THEORY OF EMULSIONS AND EMULSIFICATION

BY P. M. TRAVIS

For the past twenty years emulsions have been the subject of lively comment in chemical literature, and while no general theory for emulsification has been elucidated, many have been proposed from time to time, only subsequently to be shown to apply to special causes. There is, however, a mass of arbitrary data which can be profitably applied.

Definition: An emulsion is a system containing two liquid phases, one which is dispersed as globules in the other. That liquid which is broken up into globules is termed the dispersed phase, while the liquid surrounding the globules is known as the continuous phase or dispersing medium. The two liquids which must be immiscible or almost so, are frequently referred to as the Internal and External phases respectively, or expressed in another way. An emulsion is a mixture of two or more fluid bodies which are not soluble in each other, but kept in suspension by mechanical means. The finer the division of the particles, the better they serve the purpose they are intended for. If these particles can be divided so finely that they approach in form a colloidal state, then they will not separate on standing.

Of recent years, so-called colloidal solutions have formed the subject of numerous investigations, and are of great practical importance in both medical and industrial chemistry. These solutions were formerly known as pseudo-solutions. In true solutions, the particles are in the molecular or ionic state. The particles in collodial solution are on the whole larger aggregates than in true solution, and the similarity to a fine emulsion is very close.

In the case of an emulsion where oil and water are used, we speak of it as an oil-in-water emulsion or a water-in-oil emulsion. In the case of the oil-in-water emulsion. the oil is dispersed in the water, the water being the continuous phase, while in the water-in-oil emulsion, the reverse is the case.

Clowes[1] found that sodium, potassium and lithium soaps emulsify oil in water, while magnesium, strontium, barium, iron and aluminum soaps emulsify water in oil. The first series of soaps contain monovalent metals and are soluble in water but not in oil while the second series contain bi and tri valent metals and are soluble in oil but not in water. In other words, alkali soaps are wetted more by water than by oil, and probably the surface tension is lower on the water side than on the oil side of the globules, so the film will bend convex to the water and concave to the oil, enveloping the oil globules, as the area of the inner surface of a sphere is less than that of the outer. Similar reasoning holds for the reversing of the emulsion by the other soaps mentioned, which are more soluble in the oil. Examples of both types of emulsions are as follows:

Water-in-Oil Emulsions

Calcium and aluminum soaps are used in lubricating greases. They are, as a rule, solutions of lime soaps (15 to 25 per cent) in heavy mineral oil with 1 to 4 per cent water emulsified in them. Some lubricating greases for automobile use consist of aluminum soaps dissolved in mineral oils with water emulsified in them by the aid of rosin.

Oil-in-Water Emulsions

The most common emulsions are those in which the oil is dispersed in the water or oil-in-water emulsion. In all emulsions where the concentration is over 2% it is necessary to have a third substance present, which is known as the emulsifier or emulsifying agent. For example; in the case of dairy emulsion, such as butter fat dispersed in milk, casein is the emulsifying agent, while in the case of a chocolate emulsion the cocoa fat is emulsified in the chocolate liquor, fine particles of cocoa powder which accumulate about these fine globules of cocoa fat are the emulsifying agent.

Water-Soluble Colloid as Emulsifying Agent: Good emulsifiers of this class are sodium and potassium soaps, egg albumin, gelatin, glue and other water-soluble proteins, gum arabic, Irish moss, casein, starch, saponin and various bark extracts.

NaOH was classified as an excellent emulsifying agent for fatty oils in water, but Donnan's[1] investigation showed that its emulsifying powers were really due to the soap formed by interaction with the small amount of free fatty acid that is always present in fatty oils.

There is a very simple method of determining the type of emulsion. Upon addition of water to an emulsion of oil-in-water it will disperse. Similarly, a water-in-oil emulsion will mix with oil. In short, an emulsion will mix with more of its external phase, but not with internal phase.

The Electric Charge: The oil globules in emulsions of oil-in-water carry a negative charge, as proved by cataphoresis tests. The origin of this charge is still open to question, as is, indeed, the more general case of the electric charge of all colloid particles.

The electric charge is believed to be due to the absorption of ions, In the case of emulsions bearing a negative charge, absorption of OH ions at the surface of the oil globules is postulated. Even when emulsions are made with absolutely pure oil and pure water there should be present hydrogen and hydroxyl ions due to the ionization of the water, and consequently absorption of OH ions.

The Stability of Emulsions: We have already noted that concentrated emulsions demand the presence of an emulsifying agent. In such cases the stability of the emulsion depends on factors relating to an absorbed film at the oil-water boundary.

Pickerling[1] noted that emulsions were poor conductors of heat. It is possible to boil a beaker of such an emulsion for several minutes, while the center remains at less than 100° C. When kept in closed vessels they are permanent for months.

The absorbed ions are considered to be concentrated near the surface of the globules, in the layer of the liquid immediately bathing the globules.

The two layers of oppositely-charged ions are frequently referred to as the Helmholtz double layer. The oil globule and its double layer may be considered as a small condenser, a definite potential difference existing between the oil and the nearer ionic layer. Such a system should be self-contained and electrically neutral to an external field, and for this reason a certain "facility of slip" between the nucleus and the outer ionic layer since the oil globules in emulsions wander to the anode in an electric field, thus giving proof that they are negative. The fact that the dispersed particles do carry an electrical charge is most important when we come to the question of the stability of any emulsion.

Brownian Movement in Emulsions: Suspensions of fine particles, fine-grained emulsions, and colloidal solutions of metals all show when examined under the ultra-microscope, that the particles of the dispersed phase are in continuous zigzag motion. The phenomenon is termed the Brownian Motion, after Brown[2], who studied the movements of pollen grains in water. It is now known that the movement of finely divided particles suspended in liquids are due to the bombardment of the particles by the molecules of the surrounding liquid. This Brownian movement is not observed before the particles are split to a very finely divided state; usually below 2 u in size.

The Viscosity of Emulsions: The position regarding the viscosity of emulsions from a quantitative point of view is far from satisfactory, very little work having been done in this connection. Dilute emulsions show a viscosity not much greater than that of water. Viscosity increases rapidly as the volume of the dispersed phase increases, but in this case, of course, there arises the new factor of the emulsifying agent.

The viscosity of concentrated emulsions is intimately connected with the presence of absorbed films around the dispersed globules. This is particularly so in the homogenization of emulsions, i.e., the increased dispersion of the internal phase, whereby the presence of the absorbed emulsifying agent at the greatly magnified interface confers a marked increase of viscosity to the system.

Stability: For emulsions of oil in pure water the stability is influenced by (a) the interfacial tension, tending to bring about coalescence of the globules, whereby the total surface would be reduced (b) the Brownian movement, tending to collision of the globules, a factor against stability; and (c) the electric charge on the globules, tending to repel them on near approach.

Most of the work on emulsion stability relates to the influence of added electrolytes. When colloid particles are coagulated under the influence of electrolytes, the globules absorb oppositely-charged ions, so their charges become neutralized and at the isoelectric point, where the potential difference between the particles and the medium become zero, stability is least.

The work of Donnan[1] on neutral oil emulsions shows that there is a close similarity between such "mechanical" emulsions and colloidal suspensions. In each the particles carry an electric charge of the same order of magnitude, the limiting grain size is similar, the potential difference values are similar, and the condition for stability under the action of absorbed ions are also similar. Thus the electrical factors outweigh the effect of interfacial tension.

The preparation of stable emulsions on a commercial scale is best carried out by use of a machine known as a homogenizer. This is usually a pressure type of machine which operates at pressures of from 3,000 to 4,000 lbs. per sq. in. In recent years, however, other types have appeared on the market and in some cases the pressure type has been replaced by a high speed type in which the dispersion is brought about by a shearing action.

Homogenizers

The first uses of the homogenizer were confined to the Diary Industry and dates back to about 1905, when they were first introduced for the Homogenization of Dairy Products, such for example as Evaporated Milk, and for all uses where they did not wish the cream or fat to separate. Therefore, its purpose was just the reverse of that of a Cream Separator. Instead of separating the fat from the milk it was possible with the homogenizer to incorporate fat into the milk, thereby making any percentage of cream desired up to as high as 40%, or what is known as heavy cream.

After the homogenizer had worked successfully in this field for a few years, it was next introduced into the Ice Cream Industry, where its use obviously was to incorporate the fat, milk solids, etc., into a homogenous mass, and develop a smooth ice cream, gel, etc., which brought about a big improvement in the manufacture.

The practice of homogenizing was confined to the two industries just mentioned for a great number of years, and it is only fairly recently that machines have been perfected capable of making fairly perfect emulsions of oils, fats, etc., with water.

The present generally accepted theory of the formation of homogenized emulsions postulates the presence of a stabilizing film around the dispersed phase which prevents the particles from coalescing when they come in contact with each other, due to the Brownian motion. This protecting film is the colloid or emulsifying agent used, which surrounds each particle of the dispersed phase of the emulsion. As these particles are so finely broken up that they take on Brownian "motion" they are, of course, not affected by gravity so much.

Change in Size of Fat Globules: Wiegner[1], in his studies on homogenized milk, investigated the change in the diameters of the fat globules and the increase in their numbers following homogenization.

It is of interest now to mention the globule sizes of some typical three-phase emulsions for the purpose of comparison. Baldwin[2] found that the butter fat globules in cow's milk were from 0.005 to 0.006 mm. diameter (5 to 6 u). By homogenizing—i.e., further sub-dividing—the globules, the diameters were reduced to 1 or 2 u.

It is of interest to know that according to the tables, that the diameter of the fat globules have been reduced from 2.86 u. to 0.27 u. and from 2.94 u. to 0.17 u., the sample with the smaller fat content being split into a finer state of division.

The number of particles in the first sample has increased 1,188 times and in the second sample 1,258 times, after homogenization. The surface area of the fat globules has been increased 112 and 117 times, respectively. The viscosities of 1 ; 1.12 and 1 ; 1.15, respectively. There was no apparent change in density and no difference in electrical conductivity, though Buglia[1], in similar work, noted a slight increase in the electrical conductivity of homogenized milk. Both Wiegner and Buglia find that there is a slight increase in osmotic pressure following homogenization.

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