

EMULSIFICATION

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THE general importance of the emulsions as dispersed systems in which one kind of liquid is subdivided within a second liquid needs no emphasis before this audience. Such are all your milks and butters; your soaps and native fats; all your greases. The problem again comes up when you salt your soap kettles or dye vats and they "gum," "go stringy" or the whole mess "blows up." And why will lanolin and some of those other "peculiar" fats absorb water and go white?

I

Discussion of the emulsions is best begun by looking at their extreme examples—those systems in which the two phases are most clearly immiscible and in which more than a fractional per cent merely of the one is emulsified in the other. Why, for example, may 50 per cent (even 90 per cent) of some fatty or hydrocarbon oil be emulsified in the remaining per cent of water?

While obvious, it is a fact established but thirty years ago, that from the mixture of any two liquids, two types of emulsion may be obtained, one of *a* in *b* (as of oil in water) and another of *b* in *a* (as of water in oil). (See Fig. 1.) The two have

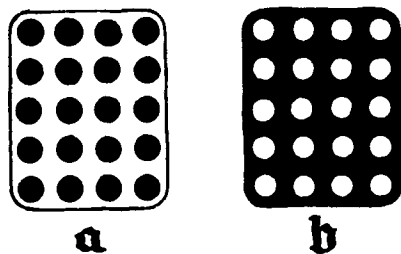


FIGURE 1.

totally different properties. Thus, if we regard milk (a 4 per cent emulsion of fat in 96 per cent water) it is found to feel "wet," to wet a piece of filter paper when dipped into it and to be miscible only with more water. On the other hand, butter (a 12 per cent

emulsion of water in 88 per cent fat) feels greasy, "oils" the paper and will mix only with more oil.

If, in illustration, an oil (like cottonseed oil) and water are chosen as the basic components of an emulsion, the first truth to appear is that the placing of the two materials in contact with each other leads to no emulsion production. As generally put, it is necessary to add a third substance, a so-called emulsifying agent, to the mixture. But even this does not "spontaneously" yield an emulsion. We have to shake or stir or pestle or beat the mixture. Or, we can dissolve one of the components (say, the oil) in a solvent (like alcohol or a phenol) and pour this into the water phase. The previously "dissolved" oil particles will then run together and we will again have our oil droplets dispersed in the aqueous phase. These facts prove that *there are no emulsifying agents* unless we call a flail or the solvent properties of a liquid such.

What then is an emulsifying agent? To put it tersely, it is a *stabilizing* agent for an emulsion formed by mechanical or chemical means. And why or how it stabilizes is the real question to be answered by the emulsion theorist.

There are hundreds of methods published which will instruct the worker as to how he may proceed to get an emulsion. Any kind of *temporary* emulsion can be produced by mechanical or chemical means; but what the emulsion chemist wants is a *permanent* one. To accomplish this some third substance must be introduced into his liquid/liquid mixture. *Invariably this substance proves to be a hydrophilic colloid* when water and oil emulsions are concerned (a *lyophilic* colloid of some sort when other than aqueous mixtures are under consideration).¹

Put another way, oil cannot permanently be beaten into water, but only into a *colloid hydrate*. The

¹MARTIN H. FISCHER and MARIAN O. HOOKER: *Science* 43, 463 (1916); *Fats and Fatty Degeneration*, John Wiley & Sons, New York (1917).

chemical constitution of the colloid is of no importance, only its ability to suck up water, to swell, in other words, its hydration capacity. Wherefore it comes to pass that the most varied types of carbohydrate have proved themselves good emulsifiers (the gums like acacia, the dextrans and starches); similarly the soaps (particularly the "soft" soaps like potassium oleate, or potassium stearate); and the "native" proteins (like egg yolk, the caseinates, or egg white). What all these compounds have in common is the quality of high hydration.

That it is specifically *this* quality which makes the emulsifying agent "work" is nicely illustrated by casein. "Neutral" casein is, as you know, a dry white powder which when thrown into water takes up but little. Technically put, its hydration capacity is low, wherefore, added to an oil-water mixture it may be beaten until the cows come home without yielding a permanent emulsion. But if a little alkali is added, an alkali-caseinate is formed which compound is highly hydratable. And now the oil-water mixture yields the finest of stable emulsions. Perhaps it is because the alkali has affected the (fatty) oil and produced a soap, some men have said. Not at all! Let us substitute an acid for the alkali. This has no action upon the oil, but just as good an emulsion is made because acid-casein is produced, which like alkali-casein, is again a hydrophilic colloid of high water-holding capacity.

The ease with which any emulsion of the oil in water type is stabilized by any hydrophilic colloid is measured primarily by this water-holding capacity. Wherefore the ammonium and potassium soaps stand above the sodium soaps and all of these very much above magnesium, calcium or still heavier metal soaps.

It is commonly forgotten, too (in spite of the definition of emulsions as liquid/liquid systems) that the stabilizing agent with its "sol-

*Stenographic report of a lecture to the American Oil Chemists' Society, meeting in Cincinnati, October 17, 1935.

vent" must yield a *liquid* in order to work best. On this account, at definite concentration, sodium stearate (because solid) may not lead to emulsification; but at once if warmed (to above 90° C. when the hydrated stearate liquefies). The substitution of potassium stearate for the sodium stearate works equally well because, at ordinary temperatures, the former is semi-liquid.

Additional proof that only a liquid hydrate (and not any "solution" of the colloid in water) acts as the emulsifier is found by comparing the effects of different soaps, or one and the same soap at different temperatures. Thus the lowermost members of the sodium soaps of the acetic series (the formate, acetate, propionate, butyrate, etc.) never emulsify because they appear only as solutions of these materials in water. Sodium caproate shows some activity (because the first to evidence hydrophilic properties in liquid form) but the higher members (like sodium stearate, arachidate, behenate, etc.) again prove largely useless because solid. By raising the temperature at which these emulsions are prepared, all move toward the right, the once effective members now failing to act as emulsifiers because they go into true solution in the water and the higher coming to exhibit such action because liquefied.

If now it is asked why an ammonium or potassium soap (or a gum or a protein glue) acts to produce an emulsion of the oil in soap type, while a calcium or barium soap acts to produce one of opposite type, we hold that the explanation is simpler than that ordinarily given. Ignoring the fact that when either phase is present in but small fraction it can constitute only an internal phase (like a small percentage of oil beaten into much water or a small percentage of water beaten into much oil)¹ that material is dispersed within any second which in response to mechanical deformation shows the shorter breaking length.² Suppose that we drag a film of oil (B of Fig 2) over a film of hydrated potassium oleate (C of Fig. 2). The former breaks before the latter wherefore oil droplets come to rest within the hydrated soap. But if we repeat the experiment



FIGURE 2.

with hydrated calcium oleate (A of Fig. 2), the soap film breaks before the oil; and the soap is dispersed within the oil.

The factors that have been here described as underlying the formation, stabilization and type of emulsion produced have been the object of much criticism. Modern protagonists of the view of the first and the oldest students of the problem (S. Plateau and G. Quincke) that emulsifying agents (or foaming agents which present the identical problem) act by lowering the surface tension or by increasing the viscosity have frequently held the ideas here proposed nonsensical; and more recent students (S. U. Pickering) have defended the idea that a third phase (a film) is formed between the essential components of the emulsion, to which thought has been added the effects of "adsorption," of "surface activity" and the "wetting" qualities of the phases in apposition. As admitted by the first authors themselves (though not by their disciples) none of these notions explains all emulsions. The colloid notion does. Its antagonists probably want no peace, though it is offered freely. There happens to be nothing mutually exclusive in the ideas of solvation as here presented and changes in surface tension of a liquid, for example. When water changes to a colloid hydrate, it is still a liquid but its physical constants have changed and these include, among others, surface tension, viscosity and "adsorption." But no one of these properties parallels qualitatively or quantitatively the efficacy of any material to act as an emulsifier.

II.

A test of the truth or falsity of the ideas here advanced is offered when study is made of the conditions necessary to break an existent emulsion. If an emulsion of oil stabilized in a hydrated soap, a protein or a carbohydrate is taken in hand, it is found that these are broken invariably by any circumstance which increases sufficiently the water content of the system or reduces sufficiently the water-holding capacity of its contained colloid. Emulsions stabilized by any of the lower soaps break, therefore, on

mere dilution (because the soap is converted from a hydrate into a true solution). Merely warming a mixture may similarly break it (because the aqueous phase is again pushed from the state of hydrated soap into that of soap-water). Finally, addition of any substance which will reduce the hydration capacity of the soap "cracks" the mixture. On this account dehydration of the soap through addition of any chemically non-reacting salt will accomplish this end. And so will the addition of a reactive salt (as one of calcium or iron) which after double decomposition leads to the formation of a soap less hydratable. Any acid will crack the emulsion (because it decomposes the soap to yield the fragments fatty acid and salt, neither of which has any hydration value). Similar rules hold for the decomposition of an emulsion stabilized, say, by an alkali proteinate. But all such attempts fail when a carbohydrate is concerned because these chemical insults are without effect upon hydrated carbohydrates.

III.

Where are we when we have said that an emulsifying agent is a lyophilic colloid? It calls for inquiry into the nature of the latter. The several theories that have been proposed have been reviewed critically by Wolfgang Ostwald.¹ In consequence I repeat here only my own,² related to this general discussion of the emulsions by the fact that the *liquid* lyophilic colloid systems prove also to be emulsions, their two phases being represented by the colloid "dissolved" in the solvent and the solvent "dissolved" in the colloid. The behavior of the system light metal soap/water is described but the general notions that cover it are applicable to all *lyophilic* colloid systems and this without regard to their chemical make-up. Thus we may have electrolytes mixed with water or with non-dissociating "solvents" (as a light metal soap with water or an anhydrous alcohol, a heavy metal

¹Mathematically the crossing line (assuming both phases to be of spherical construction) is reached when thirty-three percent of an external phase envelopes sixty-seven percent as an internal one.

²MARTIN H. FISCHER: Soaps and Proteins: 155, John Wiley & Sons, New York (1921).

¹WOLFGANG OSTWALD: Kolloid-Zeitschr. 46, 248 (1928).
²See MARTIN H. FISCHER: Soaps and Proteins, John Wiley & Sons, New York (1921); Lyophilic Colloids, Charles C Thomas, Springfield, Ill. (1933).

soap with a hydrocarbon); or we may have a nonconductor (as one of the carbohydrate gums) mixed with water; or another nonconductor (nitrocellulose) with alcohol-ether; finally, both phases may be nonconductors (caoutchouc mixed with benzene).

A twenty-five per cent mixture of potassium oleate with water when hot is limpid. With lowering of temperature the mixture increases in viscosity, loses in transparency and ends by becoming a thick-flowing, semigelatinous mass. What happens is illustrated in Fig. 3. At higher temperatures, the soap "dis-

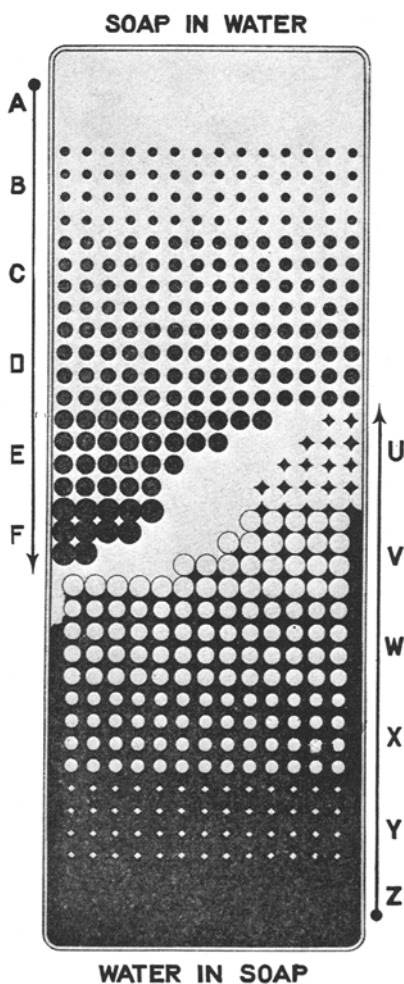


FIGURE 3.

solves" in the water and there results a true solution. This matter is represented by the region marked A in the diagram (the soap is dispersed molecularly or ionically in the solvent). As the temperature falls, the solubility of the soap in the water is decreased and as the saturation point for any lower temperature is attained, the soap particles must obviously assume more than molecular size. By definition,

therefore, we are in the realm of the colloids, or that of dispersions of one material in a second with the degree of dispersion showing dimensions greater than the molecular. This gradual increase in the size of the soap particles (or increase in their number) with lowering of the temperature is represented by the regions B, C, D, E, and F.

This agglomeration of particles, while yielding us a colloid system, does not yet tell us however whether it will be lyophobic or lyophilic. *The lyophobic colloid results when the solvent is not soluble, the lyophilic when the solvent is soluble in the precipitating phase.* When soap falls out of solution from such a solvent as allyl alcohol, the former of these possibilities is satisfied (and we get a lyophobic colloid); when it falls out from most other alcohols or, as in our illustration, from water, the latter is satisfied (and we get a lyophilic "sol" or "gel"). The black circles in Fig. 3 represent more, therefore, in the latter instance than mere precipitates of soap; they are this, plus a certain amount of the water (or other "solvent") dissolved in them.

At a sufficiently low temperature the soap aggregates will have become so large or so numerous as to touch and coalesce. This process continued sufficiently must yield ultimately a single system in which the soap has now become the solvent for the water. Diagrammatically this situation is represented by the zone Z of Fig. 3.

Between the upper extreme A of a solution of the soap in the solvent and the lower extreme Z of the solvent in the soap, there exist two main zones of mixed systems—one below the upper (B, C, D and E) consisting of a dispersion of solvated-soap in the soaped-solvent, and a second above the lower (Y, X, W, and V) consisting of soaped-solvent in the solvated-soap. These two mixed systems (if the soap is liquid) are in essence emulsions, but of opposite type and as such (even when of the same quantitative chemical constitution) possessed of totally different physical properties. The former corresponds, for example, to an emulsion of oil-in-water, the second to one of water-in-oil, and as the former (as illustrated by milk) will mix with water, wet paper and show a certain viscosity value, the latter (as illustrated by butter) will mix only with oil, will grease paper and show an entirely different viscosity.

Returning to the lyophilic soap

and the diagrams, it is obvious that as we descend, with lowering of temperature, from the region A, we pass in the regions B, C and D through increasingly viscid liquid colloid "solutions" (so-called sols) but all of them emulsions of the type solvated-soap in soap-water. In the region E, the particles of solvated soap almost touch and here the highest (liquid) viscosity is obtained. In F they do touch and now form a continuous external phase. At this point we change to the opposite type of emulsion (to one of soap-water in solvated-soap) and the previously liquid colloid further solidifies. As ordinarily put, the mixture *gels*.

IV.

May I illustrate to you the value of the notion of emulsification as I have tried to present it for an understanding of what happens in two large industrial processes in which most of you have an interest. I refer to the manufacture of the modern "greases" and the problem presented by the "livering" of paints.

Latter day greases are mixtures of various paraffin oil fractions with soap. Every kind of soap has been mixed into every kind of mineral oil to yield the cosmetic creams, the shampoos, insecticides, cleansing creams, polishes of various sorts, various varnishes and the cutting oils. These greases have any consistency from that of water up to waxlike cakes. They may be emulsions of the oil-in-water type or of the water-in-oil type. Their nature and the behavior of the emulsifying agent in such systems have already been discussed. We pick for special consideration the greases produced when one of the heavier metal soaps is mixed with just one liquid, like a paraffin oil. In this instance, too, emulsification is responsible for the characteristic increase in viscosity, the gelation and the "setting" of the whole mixture into more solid form. What underlies this? The answer is found in the fact that all methods of grease manufacture begin (a) by producing a heavier metal soap (like calcium stearate or barium rosinate) in the oil pot or (b) by adding such directly to the oil. The mixture is warmed to dissolve the soap in the oil. On cooling, this thin and liquid mixture becomes thick or actually sets. What has happened is that, on cooling, the soap has fallen out of solution, has become a solvent for the solvent, and this new solvate has either remained

emulsified within whatever oil was unabsorbed, or, becoming the external phase, is now the dispersing phase for this uncombined oil. The grease-producing activity of any soap is measured by its solvation capacity¹ wherein lies the explanation of the fact that science has discovered a whole series of metallic soaps superior to the older magnesium, calcium and barium compounds; and aluminium stearate being the cheapest of these, it today is the commonest of the soaps used in grease manufacture.

¹MARTIN H. FISCHER: *Lyophilic Colloids*, 164 and 177, Charles C Thomas, Springfield, Ill. (1933).

“Livering” in ready-to-use paints (especially the oil paints) represents a process analogous to grease formation.² Livering occurs whenever conditions are such as to allow of the formation of a solvatable colloid in the mixture which, becoming the solvent for the paint vehicle increases its viscosity, makes it semi-plastic or actually leads to its hardening.

Thus it comes about that certain paint mixtures (like the sulphides with linseed oil) never liver; others

²MARTIN H. FISCHER and WERNER J. SUER: *Kolloid-Zeitschr.* 60, 71 (1932); *Lyophilic Colloids*, 179, Charles C Thomas, Springfield, Ill. (1933).

thicken an agreeable amount (as lead white with linseed oil on standing); still others liver to the point of spoilage. The latter is invariably the case where, with time, production of the heavier metal soaps comes about, which then, “dissolving” or “combining” with the paint vehicle, leads to solidification of the whole system. High content of free fatty acid, a definitely alkaline base and this of a nature to yield a soap highly solvatable—and intense livering is to be expected. For which reason the “lake colors” (especially those made by precipitating dyes upon aluminium hydroxide carry off the banner in this field.

HYDROGEN FOR THE OIL INDUSTRY

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UNTIL 25 years ago Hydrogen was almost exclusively used for the inflation of balloons and for high temperature work in the fabrication of metals. Only comparatively little was employed for strictly chemical work. Since then ever increasing amounts of Hydrogen have been needed for the Chemical Industries. First, for the hydrogenation of oils; since the beginning of the World War, for the technic in combining it with the nitrogen of the air to make ammonia, and also for the manufacturing of wetting agents for the Textile Industry through hydrogenation of coal tar compounds. During the last ten years, also the hydrogenation of coal and crude oil has been perfected.

In view of these developments it is interesting to compare the

problems of manufacturing hydrogen for the *different* industries must of necessity be manifold. We realize this even more fully on checking the total amounts of Hydrogen needed for some of these industries.

In 1932 the American Industries made daily about

1070 tons of ²synthetic ammonia, requiring theoretically 74 million cu. ft. of H₂.

1000 tons of ³hydrogenated oils* requiring theoretically 1.5 million cu. ft. of H₂.

Low cost and not the purity of the Hydrogen is of first importance for the synthetic ammonia industry, especially since nitrogen is needed for this reaction, and we find⁴ that 60% of the Hydrogen needed in this process is supplied by means of the water gas process; only 13%

and Canada, Sweden and Norway, where low hydro-electric power is abundant.

For the hardening of oils a Hydrogen of high purity is of great importance; in our country most of it is made according to the steam iron process. Steam passing at a high temperature over iron of a spongy character is decomposed into Hydrogen and at the same time the iron is oxidized. The oxide is regenerated and then used over again. The gas made by this process has a purity of over 99%; its only drawback is the fact that it contains a very small amount of carbon monoxide which is detrimental to the catalyst. In this respect we have to compare the amount of carbon monoxide with the amount of catalyst used in the reaction⁵ and not with the oil or gas in order to clearly understand the significance of this impurity.

It is therefore not surprising that the general trend turned toward electrolytic gas which theoretically is 100% pure. This is noticeable especially in countries where large hydro-electric power plants supply cheap current or where coal and other fuel supplies are low priced.

To decompose water containing an electrolyte by electric current⁶ a minimum voltage of 1.69 is needed with caustic soda or 1.67 with caustic potash. On practical operation voltages of from 1.9 to 2.5 are used to overcome the inner resistance of

Hydrogen required:	Cu. ft. (theoretically)
To inflate an airship (size of "Akron").....	6,500,000
To produce 1 ton of:	
Ammonia, by catalytic process	63,000
Decalin, from naphthalene	28,000
Cyclohexanol, from phenol	22,500
To fully hydrogenate 1 ton of:	
Oleic acid	2,500
Linoleic acid	5,100
Linolenic acid	7,700
Coconut oil	285
Cottonseed oil	3,100
Soybean oil	3,350
To hydrogenate to consistency of lard (M. P. 98° F.):	
Cottonseed oil	1,300

amounts of Hydrogen required for some of these processes.

When comparing the widely differing amounts necessary per ton of material, we realize that the

is generated by electrolysis, f.i. in Italy, a country deficient in coal,

*Incidentally, the total amount of oils hydrogenated per year in the U. S. A. has not varied to any extent during the past year.