

Emulsions in Theory and Practice

Reviewing Some of the Literature Relating to This Chemical Phenomenon of Paramount Interest

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THE technical man often has use for a knowledge of emulsions, how to make them, how to avoid them, and how to use them. The theory of emulsions has not yet taken its final form; the present theoretical knowledge is fairly adequate from the view-point of the practical problems presented by emulsions.

An emulsion is a colloidal suspension in which both the continuous and disperse phase are liquids. It follows from the definition that the two liquids must be mutually immiscible, or nearly so, under the prevailing conditions in order to form an emulsion. Each phase of an emulsion is by definition a "distinct" and usually "separable" part. The majority of common emulsions contain three essential phases, viz; two mutually immiscible liquids and a peptizing, or emulsifying, agent. The peptizing agent is a substance which attaches itself to the globules of the disperse phase by absorption, by virtue of which the emulsion is formed, and more particularly, stabilized.

There are two general types of emulsions; the oil in water emulsion (oil droplets dispersed in water), and the water in oil emulsion (water droplets dispersed in oil). The terms water and oil are used here in a comparative sense. Theoretically, with the aid of the proper peptizing agent, any concentration of water dispersed in oil, or oil dispersed in water, is possible.⁽¹⁾

Two classes of emulsions have been recognized, simple oil in water emulsions (no osensible peptizing agent present), and concentrated emulsions of oil in water and water in oil. The disperse phase (oil) in the simple emulsions has not been found to exceed a concentration of 2%.⁽²⁾ In the case of these emulsions, only the oil in water type has been observed.⁽³⁾ The possibility that there is a peptizing agent present even in these simple emulsions is not entirely eliminated. "Stable emulsions of two pure liquids cannot be made."⁽⁴⁾

There are several theories of emulsion formation which can only be presented here very briefly. Bancroft⁽⁵⁾ believes that to form a stable emulsion there must be a tough, elas-

tic film of peptizing agent about each dispersed droplet. Further, substances which are capable of going into colloidal suspension in one of the liquids to be emulsified, and are strongly adsorbed at the liquid—liquid interface are good emulsifying agents. Holmes⁽⁴⁾ states some of his thoughts on emulsion as follows, "Having studied cellulose nitrate as an emulsifying agent⁽⁶⁾—the ideal film for an emulsion must be one which forms readily and comes quickly to an equilibrium between the peptizing action of the one liquid and the precipitating action of the other. It should be tough and elastic and should change little with age. Such a film on the solvent side should be gelatinous and swollen with that liquid. On the side of the second liquid it should be coagulated, not to the point of brittleness, yet should be 'wetted' somewhat." Quincke⁽⁷⁾ held that the main part played by an emulsifying agent is a lowering of surface tension. Fischer believes⁽⁸⁾ that in the case of the alkali soaps the peptizing agent is the important factor. Briggs, DuCasse, and Clarke⁽⁹⁾ present arguments counter to an hydration theory. Pickering⁽¹⁰⁾ showed that it is possible that the globules of the disperse phase can be kept apart by small discreet particles of an insoluble substance. Another theory is that the best emulsifying agents have long molecules, at the end of which there is a polar group.⁽¹¹⁾ Langmuir's contention⁽¹²⁾ is that in the case of organic liquids, the active groups are oriented towards the interior of the liquid. As a broad generality this theory may be somewhat inadequate.

It immediately becomes apparent that there is a variety of theories of the phenomenon of emulsification, some of which apply more to specific cases than as generalities. Some of the difficulty seems to have been in trying to define a good emulsifying agent; and the greater proportion of the work done so far seems to have been with stable emulsions. It is therefore not quite certain what the minimum specifications are that any given emulsifying agent must fulfill before it can be counted on to form a colloidal suspension of one liquid in another. In the majority of cases, for the

commercial handling of emulsions, the theories of Bancroft and Holmes will be found to be the most useful.

Methods for the formation and coalescence of emulsions are of particular interest to those working with fatty oils. In the process of refining vegetable oils and fats with alkali⁽¹³⁾ one deals with both the peptization and coalescence phenomena. When sodium hydroxide solution is added to the oil, with agitation, soap is formed. The soap then peptizes the water, forming an oil in water emulsion which is fairly unstable. Heating the emulsion causes it to "break" or coalesce. It is of interest to note that while sodium and potassium soaps form emulsions of oil in water, soaps of the alkaline earth metals form emulsions of water dispersed in oil.

If one wishes to form an emulsion, there are several methods at hand. The ingredients may be stirred up with a high speed agitator, or the dispersion may be obtained by means of the colloid mill.⁽¹⁴⁾⁽¹⁵⁾⁽¹⁶⁾ The two liquid phases may be simply shaken together in the presence of the peptizing agent. There are two ways in which this may be done by means of a shaking machine, or by hand. Intermittent shaking produces the finished emulsion in a shorter time than continuous shaking. Briggs⁽¹⁷⁾ emulsified 1% sodium oleate solution in benzene, 80% of the volume being benzene. Using intermittent shaking by hand the emulsion was formed in eighty shakes; whereas it took forty eight thousand shakes to peptize the benzene by means of continuous shaking by hand. Emulsions may be formed by trituration; this method being favored by the pharmacists.⁽¹⁸⁾ Here either the American or the Continental method may be used. The American method consists of peptizing the gum and placing the colloidal suspension in a mortar. The oil is then added a little at a time with continuous grinding in the same direction. The gum is ground with the oil, when using the Continental method, and enough water added at one time to emulsify all of the gum. Richards⁽³⁴⁾ has recently contributed an interesting method for the formation of emulsions. He emulsified water and benzene by means of intense, high frequency (3000 K.C.) sound waves. The sound waves acted as the means of agitation. Mercury was peptized into water by this method. Oil, in ether solution, can be peptized in alcohol by adding the ethereal solution to the alcohol in the presence of an emulsifying agent.

Emulsions may be coalesced, or "broken" by several means. In some cases by bringing the disperse phase to the isoelectric point (the

breaking point), the zero value of the potential of the electric double layer⁽²⁰⁾ the emulsion may be broken. It is probable that this is what happens when an emulsion of oil and water which is peptized by sodium soap is broken by the addition of calcium chloride. Of course, the calcium chloride forms the calcium soap which wants to peptize water and oil, this antagonistic fact coalesces the dispersed droplets. Emulsions can quite often be coalesced by heating. "Anything which destroys the film (of peptizing agent) destroys the emulsion."⁽¹⁾ Thus a benzene in water emulsion, peptized by sodium soap, may be broken by the addition of hydrochloric acid which decomposes the soap, and by sodium chloride which "salts out" the soap. Filtration will sometimes break an emulsion, or at any rate make it much less stable. The addition of a liquid in which both phases are soluble may be used to coalesce the particles. Freezing may cause an emulsion to be broken. Electrical methods may be employed to break water in oil emulsions.⁽²¹⁾⁽²²⁾⁽²³⁾⁽²⁴⁾ In this case high potential alternating current is generally used, although direct current will effect the desired result.

Briggs⁽²⁵⁾ has devised an excellent method for determining which phase is disperse and which continuous in a given emulsion. This method is carried out by placing a drop of emulsion on a slide under a microscope. A drop of one of the two liquid components of the emulsion is then brought up to the emulsion drop. If the emulsion and the pure drop mix, the continuous phase consists of the same material as the drop. Clayton⁽²⁶⁾ determines which phase is which by determining the electrical conductivity of the emulsion. Oil and water emulsions show a conductivity, whereas water and oil do not. Gordon and Krantz⁽²⁷⁾ add a colored foreign substance, which is soluble in only one of the phases, and observe the resulting color of the emulsion. This may have an unwanted effect upon the emulsion. Generally the Briggs method will be found most satisfactory without resorting to the more complicated methods.

Examples of a few interesting emulsions will serve to coordinate the ideas which have been discussed. Pickering⁽¹⁰⁾ prepared an oil in water emulsion using basic copper sulfate to peptize a petroleum distillate (heavier than kerosene) in water. Glycerol may be dispersed in amyl acetate, using cellulose nitrate as the peptizing agent.⁽⁴⁾ Holmes and Cameron⁽²⁸⁾ have prepared beautifully colored, "chromatic" emulsions of glycerol and benzene, using cellulose nitrate in amyl acetate. In the oil chemist's test for unsaponifiable matter by the extraction

of an alcoholic soap solution with petroleum ether, emulsions of water in petroleum ether, and petroleum ether in water, frequently co-exist. Woodman⁽²⁹⁾ has investigated this phenomenon using petroleum ether with a boiling point of approximately 120°C. Mayonnaise is an oil in water emulsion (oil in vinegar) with egg yolk as the emulsifying agent. Calcium soaps probably emulsify water in oil in the process of splitting fats by the use of calcium hydroxide and superheated steam.⁽¹⁾ Water may be emulsified in kerosene by the use of carbon black.⁽³⁰⁾ Codliver oil is an emulsion of oil in water. Milk is an emulsion of butter fat (oil) "dispersed in a water solution of caseinogen, albumins, sugar, and various salts."⁽³¹⁾ Rosin peptizes water in linseed oil to form paint. The resinous matter from certain oils will emulsify water and ether.⁽³²⁾ The emulsion is not stable due to the evaporation of the ether.

The viscosity of emulsions increases rapidly with the percentage of disperse phase; thus, very stiff emulsions containing 99% of oil as the disperse phase, in 1% sodium oleate solution, have been prepared.

The sodium salts of the low molecular weight fatty acids do not act as emulsifying agents under ordinary conditions and do not form colloidal suspensions; the sodium salts of the fatty acid series starting with lauric acid act in the reverse manner.⁽³³⁾

Combats Yellow Shortcomings

A SPECIAL rule for the consideration of the Haugen margarin bill has been granted by the House Committee on Rules, which means that this bill will not wait its turn on the legislative calendar but will be called up for action shortly. The bill, H.R. 6, was introduced by Representative Gilbert N. Haugen of Iowa, chairman of the committee on agriculture, and is similar to one reported out by this committee last year. Its purpose is to extend the oleomargarin act of 1886 to include so-called cooking compounds made in semblance of butter. Many such products are now on the market, having so far successfully resisted efforts of the Bureau of Internal Revenue to collect the tax applying to colored oleomargarin. Both butter interests and the Institute of Margarine Manufacturers have endorsed the bill.

The report submitted by Chairman Haugen states that these products are packaged like butter, resemble it closely, and are advertised as a bread spread, and are poorly suited to cooking purposes because of the deliberate addition of water, salt, and coloring matter, ingredients not found in ordinary shortening compounds. It is declared that the bill will not injure any bona fide manufacturer of oleomargarin or cooking compounds, and that it will not include unrelated products, such as ice cream, salad dressings, or puff-pastry shortenings. The bill also makes some perfecting amendments in the wording of the act, and permits the use of fish oil and fat in making oleomargarin, the committee declaring that modern refining processes make these fats edible.

Spanish Olive Oil

A further decline in prices of olive oil in Spain in the last quarter stimulated export trade, and shipments exceeded those made in the preceding quarter and in the first quarter of 1929, reaching 3,015 metric tons. Of the total exported the United States took 1,132 metric tons, or over 37 per cent, and was followed in important purchases by Italy, 504 metric tons; Great Britain, 367; Norway, 316; Cuba, 299, and Portugal, 218. In the third quarter of 1928 total exports were 5,858 metric tons, of which 3,271 went to Italy. Before prices in Spain declined sufficiently to become attractive to foreign buyers, foreign needs this year had been largely supplied by other producing countries. (*Report from Consul Brady at Malaga, Spain.*)

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