

THE THEORY OF EMULSIFICATION, V

BY WILDER D. BANCROFT

Mr. Charles E. Swett has called my attention to the fact that wool fat forms an emulsion with water in which the water is present in drops.¹ "Although insoluble in water, wool wax possesses the remarkable property of absorbing larger quantities of water than any other wax. The emulsion it forms with water has the appearance of a perfectly homogeneous mass. This wool wax can be mixed with as much as 80 percent of water. A mixture of neutral wax and water, containing about 22-25 percent of the latter, is sold in commerce under the name lanolin."

"Owing to its property of forming an emulsion with water which will not separate into two layers even after several years standing, and to the ease with which it is absorbed by the skin, wool wax is used as a basis for ointments and cosmetics. The British Pharmacopoeia recognizes two preparations, viz., *Adeps lanae, i. e.*, pure wool wax, and *Adeps lanae hydrosus, i. e.*, hydrous wool wax, better known under the trade name of lanolin."

I have not been able to find out whether other ointments containing water have the water as drops or not; but it seems probable that some do. Shoe blacking contains oil, water and other materials. It may, therefore, be considered as an emulsion; but I have not been able to find any statement as to the type and we have not yet had time to study it in the laboratory.

Mr. Swett tells me that drops of water in oil can be obtained by the use of rosin. The directions are to dissolve rosin in mineral oil, using heat. When the mixture is cold, add water in small proportions and shake. As much as one hundred percent of water may very easily be taken up in this way.

¹ Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," third edition, 2, 879, 883 (1904).

Lime and alumina soaps are used in lubricating greases. The addition of water produces some rather surprising results.¹ "Though the composition of these greases varies somewhat, most of them consist of a solution of lime soap (15-23 percent, and occasionally more) in a heavy mineral oil with the addition of a little water (sometimes as little as 0.5-0.7 percent, but usually 1-4 percent). As secondary constituents we have small amounts of unsaponified fatty oils, glycerol, free lime, free fatty acid, as well as substances added to mask the color, odor or fluorescence. In some greases there are also alkali soaps. For technical use these greases are usually manufactured by dissolving a previously prepared lime soap in mineral oil and mixing a small amount of water intimately with the resulting solution. It is only occasionally that these greases are prepared by dissolving a saponifiable oil in mineral oil, saponifying with lime, and adding enough water so as to obtain, on stirring, the vaseline-like or tallow-like consistency characteristic of lubricating greases.

"The lubricating greases offer a series of interesting problems in physical chemistry, which have not yet been studied from a scientific view-point. Among these problems are: the determination of the factors giving rise to the peculiar consistency; the determination of the reason why the greases often break up spontaneously into a thin, oily, portion and a solid portion; and the explanation of the part played by the addition of water."

"No clear understanding has yet been reached in scientific or technical circles in regard to the relation between the amount of water and the properties of the lubricating greases. Among technical men the belief is prevalent that the water combines with the soap to form a compound analogous to salts with water of crystallization. This erroneous assumption is also often made in regard to the alkali soaps. Observation shows that the water is usually present in a state of very fine mechanical subdivision. This much is certain, that a

¹ Holde: *Zeit. Kolloidchemie*, **3**, 270 (1908).

certain amount of water is necessary in the grease to produce a satisfactory permanency, since all the greases that do not contain water soon become clearly inhomogeneous. As the technical men say, they let go of the oil.

"Some experiments were made on the relation between the amount of water and the resulting consistency and transparency of the greases. A 22 percent viscous solution of a rape-seed oil lime soap was made by heating twenty-five parts of rape-seed oil with 2.13 parts slaked lime to 220°-240°, in a heavy Russian mineral oil. At room temperature, this solution would drip from a glass rod. On adding 1-2 percent water, the liquid mass became like a salve as soon as the water was distributed as a fine solution through the oily mass. On the other hand, a solution of lime soap in oil remained unchanged in consistency when rubbed in a mortar without water. In contradistinction to the clear water-free solution of the soap, the emulsion was distinctly cloudy and only began to drop at 70° in Ubbelohde's apparatus. After dropping, the very fine emulsion was found to have cracked.

"Changes in consistency, like that described, have been noticed by K. Beck¹ in a study of emulsions of gum arabic solutions with castor oil. The viscosity increased very much. A characteristic sign of the moment of maximum formation is a peculiar crackling of the rubbed mass. The increase of the viscosity as the mass changes from an oil to an ointment is probably due to surface forces which only become important when the water particles are distributed as very fine drops through the oil, since the water, before that, moved through the oil without hindrance under the influence of gravity. The dripping at higher temperatures can be accounted for on the ground that a higher temperature works against the surface forces and tends to destroy the emulsion. The salve-like consistency is obtained only when the water is distributed in microscopic particles through the grease.

¹ Zeit. phys. Chem., 58, 409 (1907).

So long as one can see droplets, the conditions are lacking for producing the consistency of a salve.

“The degree of clouding stands in a definite relation to the water content in the case of many greases. In one case, for instance, the mercury bulb of the thermometer in the Ubbelohde apparatus was distinctly visible when the cylindrical glass vessel was filled with a grease containing one percent water while it could scarcely be seen when the grease contained two percent water. On raising the temperature the transparency increases, especially in the neighborhood of the drip-point. This is evidently connected with the decreased stability of the emulsion.

“After standing a while, there is often a surprising increase along the edges of a grease which has been clouded by addition of water. Very often there separates, at these points, a small amount of a clear oil containing dissolved lime soap. This is probably due to the evaporation of water from the surface of the grease exposed to the air, because the presence of water is essential to the maintenance of the emulsion with soap and oil.

“If the amount of water is increased too much, the greases of this type become too cloudy and the viscosity decreases. This is the reason why a water content of seven percent is rarely exceeded. The amount of oil has an effect on the consistency which could scarcely be predicted. If one dilutes a stiff grease with oil so as to make a less stiff one, which does not adhere to the mortar and pestle for instance, the drip-point is not lowered appreciably but drops begin to form 30° to 40° lower than before. Similar large differences between the first formation of drops and the drip-point are also to be noticed with such greases as have been made with too thin oil or with a heavier oil under unsuitable conditions of heating. The differences between the first formation of drops and the drip-point is of considerable importance in technical work and the fluid nature of a solution of lime soap in oil before mixing with water is not considered a disadvantage in preparing a sufficiently stiff grease.

"Like other colloidal solutions, the stiff greases show hysteresis phenomena. It is easy to notice qualitatively that soft greases, which flow in a mortar when the latter is moved slowly, lose this mobility on standing and become stiffer. This shows itself numerically by a rise in the temperature at which drops begin to form, though the drip-point of a grease which has been stored remains approximately the same as that of the fresh grease.

"The changes in the softening point are obviously connected with the hysteresis phenomena which can also be observed with the water-free solutions of lime soaps in oil. These solutions are quite oily and clear when fresh; but become inhomogeneous after standing several days, and sometimes even sooner. A jelly-like lime soap separates, in the same way that jelly-like masses separate from rubber solutions or other colloidal solutions. The filtrate at room temperature proved on analysis to contain 1-2 percent soap, the original soap solution contained 22 percent soap, and the thick jelly on the filter contained 15 percent soap.¹ Similar changes in homogeneity undoubtedly take place in greases to which water has been added; but the emulsification of the drops of water prevents these changes from being visible except as they displace the temperature at which drops begin to form.

"When the anhydrous solution of 20-22 percent lime soap in heavy Russian machine oils solidifies to a gel, its drip-point is about 30°, quite different from that of the salve-like mixtures which have been rubbed with water. If the jelly is shaken, however, the drip-point drops about to room temperature. After heating and slow cooling, the drip-point rises occasionally above 30°.

"With oils containing small amounts of lime soaps, such as the filtrates previously referred to, fine films form on the surface after long standing, so that it seems probable that all these solutions of lime soap are really supercooled colloidal

¹ [It is difficult to see how a soap solution could separate into two portions, each having a lower percentage of soap than the original solution. W. D. B.]

solutions which all have a tendency to precipitate the excess of soap. The previously described lubricating greases are to be considered as salve-like emulsions of these supercooled solutions of lime soap in mineral oils and of the precipitated, jelly-like colloidal lime soap together with a little water. The drip-point of all these greases is about 70° .

“Quite different results are obtained when the lime soap is prepared by precipitating a rape-seed oil alkali soap with calcium chloride instead of by heating, and 20 percent of this precipitated soap was dissolved in a light American mineral oil containing paraffin. The precipitated soap was granular and clear yellow, quite different from the brownish, translucent, viscous and jelly-like boiled soap. It dissolved with such difficulty in oil that gelatinous, crumbly, readily-hardening masses were formed on heating, even when there was continuous stirring at 210° . When solid the mass was a deep brownish red, transparent, and stiff jelly. In it could be seen lighter particles of apparently undissolved soap. In Ubbelohde's apparatus, the drip-point was found to be about 90° , while drops began to form at 75° – 80° . When a brown emulsion was prepared from this jelly with one percent water, it remained fluid even after long standing. Since the anhydrous jelly cracked in a short time to soap and a mobile oil, the peculiar liquefaction of the originally solid mass, when mixed with water, can perhaps be explained by assuming that the solid jelly is a mechanical mixture of a mobile, soap-like oil containing a mass of crystallized lime soap which latter causes the high drip-point.

“Another sample was prepared by dissolving 6.2 percent soap in oil at 225° and rubbing into it one percent of water. It was also reddish brown and fluid while the anhydrous mass, before the water was added, was jelly-like at 28° ; but very mobile. A liquid layer separated on standing. Five other greases were prepared from the light American oil. In the first, 6.2 percent of precipitated soap was dissolved at 255° . The solution formed a thin jelly when cold and a thick layer

of it became partially liquid on standing. When ground with one percent water, there was formed a stiff vaseline-like, dark reddish-brown grease, which was transparent in thin layers and which began to form drops at 25° when freshly prepared, but which showed a drip-point of 74° . The other sample was made with boiled soap and with the same mineral oil. The boiled soap dissolved between 80° and 90° , but stiff greases were not formed unless the solution was heated higher (205°). An 18 percent solution, heated for five minutes at 205° and ground with one percent water, began to form drops at 37° and dripped at 57.5° . A similar solution was heated for 15 minutes at 205° and then ground with water. The resulting grease began to form drops at 46° and dripped at 66° . Longer heating thus raised both temperatures.

“To show the colloidal character of the lime soap solutions, some experiments were made with the ultra-microscope since a boiling-point determination was out of the question in view of the nature of the high-boiling constituents. The solution of the lime soap in the heavy mineral oil was diluted with benzene so as to make observations easier. Under the ultra-microscope it proved to be amicroscopically colloidal. Solutions of precipitated lime soap in pure benzene showed a bluish cone of light, and innumerable submicrons. Solutions of lime soap in a mixture of benzene and alcohol were seen to be colloidal when examined under the ultra-microscope. In the case of these greases we have not only a colloidal solution of lime soap in mineral oil but also a colloidal solution of resins in the oil. This was confirmed by examining the reddish-brown and black opaque mineral oils and their mixtures with benzene. The dark asphalts and the lighter resins were colloiddally amicroscopic.

“When a few drops of a dark railroad oil were dissolved in benzene and placed before the slit of the ultra-microscope, a beautiful, bluish-green cone of light was to be seen. Under the ultra-microscope the solution appeared entirely amicroscopic. If one adds concentrated alcohol to the benzene solutions of dark oils which contain dissolved asphalt, or if

one adds alcohol to an apparently amicroscopic solution of pure asphalt in benzene, the apparently clear and transparent solution shows, under the ultra-microscope, submicrons which are evidently precipitated asphalt, but which cannot be seen as such by the naked eye.

“Reddish-yellow machine oils give a bluish cone of light containing amicrons. The solution of lime soap in a Russian machine oil was also amicroscopic. A white paraffin oil gives a beautiful bluish cone of light containing amicrons. Crystallized paraffin, with a melting point of 38° , differs from asphalt in giving no sharp cone of light when small amounts are dissolved in benzene. It is only when considerable amounts of paraffin are dissolved in benzene that we get a cone of light with submicrons sparkling very beautifully. A similar result is obtained with a normal paraffin melting above 50° . The cone of light is due chiefly to amicrons and is scarcely colored. There are more submicrons, the more concentrated the solution. Submicrons were scarcely to be found in Russian petroleum in which there is almost no paraffin, but they were to be detected in the American petroleum which contains more paraffin and which solidifies more readily.”

In these lubricating greases we have water as the disperse phase, the lime soap forming the protecting film. The consistency is due to the structure of the emulsion. Since there is present about 20 percent of lime soap, the emulsifying agent it is not surprising that there is a marked change in the physical properties, especially in view of the fact that Pickering¹ obtained a practically solid mass resembling blanc-mange by emulsifying 99 parts kerosene with one part of a one percent potash soap solution. Holde does not give sufficient details to enable me to discuss the alleged difference in behavior of a lime soap made by treating rape-seed oil with lime and of a lime soap made by adding calcium chloride to a soda or potash soap. There is presumably no glycerine in the second case and there is probably some soda or potash soap carried

¹ Jour. Chem. Soc., 91, 200 (1907).

down. It is rather a pity that Holde should have changed the method of preparing the lime soap and the nature of the mineral oil at the same time.

Another instance of an emulsion in which water occurs in drops is to be found in the case of mixed paints.¹ "The manufacture of mixed paint is essentially American, having been accredited to some enterprising New Englanders who observed that when linseed oil paint was mixed with a solution of silicate of soda (water-glass) an emulsion was formed, and the paint so made showed very little tendency to settle or harden in the package. Several lay claim to this invention. The first mixed paint was marketed in small packages for home consumption and appeared about 1865.

"The addition of silicate of soda is still practised by a few manufacturers, but the tendency is to eliminate it as far as possible and to minimize as much as possible the use of an alkaline watery solution to keep the paint in suspension. The general use of zinc oxide has had much to do with the progress of mixed paint, for it is well known that corroded white lead and linseed oil settle quickly in the package, while zinc oxide keeps the heavier lead longer in suspension. Where only heavy materials are used, manufacturers are inclined to add up to four percent of water.

"In certain classes of mixed paints, particularly house paints which are made of corroded lead, sublimed lead, barium sulphate, etc., there is a likelihood or tendency of the pigment to settle. This is more marked in the case of corroded lead than in any of the other pigments. To prevent this, in a measure, water is added, and up to a certain percentage both the manufacturer and the consumer have accepted the fact that water is not injurious when added to two percent for the purpose of combining the paint; but beyond this percentage its effect is likely to be injurious.

"Sometimes for the sake of an argument, but more often

¹ Toch: "The Chemistry and Technology of Mixed Paints," **11**, 116 (1907).

for the sake of making a paint which contains no more water than the natural moisture of its constituents, a manufacturer feels the necessity of adding a combining medium other than water to prevent the paint from settling hard in the package. Among these are gutta-percha solutions, solutions of balata, para-rubber, gum chicle, etc. The rubber solutions mentioned serve their purpose very well without injuring the paint, and the percentage used is so small that it may be considered negligible. This, however, is not true of many of the mixing varnishes which are made by varnish manufacturers who have no experience in the manufacture of paint. They sell rosin varnishes neutralized with lime, lead or manganese, and while they assist very well in combining the lead with the oil, the wearing quality of the paint is proportionately reduced.

“With the last few years a new combining medium has appeared on the market which in itself is an improvement on all paints. It is made by melting a mixture of a resin (free from rosin or colophony) and heavy linseed oil and reducing with China wood oil and naphtha. Where a manufacturer uses a combining medium of this character the paint becomes more viscous as it grows older, and when it dries it produces a satin-like gloss and shows fewer brush marks than a paint containing water.

“The question of how much water shall be added to mixed paints, or how much water mixed paints shall contain, either added or incidental, is not fully decided upon, as there is a difference of opinion as to its value, and likewise a difference of opinion as to the amount necessary for certain purposes. There are some paints in which as high as 2 percent water are necessary, and in other paints less than 1 percent is purposely added. That water is of great benefit in certain paints cannot be disputed, one large railway corporation permitting the addition of 1 percent of water to its mixed and paste paints.

“A chemist in making an examination of a mixed paint must necessarily be careful in giving an opinion as to the amount of water in the paint, and great judgment must be

used in a report. For instance, a paint, made according to a certain specification, containing a large mixture of Venetian red and yellow ochre, might contain very nearly 2 percent of moisture, which was a part of the composition of the pigment. Then again, linseed oil frequently contains more than a trace of water, which the manufacturer cannot extract nor can he afford the time necessary to allow the water to settle out of the oil. A mixed paint should not contain over 2 percent water, for it is unnecessary to add more than this amount to any paint.

“The proper benefits derived from the addition of water to a pure linseed oil paint are suspension of the pigment and improvement in its working quality. Take the case of artists’ tube colors which lie on the dealers’ shelves for years and which are prone to get hard and likely to separate so completely that the color will be found on one side of the tube and the oil entirely free on the other. Water is an absolute necessity in this case and is an improvement for both seller and user. The colors made with the correct addition of water are known to pile and artists prefer a color which “piles” properly.

“There are many ways of adding water to a paint. In some instances the required amount of water, together with the oil and the drier, are placed in a churn or mixer and the paste stirred in. Where materials like calcium sulphate, calcium carbonate, ochre, Venetian red, silicate of magnesia, silicate of alumina, white lead, etc., are used, there is no necessity for adding any combining material which will form a soap with the linseed oil, there being sufficient action between these materials and the water. It is an additional advantage that there is less likely to be complete saponification in a mixed paint to which no emulsifier has been added.

“There are a large variety of materials which are used for ‘emulsifying’ paint, some of which are good and some of which tend to gelatinize the paint. The materials used for ‘emulsifying’ paint are the carbonates of all the alkalis, borax, zinc sulphate, calcium hypochlorite, manganese sul-

phate, manganese chloride, ferric chloride, lead acetate, ferrous sulphate, alcoholic solutions of these various salts, also the alcoholic solutions of these salts containing a small percentage of moisture.

“To detect water in paint, particularly in light-colored paints, is a comparatively simple matter. The method devised by the author is almost quantitative for some purposes. The first method ever published by the author consisted in placing a strip of gelatin in a mixed paint. When a measured or weighed amount of mixed paint was taken and the strip of gelatin allowed to remain for twenty-four hours a fairly correct quantitative determination was obtained. Another method described some years ago involved the use of anhydrous sulphate of copper, a bluish-white powder which on the addition of water returns to the natural dark blue color of crystallized copper sulphate.

“The author has, however, devised the scheme of using a glass plate and mixing a paint with a dyestuff known as Erythrosine B. When about $\frac{1}{2}$ gram of the dye and 5 grams of mixed paint are rubbed together with a pallet knife on a sheet of glass, a paint containing no water will produce a distinct pearl-gray color; if there is water in the paint the mixture changes almost immediately to a brilliant cerise red, and if there is much water in the paint (over 2 percent) the color changes into a crimson so that the reaction is clearly marked. The test must not be allowed to stand more than four minutes, since even paints which contain no added water but which naturally contain traces of moisture will begin to change into a rosy color, but this indication points to the absence of water.

“In a red, black, or other dark-colored paint where this color reaction cannot be seen, the oil must be separated from the pigment and a test made of the oil on a sheet of milk glass. It is always necessary to run a blank alongside of the test, the blank being of known composition. For instance, in testing a yellow paint composed of ochre, a certain amount of water will be found in the dry color. It is

therefore necessary to make a yellow paint containing ochre and test it with erythrosine and note how long it takes for the water in the ochre to attack the erythrosine. The suspected sample is then tested, and if it changes in the same time as the known sample, no added water can be reported. A white paint very largely composed of moist white lead will show the erythrosine reaction in a few minutes, and a chemist who has standard samples of known composition at hand will find this test both delicate and useful.

"There are a large variety of indicators such as nigrosine black, insoluble in alcohol but soluble in water, which are very useful indeed. Some manufacturers have been known to add a borax solution of rosin and shellac, which contains a small percentage of wood alcohol, to certain paints.

The wood alcohol in this case would give a very brilliant color with the erythrosine, but the nigrosine being insoluble in alcohol would give its color only with water."

Holley and Ladd¹ say that "many of the paints which have been sent out of late years have contained unnatural proportions of water, not intended to add value to the paint, or to serve for preventing its settling and hardening. No more than from one to two percent of water is needed, if at all necessary, for this purpose. It is not uncommon for paints to contain from ten to twenty-four percent of water in the liquid portion. This, with the small amount of added alkalies and jelly-like constituents, has produced serious results for the paint consumer."

I have not been able to find any statement as to the type of the emulsion formed when water is added; but it seemed to me self-evident that 24 percent of water would readily be detected in case the water were the external phase, and consequently it seemed justifiable to assume that in mixed paints we had water emulsified in oil. This assumption was confirmed in my laboratory by Mr. F. R. Newman who tested a sample of mixed white lead and added more water to it

¹ "Analysis of Mixed Paints, Color Pigments, and Varnishes," 5 (1908).

until the paint contained over 70 percent of water. It was also found that water emulsifies in commercial linseed oil, this undoubtedly being due to the rosin content of the oil. Since there are said to be seventy million gallons of mixed paints used per year in the United States, this type of emulsion is unquestionably the more important one commercially, and it is rather extraordinary that the writers on emulsions should have overlooked this important industry.

It seems to me that we are now in a position to consider the conditions under which one or the other type of emulsion occurs. Donnan's surface tension theory of emulsions is certainly not right in the form in which it has hitherto been given. Pickering¹ brought this out clearly when he prepared emulsions of oil in water with basic iron sulphate. On the other hand, no one will deny that the formation of an emulsion is a phenomenon involving surface tension. Consequently, some point has been overlooked in Donnan's theory. Donnan is quite right in pointing out² that the stability of an emulsion depends on the fact that a surface film with a low surface tension tends to prevent a coalescence of the drops of oils. He is also right in the reason given for it. The weakness in Donnan's theory is due to the fact that Donnan has always started with the fact that the oil is emulsified and that he has consequently never formulated the conditions under which the oil becomes the disperse phase rather than the water. Donnan considers the surface film in the case of soap emulsions as part of the water phase though differing in concentration from it. All the difficulties disappear if we consider the surface film as a separate phase, so that we have drops of oil, a surface film, and surrounding water. We must do something of this sort in the case of foams or soap-bubbles, because there it is absurd to consider the film as part of the enclosed air or of the external air. In the case of the soap-bubble, the compositions of the phases inside and outside the film

¹ Jour. Chem. Soc., 91, 2012 (1907); Zeit. Kolloidchemie, 7, 15 (1910).

² Cf. Jour. Phys. Chem., 16, 202 (1912).

are --or may be --the same, and the internal phase is the one exerting the most pressure, at any rate originally. With a real emulsion the conditions are different because we have two distinct liquids. It seems to me that it is easy to modify Donnan's theory so that it will fit the facts. Let us imagine a flexible, vertical diaphragm, which separates two liquids A and B, and which is wetted by each. Since the diaphragm by definition adsorbs each of the liquids, the surface tensions of the two sides of the wetted diaphragm will not be the same as a rule. Owing to this difference in the surface tensions, the diaphragm will bend so that the side with the higher surface tension becomes concave. This change tends to envelope the liquid on that side. Consequently we conclude that liquid A will form drops in the emulsion in case liquid B lowers the surface tension of the diaphragm more than does liquid A. The absolute and relative surface tensions of the two liquids against their respective vapors have nothing to do with the phenomenon and it is theoretically possible to emulsify benzene in water with one diaphragm and to emulsify water in benzene with another diaphragm. It all depends on the properties of the diaphragm, on the nature of the emulsifying agent. While this way of looking at the matter clears up the theoretical difficulties in regard to the type of emulsion, it is not quite clear from this how one would go to work to find a suitable emulsifying agent in any given case. I am quite willing to admit that I do not know how to formulate a rule which will cover all cases; but I can deduce one which covers a great many cases. Suppose we consider the extreme case that one of the two liquids, water for instance, lowers the surface tension of the diaphragm very much when adsorbed by it. We then have conditions favorable to the disintegration or peptonization of the diaphragm. Consequently we conclude that if a substance forms a colloidal solution with water and is coagulated by benzene, that substance will tend to emulsify benzene in water. To what extent we get an actual emulsion depends on the coherency and permanency of the film formed. This rule covers practically all the cases of

emulsions in water which have been considered in this series of papers. Soap is a hydrophile colloid and so are the gums. The insoluble salts used by Pickering approached the colloidal state the more finely they were ground, and it was under these conditions that they were the most effective. It is not possible from Pickering's experiments to tell to what extent the differences in effectiveness were due to the lack of formation of a suitably coherent film and to what extent they were due to specific relative adsorption. This point can be discussed more profitably when we get to the special case of ore flotation.

This formulation covers that of Höber,¹ previously quoted:² "Some other processes in the cell probably also come under the heading of adsorption of colloids. We saw that drops of chloroform or carbon bisulphide in solution of albumen become covered with a membrane of albumen. Such membranes, resulting from the contact of two solutions have been known in biology for a long time under the name of haptogen membranes. It is to them that we owe, in large part, the permanency of the emulsions which occur in many physiological solutions. Thus the continued, fine distribution of fat in milk is due to the existence of a film of caseine around the globule of fat. The emulsifying action of small amounts of alkali on a mixture of oil and water is due to the formation of membranes of soap at the surface between oil and water. In order to obtain a fine-grained emulsion it is not sufficient to add a substance which concentrates in the surfaces between two liquids. By addition of chloroform or acetone to oil and water, we get no emulsion. It is necessary that the added substance should be a hydrophile colloid which is adsorbed in its peculiar way with formation of a solid film."

Theoretically, it ought to be possible to form an emulsion when the emulsifying agent is soluble in water and is precipitated by the other liquid provided a film is formed; but it

¹ *Physikalische Chemie der Zelle und Gewebe*, third edition, 293 (1911).

² *Jour. Phys. Chem.*, 16, 227 (1912).

would be difficult to form a permanent emulsion unless one started with a saturated solution in water.

The theory as outlined shows that we should get an emulsion of water in oil or carbon bisulphide provided we took an emulsifying agent which formed a colloidal solution in the non-aqueous solvent. Instances of this have already been cited, rosin with linseed oil and water, lime soap with mineral oil and water. Using a magnesium soap plus a little sodium oleate Mr. F. R. Newman succeeded in emulsifying 90 percent of water in carbon bisulphide. The details of this work will be published by Mr. Newman at some future date.

There is one case cited by Pickering¹ which calls for special comment. He found that potassium cupric tartrate will emulsify a mixture of alcohol and water. Since alcohol and water are miscible in all proportions, this seemed a trifle uncanny until we repeated the experiment and found that potassium cupric tartrate causes aqueous alcohol to separate into two liquid layers. If anybody is interested in this special problem, it is evidently possible to make emulsions of acetone in water or of water in acetone by first adding some such salt as potassium carbonate to cause the formation of two liquid layers and then adding a suitable emulsifying agent.

Since the object of the emulsifying agent is to keep the drops of the dispersed phase from coalescing, anything which will act in this way will serve more or less as an emulsifying agent. As an extreme case we may have an electrical charge caused by the adsorption of an ion. Under these circumstances an emulsion will behave like a colloidal suspension. This has been realized by Ellis.² The interface potential was found to be little affected by organic impurities in the oil but to be altered enormously by acids, and to a lesser degree by alkalis. The maximum interface potential was found to correspond to a concentration of about $N/1000$ alkali, and this

¹ Zeit. Kolloidchemie, **7**, 11 (1910).

² Zeit. phys. Chem., **80**, 597 (1912).

was found to be the point of maximum stability of the emulsion. Surface-tension measurements showed that the stability did not depend on the surface tension, but on the interface potential.

The question of the factors determining the stability of an emulsion is an important one from the point of view of the maker of emulsions; but it cannot be taken up in this series of articles because it depends on the theory of jellies. I propose to discuss it later under that head. A few words on the subject will suffice for the present. It is well known that jellies contract in time and exude liquid or even go all to pieces. If the surface film around the drops behaves in this way it is clear that the emulsion cannot be stable. Other things being equal an emulsion will be more stable, the smaller the drops. By use of a homogenizer it is possible to break up the globules in fresh milk so that the cream does not come out in a separator. I am told that it is also possible to start with skimmed milk and renovated butter fat, and to make an excellent imitation of fresh milk therefrom.

The general results of this paper are as follows:

1. Lanolin is an emulsion with water as the disperse phase.
2. Some of the properties of lubricating greases are due to the presence of emulsified water. The emulsifying agent is apparently the lime soap.
3. In mixed paints the water is the disperse phase. The emulsifying agent is apparently the dissolved rosin.
4. If the surface tension between liquid A and the emulsifying agent is lower than the surface tension between liquid B and the emulsifying agent, liquid A will be the dispersing and liquid B the disperse phase.
5. A hydrophile colloid will tend to make water the dispersing phase while a hydrophobe colloid will tend to make water the disperse phase.
6. In order to emulsify two liquids which are miscible in all proportions, it is necessary to add a substance which will make them only partially miscible.

7. As a limiting case, drops may be kept from coalescing by an electrical charge due to the adsorption of an excess of some ion. Such an emulsion will behave like a typical colloidal suspension.

8. Anything which destroys the film round the drops in an emulsion or which neutralizes the charge on the drops will make the emulsion less stable.

9. The cracking of an emulsion is often due to the ageing of the film round the drops. The discussion of this belongs properly under the theory of jellies and will be taken up there.

10. Other things being equal, an emulsion will be more stable, the smaller the drops.

In the next paper of the series I intend to consider the flotation of ores as a special case under the general theory of emulsification.

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