

CONTRIBUTED AND SELECTED

THE PHYSICAL SIGNIFICANCE OF EMULSIONS.*

BY LEO ROON.

Colloid and physical chemists have for many years, and especially so in recent years, carried out many investigations on emulsions with the idea of bringing to light the many missing links in the emulsion theory chain.

On the other hand, the pharmacists have done excellent work on emulsions for a greater number of years, but this was purely on the practical side. It is of interest to note, however regrettable, that the younger generation of pharmacists does not attempt to contribute even to our practical knowledge of the subject. This was brought out by a perusal of the proceedings of the American Pharmaceutical Association, which reveals the fact that almost all emulsion experimentation by pharmacists was done in the period between 1870 and 1900, and practically no work of value has been done since.

Therefore, for the explanations of the "why" of emulsions, we must of necessity turn to the physical chemists, and then, having in our minds a bird's-eye view of what they have tried to explain, perhaps we shall be able to apply *their theory to our practice*.

The object of this paper, then, is to give a brief résumé in chronological order of the development of those portions of the theory of emulsification which might be of practical application and of general interest to the pharmacist.

Several terms, which will appear frequently in this paper, will be defined first:

Each different, homogeneous part of a system is called a *phase*. For instance, pure water and olive oil are two different liquid phases.

If we now add the oil to the water and shake vigorously, we obtain a very fine distribution of a liquid phase (olive oil) in another liquid phase (water). Such a heterogeneous system is called an *emulsion*.

The phase which is divided into small separate volumes (in this case, the olive oil) is called the *disperse phase*.

The phase in which the disperse phase is distributed (in this case, the water) is called the *dispersion medium*.

The surface of a liquid has different properties from its interior, and acts like an elastic bag, tending to diminish the surface area. This effort or force exerted to diminish the surface of a liquid is its *surface tension*.

In adding to water as little as 0.01 percent of soap, the surface tension of water is decreased to 40 percent of its original value. If to such a solution oil is added and the mixture shaken, the tendency for the oil globules to gather together and the water particles to gather together is diminished. Substances, such as soap, that lower surface tension also cause *surface concentration*, and this phenomenon is an important factor in stabilizing emulsions, as will be shown later.

Surface tension \times surface = surface energy.

For instance, 1 Cc. (mil) of oil has approximately a surface of 6 sq. cm. If this 1 Cc. (mil) of oil is subdivided into globules having a diameter of about 1 micron (1/1000 mm.), then that same quantity of oil has a surface of 60,000 sq. cm., or, in other words, if the surface tension has not changed, then the surface energy is now 10,000 times as great as before subdivision. This is evidenced in

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making an emulsion nucleus. The trituration at first is very easy. As the particles become more and more finely subdivided, the total surface, and also total surface energy, increase tremendously, and the work in trituration necessary to overcome the increased energy is very great indeed.

In 1870, E. v. Brucke¹ announced the fact that when rancid oil, or, in other words, oil containing free fatty acid, is shaken with a solution of sodium carbonate and certain other alkaline liquids, an immediate emulsion results. He believed that the oil was broken into fine globules by shaking, and that the soap formed served to hold the emulsion by preventing the oil globules from coming together.

In the same year, L. Plateau,² after investigating various emulsions, came to the conclusion that the formation of emulsions depends on low surface tension and a high viscosity, the decrease in surface tension permitting greater miscibility, and the high viscosity hindering the coalescence of the oil globules.

In 1873, Donath³ made practical use of the formation of emulsions as a means of detecting adulterants. He boiled for five minutes a piece of beeswax, about the size of a nut, with a concentrated solution of sodium carbonate. If an emulsion remained on cooling, the wax was considered adulterated with rosin, tallow, stearic acid, or Japanese wax.

In 1878, Johannes Gad⁴ called attention to the fact that, when oil containing the proper percentage of fatty acid was placed on the surface of a sodium carbonate solution a beautiful spontaneous emulsion resulted, and from this he held that neither shaking, nor any other outside mechanical force was necessary to the formation of an emulsion, but that the chemical force developed by the soap formation of itself was sufficient, under favorable circumstances, to break the oil drops into the finest emulsion globules.

Gad's method, used in his study of spontaneous emulsions, consisted in taking a series of watch glasses containing a 0.25 percent solution of sodium carbonate. Drops of oil containing different percentages of fatty acids were gently placed upon the surface of the solutions in the watch glasses, and the amount of spontaneous emulsification noted. Gad found, at room temperature under the conditions named above, that the oil which contained about 5.5 percent of fatty acid emulsified spontaneously, and that oils with very little more or less than 5.5 percent of fatty acid yielded incomplete emulsions. He therefore determined that the limits of good spontaneous emulsibility were not only constant, but quite narrow.

The essence of Schischkoff's⁵ work, published in 1880, is as follows:

1. He found also that fats and oils with free fatty acid were emulsifiable with dilute alkaline solutions.

2. He could emulsify oil of turpentine, mineral oil, etc., by alkaline liquids, if a small amount of stearic acid were added to the oils.

3. He observed that butter fat, freed from free fatty acid, could not be emulsified by an alkaline liquid.

4. Finally, he discovered in whey an albuminoid, which is different from common albumen and casein. His synthetic experiments tended to show that casein, without this albumen, may form milk, but not cream.

In 1888, Quincke⁶ discusses emulsions as follows:

"By shaking oil with soda or gum arabic solution, one can prepare emulsions which look like milk. When fatty oils are emulsified in soda solution, the coalescing of the fat globules is prevented by a thin layer of soap solution, any opening in which is at once closed by the molecular forces." He also shows in a table that the surface between the fatty oils and the gum arabic solution is less than the surface tension of the fatty oils against water. Further, he states that "if one shakes

together mercury, water and olive oil, there is formed a grayish-white viscous mass, an emulsion of mercury, formed of many small globules of mercury, each one covered with a film of oil. . . ." According to Quincke, "gray mercury salve is really an emulsion of mercury in viscous lard."

In 1891, Rachford⁷ published an exceedingly interesting paper entitled, "The Influence of the Bile on the Fat-splitting Properties of the Pancreatic Juice," which, because of its wealth of emulsion study, will be briefly abstracted herewith:

Rachford employed in his experimental work Gad's method of determining the spontaneous emulsibility of oils. He showed that heating an animal or vegetable oil split off free fatty acid, so that a neutral oil, incapable of being emulsified with alkaline liquids, when heated, developed sufficient free fatty acid to form a good emulsion with sodium carbonate solution.

Rachford says, "It is a physiological fact beyond dispute that the splitting of fatty acids is a most important preliminary step in fat digestion. That the cooking of fats will develop in them fatty acids is therefore a fact of considerable physiological importance and one that, so far as I know, has not previously been noticed."

With these as preliminaries, the author goes on with his investigations with the pancreatic juice. He inserts a small glass cannula through the pancreatic papilla into the pancreatic duct of a living rabbit, and collects about 1 Cc. of juice "uniform and powerful in physiological action." He arranges a series of watch glasses with 0.25 percent sodium carbonate solution in them (Gad's method). Into a 2 Cc. tube, $\frac{1}{3}$ Cc. of pancreatic juice and $\frac{2}{3}$ Cc. of neutral olive oil is placed and shaken, and the oil allowed to separate. One drop of this oil is pipetted on the surface of solution in watch glass No. 1. The tube is shaken again, mixture allowed to separate, and a drop of the oil pipetted on solution in watch glass No. 2. This is repeated every three or four minutes until the experiment is completed. Gad had found that oil containing 5.5 percent of free fatty acid emulsified spontaneously in 0.25 percent sodium carbonate solution, and Rachford used this fact as a measure of the fat-splitting action of the juice. The results may be shown as follows:

Sodium carbonate solution, 0.25 percent, to which is added drop of

Oil with no fatty acid.....	no emulsion.
Oil with steadily increasing amounts of fatty acid....	more and more emulsion.
Oil with 5.5 percent fatty acid.....	spontaneous emulsion. .
Oil with increasing amounts of fatty acid.....	less and less emulsion.
Oil split to all fatty acid and glycerin.....	no emulsion, only turbidity due to soap.

All the oil is split to fatty acid and glycerin in one to two hours' action of the pancreatic juice.

"The action of the juice on most of the fats is rapid and complete. Castor oil is an exception to the rule, as only a very small quantity of acid is developed in it by the action of pancreatic juice for 5 hours at 37° C. Castor oil is therefore practically indigestible, and this may in part account for its cathartic action."

In 1898, Moore and Krumholz⁸ published their paper "On the Relative Power of Various Forms of Proteid in Conserving Emulsions," in which their experimental data, dealing with emulsions made with white of egg, blood serum, acid and alkali albumen prepared from each of the above, and with Witte's peptone (chiefly deutero-albumose), shows an order of emulsifying value as follows:

Alkali and acid albumen	very effective.
White of egg and blood-serum	very little action.
Albumose	practically inert.

The theory of emulsions interested Donnan⁹ for a number of years, and, in a paper on soap emulsions, he says:

“The formation of emulsions of fatty oils and alkaline liquids is a phenomenon well known to physiologists. So far as I know, this subject has never received quantitative treatment, and there seems to be no general theory on the subject. . . . The problem is an especially interesting one, because it will probably lead some day to a rational theory of colloidal solutions.”

Now, Donnan proceeded by taking a stop-cocked pipette with a curved tip, and filled it with rape-seed oil. This was lowered into water, the oil allowed to flow, and the number of drops rising to the surface counted. Additions of sodium hydroxide were made, and the effect noted as shown in table.

Rape-seed Oil and NaOH.

Gm.-mol. NaOH per liter.	No. of drops.
0	88
0.0008	213
0.0011	430
0.0013	stream

Similar results were obtained with sodium carbonate. From this we see that surface tension plays an important part in the phenomenon, and that this decreases very rapidly with increasing concentration of alkali.

Commenting on his result, Donnan says: “This decrease in surface tension is due to the formation of soap at the surface. . . . At first one might be inclined to suspect a surface saponification of the glyceride, but most of the textbooks on physiology state that the natural oils almost all react acid and that the emulsifying action of the alkaline liquids is the result of the formation of soap by simple neutralization (of the free fatty acid).”

To prove this view, Donnan prepared an absolutely neutral olive oil and repeated the above experiments with these results:

	No. of drops in water.	No. of drops in N/1000 NaOH.
Commercial oil (acid reaction)	58	331
Purified oil (neutral)	55	58

The difference in the number of drops of the neutral oil is negligible.

Treating a neutral hydrocarbon of the paraffin series in the same way, he got no appreciable increase in the number of drops with alkali. However, on dissolving 0.6 percent of stearic acid in the hydrocarbon, soap was formed and the number of drops increased.

	No. of drops.
Pure hydrocarbon:	
In water	47
In N/100 NaOH	52.7
Pure hydrocarbon with 0.6 percent stearic acid:	
In water	48.5
In N/1000 NaOH	320.0

In 1903, Hillyer,¹⁰ in his study of the cleansing power of soaps, discusses emulsions on lines similar to those of Donnan. He brings out the fact that a soap solution, even though very dilute, has a lower surface tension than any other aqueous liquid, its surface tension being only 40 percent that of pure water.

“Can emulsification be explained by the viscosity of the emulsifying agent? In the case of very thick liquids, like the gum solutions used by the pharmacists, it is

probable that the extreme viscosity is a very large factor in giving permanence to the oil droplets which have been formed mechanically. That even very large internal viscosity will not make a permanent emulsion is shown by the fact that 50 percent glycerin, or 6 percent gum solution, will not emulsify kerosene or a viscous oil, like cotton-seed oil. Saponin or albumen solution with high surface viscosity will give permanent emulsions. Dilute soap solutions, which have not a great viscosity, have very great emulsifying power, and the same is true to a less degree of some other solutions. From these facts it must be decided that internal viscosity of a liquid will not account for its emulsifying power."

Hillyer's conclusion is "that emulsification is largely due to the small surface tension between oil and emulsifying agent, which allows the emulsifying agent to be spread out in thin films, separating the oil droplets. The surface tension is not strong enough to withdraw the film from between the droplets except slowly, and if the emulsifying agent has shown great internal viscosity, or if great surface viscosity is shown between the liquids, the thinning out of the film becomes so slow that the emulsion is permanent."

In 1907, K. Beck¹¹ made a study of emulsions of gum arabic solutions with castor oil, and noticed, on mixing the two, a great increase in viscosity. He believes the increase of viscosity to be due to surface forces which only become important when the water particles are distributed as very fine particles through the oil, since the water, before that, moved through the oil without hinderance under the influence of gravity.

An exceedingly fine contribution to the theory of emulsification was made by Pickering¹² in 1907, but, due to the length of the paper, only a few important points can be brought out here. Many of his emulsions were made with a solution of soft soap as the emulsifier, and it is interesting to note that he was able to obtain with it an emulsion containing as high as 99 percent of paraffin oil. Pickering tried solutions of glue, starch, egg-albumen, saponin, etc., as emulsifiers, but he found that none gave emulsions of such fine texture as soap.

"The basic sulphates of iron and copper are among those substances which give excellent emulsions. They may be formed by adding lime, or lime-water, to the normal sulphates, and then the paraffin oil, when the slightest churning, or even shaking, of the mixture, produces emulsification. Besides the ease of manufacture, and the absence of spontaneous de-emulsification, these emulsions possess the advantage of not being decomposed by the addition of caustic soda. . . . When the copper salt is used, the emulsion possesses all the fungicidal properties of Bordeaux mixture."

Based on his experimental data, Pickering has classified the emulsifying agents under three heads according to their value. We quote what he has to say about good emulsifiers:

"*Good Emulsifiers.*—Among soluble, or partially soluble substances, soft soap seems to be the best; dissolved starch, milk and flour are good, although the latter forms a flocculent, not a creamy, emulsion, and milk gives rise to solid clots; glue emulsifies well, and so does egg-albumen, but the emulsion of the latter is rather frothy, owing to enclosed air bubbles; saponin and quillaya bark give good emulsions when the proportion of oil present is not large.

"Among the insoluble emulsifiers, the basic sulphate of iron is the best, followed by those of copper and nickel; the basic sulphates of zinc and aluminum give good emulsions at first, but aggregation of the particles seems to occur, and causes partial de-emulsification. Ferrous hydroxide and higher hydrated oxides of iron are good. The precipitate obtained by adding sodium carbonate to copper sulphate is a

very good emulsifier, so are calcium carbonate and arsenate when first precipitated, but the latter soon becomes crystalline and de-emulsification follows; lead arsenate, freshly precipitated, is good, and zinc oxychloride, or basic chloride, is fair, although the emulsion with it is somewhat flocculent; some fine clays (unheated) give good emulsions, but they naturally contain many gross particles which sink to the bottom unemulsified; ferrous hydrosulphide gives a good emulsion if the proportion of oil present is small."

Holde¹³ shows that lime and alumina soaps are used in lubricating greases, but of this very interesting paper, we can quote but a few lines.

"Though the composition of these greases varies somewhat, most of them consist of a solution of lime soap (15-23 percent and sometimes 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).

"The lubricating greases offer a series of interesting problems in physical chemistry, which have not yet been studied from a scientific view-point.

"Observations show that the water is usually present in a state of very fine mechanical subdivision. This much is certain, that a small amount of water is necessary in the grease to produce satisfactory permanency, since all greases that do not contain water soon become inhomogeneous. As technical men say, they let go of the oil."

Another instance in which water is the disperse phase is to be found in the case of mixed paints. Toch, in "The Chemistry and Technology of Mixed Paints," is quoted here.

"The manufacture of mixed paints 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.

". . . A mixed paint should not contain over 2 percent water, for it is unnecessary to add more than this amount to any paint.

"The materials used for 'emulsifying' paint are the carbonates of all the alkalis, borax, zinc sulphate, calcium hypochlorite, manganese sulphate and 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."

In working with soap emulsions, Donnan found that the salts of the lower fatty acids, formic, acetic, butyric, etc., had not the same action in reducing surface tension as have salts of oleic, stearic and palmitic acids. This very interesting fact was also observed in 1908 by Mayer, Schaeffer and Terroine.¹⁴ The alkali salts of the lower fatty acids, formic, acetic, etc., form homogeneous, optically empty solutions, while in the neutral solutions of capronic, caprylic and lauric acids, ultra-microscopic suspensions are to be observed. "When considering aqueous solutions of the alkali salts of the normal saturated fatty acid, we are not far from the truth when we say that 'soapiness' begins about with caprylic acid and is clearly marked with lauric acid." It would seem from this that only those fatty acid salts that lie in the realm of colloids have the property of soapiness, and the ability to emulsify.

In 1909, Lewis,¹⁵ a worker in Donnan's laboratory, discusses in his paper another side of the general theory. "He worked with an emulsion of mineral oil in water because that eliminated secondary reactions. He appears not to have added

any third substance intentionally, which perhaps accounts for his getting only weak emulsions." He simply shakes the oil with water in a mechanical shaker for 48 hours, and gets an emulsion, whose oil particles exhibit Brownian movements and other phenomena similar to that shown by colloidal metals.

In 1910, Robertson¹⁶ published some results on emulsions of olive oil and water which are of special interest because he succeeded in obtaining an emulsion of water in oil. We quote a portion of his article.

"If one shakes up, thoroughly, equal parts of slightly alkaline water and olive oil, a very stable emulsion is formed in which the olive oil forms the internal phase, and water the external; that is, the olive oil is suspended in the form of spherical droplets within the water. If we decrease the proportion of water, the resultant emulsion still continues to consist of droplets of oil suspended in water until the proportion of water to oil reaches a definite critical value. When this critical ratio is reached, the character of the emulsion undergoes an abrupt change. From being a viscous, creamy-white emulsion of oil in water, it becomes a fluid, yellow emulsion of water in oil. The oil is now the external phase, and the water the internal phase. One can readily detect which phase of the emulsion is external, without microscopic examination, by means of the following simple device: The bright red dye Soudan III is insoluble in water, but readily soluble in oils; on sprinkling a few grains of Soudan III on the surface of an emulsion of water in oil, the color rapidly spreads over the surface. If, however, one sprinkles the Soudan III on the surface of an emulsion of oil in water, the color remains confined to the droplets of oil with which the grains are in actual contact, since it cannot spread from them to the adjacent drops through the intervening water."

In 1910, Pickering¹⁷ published another paper in which he brings out the rather startling fact that potassium cupric tartrate will emulsify a mixture of alcohol and water, even though we know them to be miscible in all proportions. Bancroft found on trying this that the potassium cupric tartrate causes the aqueous alcohol to separate into two layers. Thus, he shows that it is evidently possible to make emulsions of acetone in water by first adding some such salt as potassium carbonate to cause the formation of two layers, and then adding a suitable emulsifying agent.

Based on his experimental data in this and in his former paper, Pickering sums up his notion of the effect of surface tension and viscosity in the formation of emulsions.

"The conclusion to be drawn is that emulsification may take place in a liquid when the viscosity is not high and the surface tension is not low, though it is admitted that a high viscosity and a low surface tension often facilitate the formation of emulsions. The only, or rather chief, cause of emulsification seems to be the presence in the liquid medium of small insoluble particles, which form a film around the drops. In order that such particles have the power of forming an emulsion, they must have only a slight tendency to agglomerate, they must be more readily wetted by the water than by the oil, and they must not be crystalline."

A few months later, Donnan¹⁸ comments on Pickering's paper as follows:

"In a recent article, S. U. Pickering discusses the theory of emulsions, and apparently comes to the conclusion that surface tension has very little to do with the phenomenon of emulsification and that emulsions owe their formation chiefly to solid particles. S. U. Pickering has made no accurate measurements on this point and seems also not to know about the close relation between surface adsorption and lowering of the surface tension. He also does not consider the electrical forces which we know to be acting. We do not believe that the true nature of emulsions is explained by S. U. Pickering's theory of solid particles."

In 1911, Ellis ¹⁹ prepared theoretical emulsions of lubricating oil and water only, and worked on the electrical charge of the particles and their migration. The paper does not add much to our knowledge of actual emulsions, working as Ellis does with an emulsion containing only about one part of oil in 10,000 of water.

Pharmaceutical text-books invariably refer to milk as the type of perfect emulsion, and for this reason it is interesting to note what Bancroft ²⁰ says on this point.

"It is a common thing for people to speak of milk as a perfect emulsion; but the facts do not warrant this. Cream starts to rise almost at once, and nobody would call a synthetic emulsion a success which went to pieces as quickly as milk does. By passing milk through a homogenizer, and thus decreasing the size of the globules, man improves on nature so far as the stability of the emulsion is concerned."

Bancroft ²¹ states that Mr. C. E. Swett called his attention to the fact that wool fat forms an emulsion with water in which water is present as the internal phase. He quotes Lewkowitsch in the "Chemical Technology and Analysis of Oils, Fats and Waxes." "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."

Further on Bancroft writes, "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 70,000,000 gallons of mixed paints used in the United States, this type of emulsion (water in oil) is unquestionably the more important one commercially, and it is rather extraordinary that the writers on emulsions should have overlooked this important industry."

F. R. Newman, ²² working in Bancroft's laboratory, did some admirable work in the study of the nature of emulsions and the identification of the phases. He brings out the three methods for determining which of two liquids is the external phase in an emulsion. They are the unsatisfactory inspection method, the fairly good Robertson's Soudan III dye method, which has already been taken up, and finally, Briggs' drop method. The latter consists in placing a drop of emulsion on a glass plate by means of a rod, and adding a drop of water on top of the drop of emulsion. The two are stirred together. If the emulsified globules spread in water, it is an emulsion of oil in water, but if there is no spreading, it is an emulsion of water in oil. The principle involved is that one can dilute an emulsion by adding more of the external phase.

Of the many other interesting points in Newman's paper, only a few can be taken up here. They are as follows:

"Magnesium oleate is the best emulsifying agent yet tried for making an emulsion of water in benzene. The emulsions are much more stable if a little sodium oleate is also present.

"In mixed paints, water is the internal phase and oil the external one. By shaking commercial white lead together with raw linseed oil and water, a water-in-oil emulsion was obtained containing 87.5 per cent. water and 12.5 per cent. oil by volume.

"Whether one liquid is emulsified in the second, or the second in the first, depends upon the nature of the emulsifier." A hydrophile (affinity for water) colloid, like gum arabic, sodium oleate, etc., will tend to make water the external phase. A hydrophobe (aversion for water) colloid, like magnesium oleate, rubber, etc., will tend to make water the internal phase.

In 1915, T. R. Briggs, ²³ and a short time after, Briggs and Schmidt, ²⁴ published

two very thorough pieces of work on benzene emulsions, although no new theory was introduced. Briggs also devised a simple method for homogenizing emulsions.

The last word in the theory of emulsions comes from no less an authority than Martin H. Fischer,²⁵ who, in conjunction with Miss M. O. Hooker, publishes in Science of March 31, 1916, an article entitled, "On the Physical Chemistry of Emulsions and its Bearing on Physiological and Pathological Problems," the details of which are soon to appear in the Kolloid-Zeitschrift. Fischer's article, in the estimation of the writer, is the most remarkable and most interesting paper contributed to the subject of emulsions, first, because of the formulation of a brand-new theory, and, secondly, because of its ingenious applications in physiological problems.

Part I consists of a brief discourse on our knowledge of the emulsion theories. It shows that the low-surface-tension theory, the high-viscosity theory and Pickering's theory of films of insoluble particles are admittedly inadequate, and that each plays its part in selected cases of emulsions.

Part II begins as follows: "In reviewing the empirical instructions available for the preparation of emulsions, and in our own attempts to formulate such as would always yield good results, we were struck with the fact that their production is always associated with the discovery of a method whereby *the water (or other medium) which is to act as the dispersing agent is all used in the formation of a colloid hydration (solvation) compound.* In other words, when it is said that the addition of soap favors the formation and stabilization of a division of oil in water, it really means that soap is a hydrophilic colloid which, with water, forms a colloid hydrate with certain physical characteristics, and the oil is divided in this. *The resulting mixture cannot, therefore, be looked upon as a subdivision of oil in water, but rather as one of oil in a hydrated colloid.*"

Part III deals with the cracking of emulsions, and this general statement is made: "An emulsion breaks whenever the hydrophilic colloid which holds the aqueous dispersion means is either diluted beyond the point at which it can take up all the offered water, or is so influenced by external conditions that its original capacity for holding water is sufficiently reduced."

Part IV deals with the application of this new theory to an explanation of fatty degeneration. In part it states: "While the fat in the cells of the body is not ordinarily visible in the state in which it exists there normally, certain pathological conditions popularly termed 'fatty infiltration' or 'fatty degeneration' suffice to make the fat readily visible. . . . In the majority of instances, chemical analysis fails to show that the affected cells contain any more than their normal fat content. *In essence, therefore, 'fatty degeneration' no longer represents a chemical, but a physical problem, which asks how a given quantity of fat usually so distributed in a cell as to be invisible, becomes redistributed in such fashion as to be readily visible.*

" . . . Seven percent potassium soap and cotton-seed oil, for instance, are both relatively mobile liquids, but when mixed in proper proportion they yield an emulsion so stiff that it will stand alone. This is the analogue of the 25 percent emulsion of fat and lipoid which we call the brain. If the oil-in-soap emulsion is broken through the addition of a little acid, it yields an impure mixture of oil, water and precipitated colloid material—the analogue of the liquid contents found in any area of brain 'softening.'"

In the face of all this work which has been done on emulsions, is not our definition of an emulsion, as given in most pharmaceutical texts, wholly inadequate and entirely too narrow? We read in our texts that, "Emulsions are aqueous liquid

preparations in which oily or resinous liquids are suspended by the agency of gummy or viscid substances." Let us analyze the definition:

"*Emulsions are aqueous liquids.* . . ." The official hydrous wool fat is an emulsion of water (or, according to Fischer, an emulsion of a hydrated colloid) in wax. This is not an aqueous liquid. ". . . *in which oily or resinous liquids are suspended.* . . ." We have the official emulsion of chloroform, and surely chloroform is not an oily or resinous liquid. Also, as has been shown, many of our emulsions are suspensions of water in oils. ". . . *by the agency of gummy or viscid substances.*" . . . It has been seen that very dilute soap solutions, precipitates of basic sulphates, and many other substances which are not viscid or gummy, have been used as emulsifying agents with success. Their successful use in pharmacy is only a matter of experiment and application.

HAVEMEYER CHEMICAL LABORATORIES,
NEW YORK UNIVERSITY.

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