.

The question we now would like to answer is, how do a_A and a_B vary with time? First let us examine the driving force responsible for degradation with which we are concerned.

It is well known (1) that the chemical potential of a component in a phase is a function of the molal interfacial area of the phase. Thus small crystals are more soluble than large ones, and the vapor pressures of small droplets are greater than the vapor pressures of large ones. Analogously, the miscibility of the internal phase material is a function of its molal interfacial area.

For a one-component droplet of radius r in equilibrium with the external phase solution the miscibility of the internal phase material with the external phase may be expressed by the following

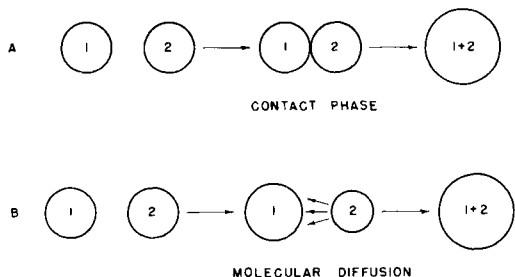


Fig. 1.—Illustration of emulsion degradation via coalescence (A) and via molecular diffusion degradation (B).

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equation in the Henry's law region

$$c_r = c_\infty \exp(K/r) \quad (\text{Eq. 1})$$

Here c_r is the miscibility of the r -size droplet, c_∞ is the miscibility of the infinitely large droplet, and K is given by

$$K = (2\gamma M)/(\rho RT) \quad (\text{Eq. 2})$$

where γ is the interfacial tension of the interface between the two phases, M and ρ are the molecular weight and density of the internal phase material, R is the molar gas constant, and T is the temperature in $^\circ\text{K}$.

It is clear from Eq. 1 that if more than one droplet size is present in an emulsion the chemical potential of the internal phase material in all of the droplets cannot be equal, i.e., the smaller particles will be thermodynamically unstable with respect to the large ones. Thus the smaller ones will tend to dissolve, and the larger ones will tend to grow at the expense of the former.

Let us now examine the mechanism of the rate process which we call molecular diffusion degradation. For a quantitative analysis of the problem we must assume that the system is dilute, i.e., a few per cent or less volume fraction of the internal phase.¹ Also we must assume that the miscibility of the internal phase material in the external phase is low, i.e., $\lesssim 1\%$ or so. Another simplifying assumption is that each particle must seek an environment which is both a time average and a space average distribution of other particles. This is a good assumption for not too viscous emulsions (dilute oil-in-water or dilute water-in-light oil emulsions) but not so good for, say, most heavy base ointments. Even for the latter however, to the extent that we are interested in approximate degradation rates, the assumption does not endanger our conclusions.

Now the rate of dissolution or the rate of growth of a sphere of radius a may be expressed (2) by the following equation when the process is diffusion controlled in the external phase and when ($c_s - c_0$) is smaller than $ca \cdot 1 \times 10^{-2}$ Gm. per ml.

$$G = 4\pi Da(c_s - c_0) \quad (\text{Eq. 3})$$

Here G is the rate, D is the molecular diffusion coefficient of the internal phase material in the external phase, c_s is the miscibility of the dissolving or growing phase, and c_0 is the concentration of the material at some distance from the sphere, large compared to a .

Implicit in the derivation of Eq. 3 are several assumptions which now must be discussed. First, Eq. 3 assumes that no interfacial barrier is present. Studies (3) have indicated that for micron-size droplets or greater, mass transfer between two liquid phases is governed primarily by diffusion rates in the external phase. Even relatively strong interfacial monolayer films provided by conventional low molecular weight surfactants probably do not affect these rates (3). Thick viscous films provided by polymeric surfactants or by polymolecular films of low molecular weight surfactants may be important, however. There is a great need for good

experimental work to solve these problems satisfactorily. We can only state at the present that in many, and in probably most, cases interfacial barriers against molecular mass transfer are not important in emulsion systems. Second, Eq. 3 assumes that hydrodynamic effects are not important. Nielsen's recent studies (2) show that fluid flow effects upon dissolution rates or growth rates caused by sedimentation or creaming of aqueous emulsion (density difference between particle and water less than unity) are unimportant for particle sizes $ca. 25 \mu$ or less. The same conclusions apply to moderately agitated systems where local fluid accelerations and decelerations do not exceed by very much that due to gravity. By the same type of analysis it can be shown that velocity gradients in the system up to about 10 sec.^{-1} remain unimportant.

Now c_s in Eq. 3 is given by Eq. 1, so that for particles of size a_A

$$c_s = c_A = c_\infty \exp\left(\frac{K}{a_A}\right) \quad (\text{Eq. 4})$$

and for particles of size a_B

$$c_s = c_B = c_\infty \exp\left(\frac{K}{a_B}\right) \quad (\text{Eq. 5})$$

We get by combining Eqs. 3, 4, and 5

$$G_A = 4\pi Da_A \left[c_\infty \exp\left(\frac{K}{a_A}\right) - c_0 \right] \quad (\text{Eq. 6})$$

and

$$G_B = 4\pi Da_B \left[c_\infty \exp\left(\frac{K}{a_B}\right) - c_0 \right] \quad (\text{Eq. 7})$$

which are the rates of dissolution (positive G) or growth (negative G) for particles of sizes a_A and a_B , respectively. It is a result of the assumption that all particles seek an average environment which makes Eqs. 6 and 7 applicable. Otherwise there should be a distribution of dissolution or growth rates even for particles of the same initial size.

We may now obtain a further relationship for c_0 on the basis of the mass conservation law. Clearly mass balance requires that

$$n_A G_A + n_B G_B + (d\bar{c})/dt = 0 \quad (\text{Eq. 8})$$

where t is the time and \bar{c} is the average amount of dissolved internal phase material in the external phase per unit volume of emulsion. Combining Eqs. 6, 7, and 8 we get

$$4\pi Da_A n_A \left[c_\infty \exp\left(\frac{K}{a_A}\right) - c_0 \right] + 4\pi Da_B n_B \left[c_\infty \exp\left(\frac{K}{a_B}\right) - c_0 \right] + d\bar{c}/dt = 0 \quad (\text{Eq. 9})$$

It can be easily shown from our final results that $d\bar{c}/dt$ is negligible in comparison to the other two terms. This greatly simplifies our task, since then from Eq. 9 we may write

$$c_0 = \frac{n_A a_A \exp(K/a_A) + n_B a_B \exp(K/a_B)}{n_A a_A + n_B a_B} \quad (\text{Eq. 10})$$

¹ However even up to high concentrations ($\sim 40\%$), the rates will probably not increase by more than a factor of two or so.

Now if the exponential terms in Eq. 10 are expanded in series form according to

$$\exp(x) = 1 + x + (x^2/2) + x^3/6 + \dots \quad (\text{Eq. 11})$$

we get from Eq. 10

$$c_0 = c_\infty \left[1 + \frac{K(n_A + n_B)}{n_A a_A + n_B a_B} + \text{higher order terms} \right] \quad (\text{Eq. 12})$$

When $K/a \ll 1$, as it is for emulsions in the size range of interest to us, the higher order terms are always negligible.

Now the c_0 expression may be substituted into Eqs. 6 and 7. The exponentials in the resulting equations may be expanded again according to Eq. 11 to give

$$G_A = \frac{4\pi D c_\infty K n_B (a_B - a_A)}{n_A a_A + n_B a_B} \quad (\text{Eq. 13})$$

and

$$G_B = \frac{-4\pi D c_\infty K n_A (a_B - a_A)}{n_A a_A + n_B a_B} \quad (\text{Eq. 14})$$

Because the rate of growth or dissolution of a particle must be equal to its rate of change of mass, we may also write

$$G_A = -4\pi \rho a_A^2 \frac{da_A}{dt} \quad (\text{Eq. 15})$$

and

$$G_B = -4\pi \rho a_B^2 \frac{da_B}{dt} \quad (\text{Eq. 16})$$

When these last two equations are combined with Eqs. 13 and 14 we get

$$\frac{da_A}{dt} = \frac{D c_\infty K}{\rho a_A^2} \left[\frac{n_B (a_B - a_A)}{n_A a_A + n_B a_B} \right] \quad (\text{Eq. 17})$$

and

$$\frac{da_B}{dt} = \frac{D c_\infty K}{\rho a_B^2} \left[\frac{n_A (a_B - a_A)}{n_A a_A + n_B a_B} \right] \quad (\text{Eq. 18})$$

These Eqs. 17 and 18 give the rates of change of the radii of the two sizes in the emulsion.

In Fig. 2 plots of a_A and a_B are presented for the case $n_A = n_B, a_{A0} = 0.5 \mu$, and $a_{B0} = 1.0 \mu$. Here

$$t' = D c_\infty K t / \rho \quad (\text{Eq. 19})$$

The curves in Fig. 2 were obtained by numerically solving Eqs. 17 and 18. These results show that at $t' \sim 9 \times 10^{-14}$, all of the originally 0.5μ particles have completely disappeared. By means of Eqs. 19 and 2 let us see how small c_∞ must be in this case in order to have a_A change only slightly, say 10%. We have then

$$c_\infty = \frac{\rho^2 t' R T}{2 D t \gamma M} \quad (\text{Eq. 20})$$

Let us select $t' = 4 \times 10^{-14}$ (about 10% change in a_{A0}), $t = 3 \times 10^7$ seconds (1 year's time), $M = 100$, $\rho = \text{unity}$, $D = 5 \times 10^{-6} \text{ cm.}^2 \text{ sec.}^{-1}$ (water viscosity in the external phase), and $\gamma = 1.0 \text{ dyne cm.}^{-1}$. Insertion of these values into Eq. 20 gives $c_\infty = 3 \times 10^{-8} \text{ Gm./ml.}$ This rather low upper

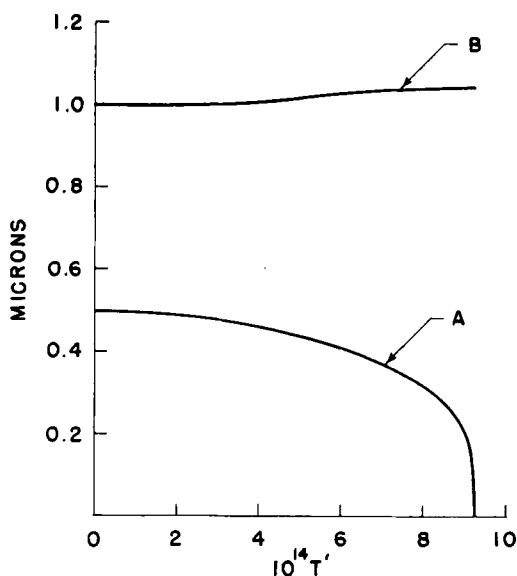


Fig. 2.—The degradation of an emulsion initially composed of a mixture of 0.5μ and 1μ radius droplets of equal number concentration. Curves A and B give droplet diameters as function of time (see Eq. 19 for definition of t').

limit value for c_∞ indicates that this mode of emulsion degradation can be a very important one. Thus substances in the micron size range with $c_\infty > 3 \times 10^{-8} \text{ Gm./ml.}$ may undergo appreciable change in size distribution.

Examination of Eq. 19 shows that the situation with respect to degradation can be improved by decreasing D which might be accomplished by increasing the viscosity of the external phase since, approximately

$$D = \frac{kT}{6\pi\eta\alpha} \quad (\text{Eq. 21})$$

where $\eta = \text{viscosity of the external phase}$, $\alpha = \text{molecular radius of diffusing material}$, and $k = \text{Boltzmann's constant}$.

Since the rate is proportional to γ , another way to retard degradation is to reduce γ by means of a suitable surfactant. However, one must avoid solubilization of the internal phase material in the external phase when using surfactants; otherwise the increase in c_∞ may offset the decrease in γ . Most water-oil interfacial tensions with surfactants are in the 0.1 to 10 dyne per cm. range.

The calculation for c_∞ just presented applies to the mixture of the 0.5 and 1.0μ radii particles. If the emulsion is a mixture of 0.05 and 0.10μ radii particles, the corresponding changes will occur a thousand times faster; i.e., the particle stability is proportional to the-cube of its radius. Hence $c_\infty < 3 \times 10^{-11} \text{ Gm./ml.}$ is the criterion for the 0.05 - 0.10μ mixture, everything else remaining the same. This conclusion is apparent from Eqs. 17 and 18.

A careful examination of Eqs. 17 and 18 reveals that control of the size distribution in the preparation of the emulsion will not be too helpful with respect to the retarding of molecular diffusion degradation unless the distribution is made very nar-

row. Whether a_B is initially only a factor of two greater than a_A or whether it is many times greater makes only about a factor of two difference in the disappearance rate of the smaller particles. On the other hand, if $(a_B - a_A)$ is made very much smaller than a_A the rate will be inversely proportional to the narrowness of the distribution. Since most emulsions cannot be prepared with distributions so narrow, the narrowness of the distribution is generally not an important factor.

Fictitious as it may be, the emulsion composed of two particle sizes, $a_{A0} = 0.5$ and $a_{B0} = 1.0 \mu$, of equal number concentration gives us a quantitative "feel" for the problem. The preceding analysis clearly shows that this route of degradation cannot be overlooked in emulsion stability studies.

Case II. More Complex Single Component Droplet Case.—To analyze a more realistic size distribution consider the emulsion with an initial ($t = 0$) distribution of radii following the law

$$n_i da_i = \frac{\bar{K}}{a_i^3} da_i \quad (\text{Eq. 22})$$

over the range $a_m \leq a_i \leq a_n$ at $t = 0$. For other, $t = 0$, a_i values assume $n_i = 0$. Here n_i is the concentration of particles in the size range between a_i and $a_i + da_i$ at $t = 0$, and \bar{K} is a constant. The distribution given by Eq. 22 is a good approximation to the log-normal distribution.

The complexity of this problem limits the calculations to only the initial rate of degradation of the system. The rate of dissolution or growth of the i^{th} particle at zero time is (analogous to Eqs. 6 and 7)

$$G_i = 4\pi Da_i \left[c_\infty \exp\left(\frac{K}{a_i}\right) - c_o \right] \quad (\text{Eq. 23})$$

where c_o is defined by a relationship similar to Eq. 10 but more general, *viz.*

$$\int_{a_m}^{a_n} 4\pi n_i Da_i \left[c_\infty \exp\left(\frac{K}{a_i}\right) - c_o \right] da_i = 0 \quad (\text{Eq. 24})$$

As before, the $d\bar{z}/dt$ term is neglected in deriving Eq. 24.

Substituting Eq. 22 into Eq. 24 and integrating for $t = 0$, we get

$$c_o = c_\infty \left[1 + \frac{K}{2} \left(\frac{1}{a_n} + \frac{1}{a_m} \right) \right] \quad (\text{Eq. 25})$$

with the neglect of higher order terms. Now if Eqs. 25 and 23 are combined we obtain

$$G_i = 4\pi Da_i c_\infty K \left(\frac{1}{a_i} - \frac{1}{2a_n} - \frac{1}{2a_m} \right) \quad (\text{Eq. 26})$$

for the i^{th} particle at zero time. Equating G_i to the rate of change of mass of the i^{th} particle

$$G_i = -4\pi\rho a_i^2 \frac{da_i}{dt} \quad (\text{Eq. 27})$$

and setting $a_i = a_m$ we get

$$\frac{da_m}{dt} = -\frac{Dc_\infty K}{2\rho a_m} \left(\frac{1}{a_m} - \frac{1}{a_n} \right) \quad (\text{Eq. 28})$$

which is the expression for the initial rate of size decrease of the smallest particles in the distribution.

Setting $a_i = a_n$ we get

$$\frac{da_n}{dt} = -\frac{Dc_\infty K}{2\rho a_n} \left(\frac{1}{a_n} - \frac{1}{a_m} \right) \quad (\text{Eq. 29})$$

which is the expression for the initial rate of growth of the largest particles in the distribution. It must be remembered that Eqs. 28 and 29 apply to only the initial rates while Eqs. 17 and 18 are valid for all times.

The quantitative similarity between Eqs. 28 and 29 and Eqs. 17 and 18 shows that a system with a continuous distribution of particle sizes does not behave too differently from the simple system consisting of only two sizes as far as the degradation rate is concerned. Thus, the general quantitative conclusions deduced for Case I are approximately applicable to more complex cases.

Case III. The Two Component Droplet Case.—While for both case I and case II the internal phase was treated as one component, in general one should consider the miscibility of the external phase material with the internal phase. Let us briefly outline the problem and discuss the conclusions for the case in which the external phase material is only slightly (say less than about 1%) miscible with the internal phase. The general case is much more difficult to analyze.

Figure 3 illustrates the problem. Component x makes up the bulk of the internal phase and component y makes up most of the external phase. c_{xI} and c_{yI} are the concentrations of the two components in the particle, c_{xS} and c_{yS} are the concentrations at the interface but on the external phase side, and c_{xO} and c_{yO} are the concentrations at some large distance from the particle.

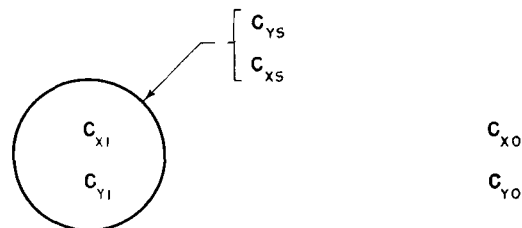


Fig. 3.—The two-component emulsion system. See text.

We may write for a particle of radius a

$$c_{xS} = k_x c_{xI} \exp\left(\frac{K_x}{a}\right) \quad (\text{Eq. 30})$$

and

$$c_{yS} = k_y c_{yI} \exp\left(\frac{K_y}{a}\right) \quad (\text{Eq. 31})$$

where k_x and k_y are the respective distribution coefficients, $K_x = 2\gamma\bar{V}_x/RT$, and $K_y = 2\gamma\bar{V}_y/RT$, with \bar{V}_x and \bar{V}_y the partial molal volumes of components x and y in the droplet. Equations 30 and 31 are simply the two component versions of Eq. 1. Both k_x and k_y can be expected to remain constant if each of the phases remain dilute with respect to one of the components (Raoult's law and Henry's law).

While we will not present the arguments, it can

be shown by Eqs. 30 and 31 and by the other conditions assumed above that the rate of growth or dissolution of the droplets in the emulsion is entirely controlled by the rate of diffusion of component x only. Furthermore it can be shown that

$$c_{ys} \simeq c_{y0} \quad (\text{Eq. 32})$$

in the steady state.

Therefore we may write

$$G_x = 4\pi D_x a (c_{xs} - c_{x0}) \quad (\text{Eq. 33})$$

for the rate of diffusion of component x toward or away from the particle. This becomes

$$G_x = 4\pi D_x a \left[k_x c_{xl} \exp\left(\frac{K_x}{a}\right) - c_{x0} \right] \quad (\text{Eq. 34})$$

when Eq. 30 is substituted for c_{xs} . Now because of Eq. 32

$$G_x = -4\pi a^2 c_{xl} \frac{da}{dt} \quad (\text{Eq. 35})$$

Then Eqs. 34 and 35 may be handled in the same way as was done in case I and the change in particle size may be evaluated as a function of time.

We may conclude that the two component droplet emulsion system behaves essentially the same as the one component droplet emulsion when the amount of the second component in the droplet is low, the second component being the predominant component of the external phase. This assumes, of course, that the appropriate γ and K_x are employed.

Case IV. Special Case of the Three Component Emulsion.—We shall not attempt a discussion of the general three component case. Let us, however, examine a special three component case which is of considerable importance to the question of emulsion stability.

In Fig. 4 the three component case is illustrated with the same symbolism as that used in Fig. 3 for the two component case but with addition of z values.

As before, let x and y represent the major internal phase and the major external phase components, respectively, with z being a minor component in both phases. As was found in case III (two component case) let the effect of y be negligible as far as the rates of change of the droplet sizes are concerned. These statements mean that

$$\left. \begin{aligned} c_{yl} &\ll c_{xl} \\ c_{ys} &\gg c_{zs} \\ c_{y0} &\gg c_{z0} \\ c_{zs} &\ll c_{ys} \\ c_{z0} &\ll c_{y0} \\ c_{zl} &\ll c_{xl} \end{aligned} \right\} \text{conditions (Eq. 36)}$$

and that

$$c_{ys} \simeq c_{y0} \text{ always}$$

We may write (as for the two component case)

$$c_{xs} = k_x c_{xl} \exp\left(\frac{K_x}{a}\right) \quad (\text{Eq. 37a})$$

and

$$c_{zs} = k_z c_{zl} \exp\left(\frac{K_z}{a}\right) \quad (\text{Eq. 37b})$$

Here k_x and K_x have the same meanings as before,

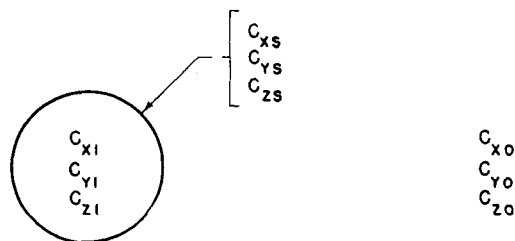


Fig. 4.—The three-component emulsion system. See text.

k_z is the corresponding distribution coefficient for the z component, and $K_z = 2\gamma \bar{V}_z/RT$ with \bar{V}_z being the partial molal volume of component z in the droplet. The validity of Eqs. 37a and 37b may be easily demonstrated if it can be assumed that z does not interact with y to form a compound or complex in the internal phase and that z and x do not appreciably interact with each other in the external phase. In other words, for Eqs. 37a and 37b to apply, the solvent properties of each phase must be determined primarily by the major component in that phase. In the other extreme, i.e., when complex or compound formation between y and z in the internal phase or between x and z in the external phase occurs, more complex relationships than Eqs. 37a and 37b must be employed. However, even for these cases the general conclusions of this section will apply provided that the variations in k_x and k_y are taken into account.

Following the results for case III we may conclude that the condition, $c_{ys} \simeq c_{y0}$, is established very rapidly in any system for which $c_{ys} \neq c_{y0}$ initially. Then a period, τ , will ensue during which a pseudo-steady state is established. In the pseudo-steady state the rate of degradation of the system will depend upon either the rate of diffusion of x or that of z , or possibly upon both of these rates. If $k_x \ll k_z$ and if the diffusion coefficients for x and y are about the same, the degradation rate will not be markedly different from the one-component case. On the other hand, if $k_x \ll k_z$ the diffusion rate of z will govern the degradation rate of the particle at $t > \tau$. Physically what happens is that the relatively very slow rate of diffusion of z permits the x component to remain essentially equilibrated among all the droplets. Therefore, changes in the system occur only as fast as the change in the distribution of the slowest diffusing component. Thus, the degradation rate may be retarded by a factor

$$K_p = \frac{k_x}{k_z} \quad (\text{Eq. 38})$$

after a time τ . This result is significant to the extent that a system with a very large K_p value may be employed to stabilize emulsions which otherwise would degrade if the third (z) component were absent.

Having now established that in the pseudo-steady state ($t > \tau$) the degradation rate depends primarily upon K_p , let us now examine the period $t \lesssim \tau$, when K_p is infinitely large. For this purpose consider the three component emulsion containing only two sizes of particles. The situation is illustrated in Fig. 5. The symbolism is the same as in

Fig. 4 except the third subscripts A and B refer to the two particle sizes.

The initial boundary conditions ($t = 0$) for the two kinds of particles A and B or the number concentrations n_A and n_B are

$$\begin{aligned} a_A &= a_{A0} \\ a_B &= a_{B0} \end{aligned} \quad (\text{Eq. 39})$$

with

$$a_{A0} < a_{B0}$$

let also

$$\begin{aligned} c_{xIA} &= c_{xIA0} \text{ and } c_{xIB} = c_{xIB0} \\ c_{zIA} &= c_{zIA0} \text{ and } c_{zIB} = c_{zIB0} \end{aligned} \quad (\text{Eq. 40})$$

at $t = 0$.

Now immediately after the emulsion is prepared component y equilibrates rapidly to give $c_{ySA} \approx c_{ySB} \approx c_{y0}$. The main process with which we are now concerned is then that of the diffusion of x out of the A particles and into the B particles until the equilibrium condition

$$c_{zSA} = c_{zSB} \quad (\text{Eq. 41})$$

is reached. Since we have chosen $K_p \approx \infty$, none of the z can leave or enter the droplets.

A practical and meaningful way to present the analysis is to determine the necessary initial concentration of z in the internal phase, $c_{zI0} = c_{zIA0} = c_{zIB0}$, which permits only a small change in a_A (say 10%) during the period, τ .

Substituting Eq. 37a into Eq. 41 we get

$$k_x c_{xIA\infty} \exp\left(\frac{K_x}{a_{A\infty}}\right) \approx k_x c_{xIB\infty} \exp\left(\frac{K_x}{a_{B\infty}}\right) \quad (\text{Eq. 42})$$

where $c_{xIA\infty} = c_{xIA}$, $c_{xIB\infty} = c_{xIB}$, $a_{A\infty} = a_A$, $a_{B\infty} = a_B$, all at $t \gg \tau$. Upon expansion of the exponential, Eq. 42 gives

$$\frac{c_{xIA\infty}}{c_{xIB\infty}} = 1 + K_x \frac{(a_{A\infty} - a_{B\infty})}{a_{A\infty} a_{B\infty}} + \dots \quad (\text{Eq. 43})$$

we may also write

$$\bar{T} = \nu_{zI} c_{zI} + \nu_{zL} c_{zL} \quad (\text{Eq. 44})$$

Where \bar{T} is a constant, and ν_{zI} and ν_{zL} are the partial specific volumes of z and x in the internal phase, respectively. Equation 44 is a good assumption for dilute solutions as specified under conditions (Eq. 36). It is valid for systems in which Raoult's law is obeyed for x and Henry's law is obeyed for z , i.e., for the case in which solute-solute interactions are unimportant.

Then for $t \gg \tau$

$$\bar{T} = \nu_{zI} c_{zIA\infty} + \nu_{zL} c_{zLA\infty} \quad (\text{Eq. 45})$$

and

$$\bar{T} = \nu_{zI} c_{zIB\infty} + \nu_{zL} c_{zLB\infty}$$

where $c_{zIB\infty}$ and $c_{zLA\infty}$ are the c_{zIB} and c_{zIA} values at $t \gg \tau$.

It is also apparent that

$$c_{zIA\infty} = \frac{a_{A0}^3}{a_{A\infty}^3} c_{zI0} \quad (\text{Eq. 46})$$

and

$$c_{zIB\infty} = \frac{a_{B0}^3}{a_{B\infty}^3} c_{zI0}$$

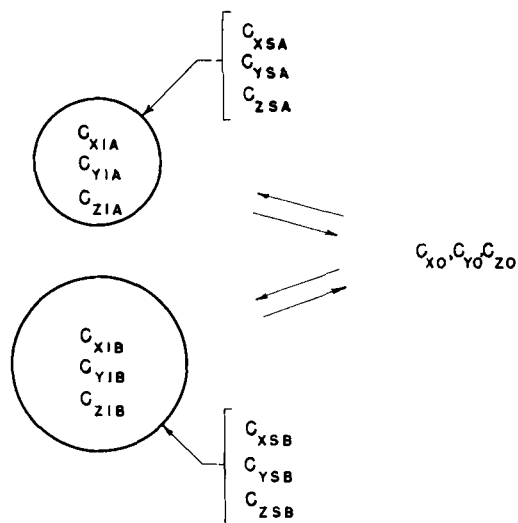


Fig. 5.—The three-component emulsion composed of a mixture of two sizes. See text for symbols.

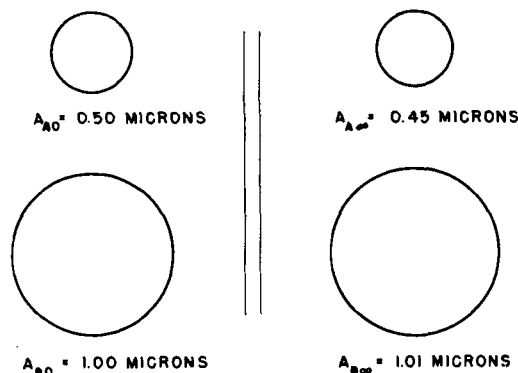


Fig. 6.—Illustration of the stabilization of an emulsion by a third component which is immiscible in the external phase. See text.

Now Eqs. 46, 45, and 43 may be combined to give

$$\frac{\bar{T} - \nu_{zI}(a_{A0}^3/a_{A\infty}^3) c_{zI0}}{\bar{T} - \nu_{zI}(a_{B0}^3/a_{B\infty}^3) c_{zI0}} = 1 + K_x \frac{(a_{A\infty} - a_{B\infty})}{a_{B\infty} a_{A\infty}} \quad (\text{Eq. 47})$$

Then with the help of a final expression for the conservation of mass, viz.

$$n_A a_{A0}^3 + n_B a_{B0}^3 \approx n_A a_{A\infty}^3 + n_B a_{B\infty}^3 \quad (\text{Eq. 48})$$

c_{zI0} may be evaluated.

Suppose as in case I we take $n_A = n_B$, $a_{A0} = 0.5 \mu$ and $a_{B0} = 1.0 \mu$ (See Fig. 6). Let us see what c_{zI0} must be so that $a_{A\infty} = 0.9 a_{A0}$, i.e., so that only a 10% change takes place during the period τ . Now $\bar{T} \sim$ unity, and for most organic compounds $\nu_{zI} \sim 1$. K_x will have values ranging from around 1×10^{-7} to 1×10^{-9} , depending primarily upon γ , since $\bar{V}_x \sim 100$, $RT \sim 2 \times 10^{10}$, and γ may generally vary from about 0.1 to 10 ergs per cm^2 . Employing these values with Eqs. 47 and 48 we find that $c_{zI0} \sim 3 \times 10^{-5}$ Gm. per ml. for $\gamma = 0.1$

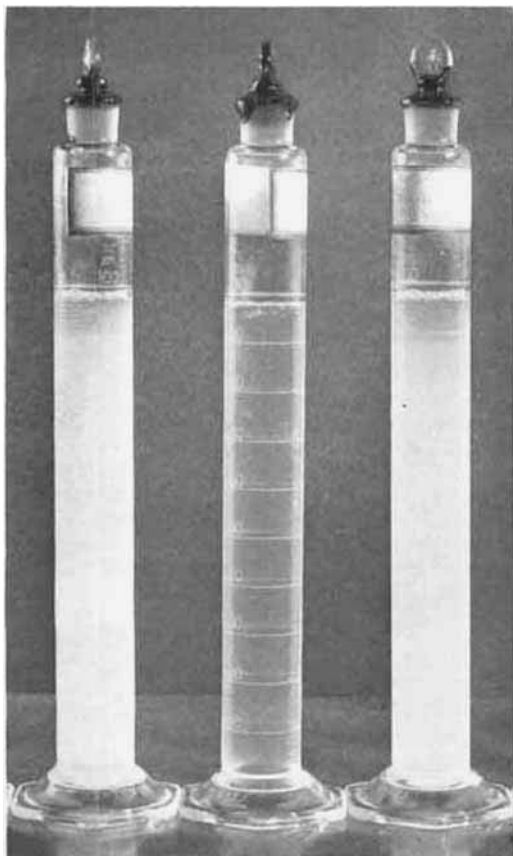


Fig. 7.—Photograph of 0.20% carbon tetrachloride-in-water emulsions containing 0.02% Aerosol OT, 12 hours after ultrasonic preparation. The center graduate, B, contains no other additive, while the graduates to the left, A, and right, C, contain 0.002% Nujol and hexadecane, respectively.

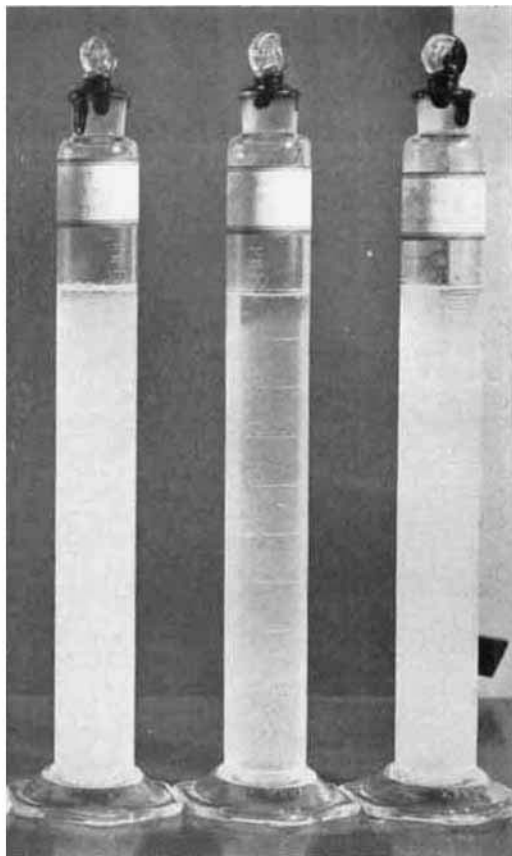


Fig. 8.—Photograph of 0.20% carbon tetrachloride emulsions containing 0.05% Aerosol OF 12 hours after preparation. Center graduate, B, contains no other additive while the graduates to the left, A, and right, C, contain 0.002% Nujol and hexadecane, respectively.

dyne per cm. and $c_{20} \sim 3 \times 10^{-3}$ Gm. per ml. for $\gamma = 10$ dynes per cm.

These values for c_{20} suggest that emulsions degrading via the molecular diffusion route may be stabilized by the incorporation of a small amount of a third component in the internal phase if this additive possesses a sufficiently large K_p value. About 1% additive should be more than ample for stabilizing most emulsions in the micron range. It is noteworthy that if γ is very low, say 0.01 dyne per cm., less than 0.01% additive is needed for stabilization.

For smaller size ranges Eq. 47 shows that c_{20} must be proportionately greater to provide the same stability. Therefore, if in the preceding calculations $a_{A0} = 0.05 \mu$ and $a_{B0} = 0.10 \mu$, the corresponding c_{20} values must be ten times greater.

EXPERIMENTAL STUDIES

Selection and Design of Experiment.—To test some of the ideas developed in the preceding sections of this report it was decided that dilute emulsions of carbon tetrachloride in water, stabilized against coalescence and aggregation, would be most appropriate for the following reasons: (a) According

to Stokes' law the sedimentation rates of micron size particles of carbon tetrachloride in water would be great, i.e., ca 1×10^{-4} to 1×10^{-5} cm. sec.⁻¹. Thus, the presence or absence of sub-micron particles could be determined easily by visual observations. (b) The miscibility of carbon tetrachloride with water is high enough ($c_{\infty} \sim 1 \times 10^{-3}$ Gm. per ml.) so that submicron size particles in the presence of larger particles should disappear in about 1 hour according to our theory. (c) Additives such as hexadecane or Nujol may be employed to test the third component stabilization theory. These substances are miscible with carbon tetrachloride but possess very low miscibility with water, i.e., K_p is very great.

Materials and Procedure.—Carbon tetrachloride used was redistilled Baker reagent grade. Hexadecane was redistilled Eastman practical grade. Plough's pure Nujol was used without further purification. Aerosol OT (AOT) was purified (4) by fractional precipitation with methanol and a water-methanol solvent mixture. Water was redistilled with care to avoid any contamination by oil-miscible, water-immiscible materials.

The emulsions were prepared by ultrasonically emulsifying 0.2 ml. carbon tetrachloride (without

and with hexadecane or Nujol) in 100 ml. of water containing varying small amounts of Aerosol OT (0.02 to 0.10%). The carbon tetrachloride was pipetted into the detergent solutions in 100-ml. graduated cylinders (precleaned ultrasonically) with ground-glass stoppers. The stoppers were sealed with Cementyte to prevent any diffusion losses of the carbon tetrachloride vapor. The cylinders were then subjected to about 30 minutes of 40 kc. ultrasonic energy generated by the model DR-125AH Acoustica cleaning unit.² The emulsions were then removed from the ultrasonic bath and allowed to stand. The amount of sedimentation and the turbidity were observed from time to time for periods extending to several days.

Results.—In all cases where the additive, hexadecane or Nujol, was absent in the carbon tetrachloride the emulsion particles visibly coarsened relatively rapidly and settled. The rate of this process of coarsening and settling was greatest for the 0.02% AOT, in which case a clear liquid region at the top of several mm. formed in less than 1 hour. For the 0.10% AOT emulsions, the corresponding length of time was always several hours. Within about 8 hours nearly all of the particles in the 0.02% AOT emulsion settled completely, while it took several days in the case of the 0.10% AOT. Emulsions with intermediate concentrations (0.05%) of AOT showed intermediate rates.

In contrast to the above behavior, emulsions prepared from carbon tetrachloride containing 1% Nujol or hexadecane remained turbid longer and settled much more slowly than those emulsions free of these additives. It is noteworthy that the total hexadecane or Nujol in these cases was only 0.002%.

Figures 7 and 8 are photographs taken 12 hours after the preparation of emulsions for the 0.02 and 0.05% AOT, respectively. The center graduate, B, in each case is the emulsion without the additive; A and C containing Nujol and hexadecane, respectively. In the case of the 0.10% AOT, the situation was much like that of 0.05% AOT (Fig. 8) but after 4 days of standing.

The significant point here is that when the additive was present the small particles in the emulsion were most noticeably affected. Immediately after

the preparation, the emulsions containing the same concentration of AOT had about the same appearance (turbidity). The large particles (1–10 μ) in the system, whether the additive was present or not, appeared to settle as expected (these can be seen in Figs. 7 and 8). The small particles (sub-micron) in the initial distribution were much more stable visibly, however, when the additive was present.

It was very difficult to ascribe these experimental findings to anything but molecular diffusion degradation and the prevention thereof. In all of these studies, visual examination of the sediment indicated that coalescence was unimportant, even for the 0.02% AOT cases. Even if some coalescence or aggregation were present, it is unreasonable to expect the presence of so little nonsurface-active ingredient as hexadecane or Nujol to influence coalescence or aggregation markedly over a wide range of surfactant concentration. Finally, the quantitative agreement (to an order of magnitude, of course) of the rate of degradation with theory should eliminate final doubts.

For emulsions not containing the additives, the increase in the apparent degradation rate with decreasing surfactant concentration may be explained on the following bases: first, the interfacial tension decreases with increasing surfactant concentration. The range of surfactant concentration employed, *viz.*, 0.02 to 0.10%, is commonly in the range in which γ changes rapidly. Thus, this is probably the main effect, following the theory. Second, it is possible that, at 0.10%, AOT may be involved in the formation of a polymolecular film at the interface. Cockbain (5) has proposed the multimolecular absorption idea to explain some of his findings on the aggregation of paraffin and benzene emulsions in AOT solutions. Mass transport through this film may be slow enough to affect the overall rate.

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² Acoustica Associate, Inc., Mineola, N. Y.