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# THE CAUSES OF THE STABILITY OF EMULSIONS

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CONTENTS


I. Stability of emulsions stabilised by soaps
II. Stability of inverse emulsions
III. Stabilisation of emulsions by substances other than soaps


A great number of investigations has been devoted to the causes of the stability of emulsions to aggregation, nevertheless, at the present time, there is no single opinion even on the causes of the stabilility of the classical emulsions stabilised by ordinary soaps. An attempt is made in

the present paper, on the basis of a critical comparison of the accumulated experimental material, to discuss the question of the stability of emulsions and, in this way, to arrive at some general conclusions.

## I. STABILITY OF EMULSIONS STABILISED BY SOAPS

An analysis of the scientific literature shows that, if theories of only historical interest discussed in detail in special monographs [1-3] are not taken into consideration, the stability of emulsions stabilised by soaps has been interpreted generally from two viewpoints: either from the so-called physical theory of stability, which specifies the presence of an electrical double layer on the surface of the globules, or from the presence round the globules of a coating of stabiliser possessing structural and mechanical properties. Both conceptions start from premises on the formation of adsorbed films; however, the properties and structure of the films, and also the very basis of stability, according to these theories, are completely different. We shall consider these two theories separately.

Stability of emulsions as a result of the presence of an electrical double layer round the globules. This theory of the stability of emulsions arose from general ideas on the stability of colloid systems developed as early as the beginning of the present century by Hardy [4]. According to this conception, the stability of colloid and micro-heterogeneous systems to aggregation is a consequence of the formation on the surface of the particles of an electrical double layer of ions, which produces an energy barrier obstructing the approach of similarly charged particles to a distance where the intense molecular forces of attraction operate. This layer, the external surface of which generally possesses a diffuse character, usually arises on the surface of the particles as a result of selective adsorption of one of the ions of an electrolyte present in the system. This idea was used by Ellis [5] and Powis [6] to explain the stability of dilute emulsions, and has subsequently been widely used also to explain the stability to aggregation of concentrated emulsions stabilised by soaps [7,8]. At the present time, such prominent scientists as Kruyt [9], Verwey [10], Overbeek [11], Van den Tempel [12], Becher [13], etc., prefer to explain the stabilisation of emulsions by ionic materials on this basis.

A persuasive argument for the correctness of this approach is the behaviour of emulsions stabilised with soaps when electrolytes of different valencies are added to them. Dilute emulsions were shown by Powis [6] to obey the Schultze–Hardy rule. In the Soviet Union, Kharin and Takking [14] have come to the same conclusions.

Martin and Hermann [15] have shown that the Schultze–Hardy rule is also applicable to emulsions of xylene stabilised by sodium oleate. Somewhat later, Van den Tempel [12], investigating the stability of normal emulsions stabilised with sodium salts of esters of sulphosuccinic acid, and with sodium laurate, to the action of electrolytes, also found that his results were in complete agreement with the Schultze–Hardy rule, according to which the concentration of a cation necessary to ensure a predetermined rate of coagulation of a sol with negatively charged particles is determined by the charge, and to a considerably smaller degree, by the specific nature of the cation. Voyutskii and Panich [16], studying the influence of electrolytes on the $\zeta$-potential of particles of synthetic latices stabilised with salts of naphthenic acids, also found an extremely marked influence of the valency of the cation on the threshold concentration for coagulation. According to their results, the threshold concentration for coagulation was generally inversely proportional to the sixth power of the valency of the cation, in agreement with the formula deduced by Deryagin and Landau from the physical theory of the stability of lyophobic sols, which gives greater precision to the Schultze–Hardy rule.

Another indication that emulsions are stabilised by the electrical double layer formed on the surface of the hydrocarbon droplets is the dependence of the emulsifying power of soaps on the nature of their cation observed by Kremnev and Kagan [17]. These authors established that, for normal emulsions, the aqueous phase of which consisted of 0.32 $N$ solutions of the oleates of various alkali metals, the critical thicknesses $\delta$ of the stabilising layers of systems of limiting concentration and the relative emulsifying power of the corresponding soaps had the values given in Table 1.

The relative values of the critical thicknesses $\delta$ of the layers of emulsions of limiting concentrations obtained using oleates with different cations are remarkably similar to the ratios of the coagulation thresholds determined by the same cations when they are added to typical lyophobic sols with negatively charged particles [9,18]. This can be seen, for example, from a comparison of the data of Table 1 with the values for the coagulation threshold $\gamma$ of suspensions of various clays for various cations found by Jenny and Reitemeier (see ref. 18) and given in Table 2.

The similarity observed is most simply explained by a general cause — an increase in the condensation of the electrical double layer as a result of an increase in polarisability and a diminution in the hydration of the ions with an increase in their true radius. Finally, complete correlation cannot be expected here in consequence of the universally known low accuracy of the determinations of $\gamma$ and their poor reproducibility.

TABLE 1. Critical thicknesses of the stabilising layers $\delta$ and relative emulsifying power of various salts of oleic acid.

| Emulsifier | $\delta$, Å | Relative emulsifying power |
|---|---|---|
| Sodium oleate | 100 | 1 |
| Potassium oleate | 50 | 2 |
| Rubidium oleate | 35 | 2.85 |
| Caesium oleate | 20 | 5.0 |

TABLE 2. Values of the coagulation threshold ($\gamma$) of suspensions of various clays by different cations.

| Cation | Ca-clay | | H-clay | |
|---|---|---|---|---|
| | $\gamma$, mM | $\gamma$, % of $\gamma$ for $Na^+$ | $\gamma$, mM | $\gamma$, % of $\gamma$ for $Na^+$ |
| $Na^+$ | 4.5 | 100 | 2.7 | 100 |
| $K^+$ | 3.0 | 66 | 1.5 | 55 |
| $Rb^+$ | 1.9 | 42 | 1.2 | 44 |
| $Cs^+$ | 1.2 | 26 | 0.7 | 25 |

The fact that a diminution in the critical thickness of the stabilising layer and a parallel increase in the emulsifying power is observed when the true radius of the ion of the alkaline metal increases is explained, finally, by an increase in the adsorption of the soap (the adsorbability of soaps rises in parallel with their hydrophobic properties from sodium soap to caesium soap). As a result of this increase in adsorption, the charge density at the inter--phase boundary rises, and the electrical double layer retains its capacity for preventing the agglomeration of the particles at a lower layer thickness.

A third argument in favour of the view that the stability of emulsions is determined by electrical forces of repulsion is the presence in emulsions stabilised by ionic materials of an isoelectric point and the possibility of reversing the charge on their particles. This was noted for dilute emulsions in the early investigations of Ellis[5] and Powis[6]. The same dependence has been established for natural latex by Belgrave[19], Sarrut[20], Fullerton[21], and Rhodes and Secar[22], and for synthetic latices by Voyutskii and coworkers[16]. During the charge reversal, the latex passes through the isoelectric point and the system may coagulate. To prevent this, the charge-reversing electrolyte must be added to the latex as rapidly as possible, and a protective colloid should be added to the latex first. Latex with particles on which the charge is to be reversed must not be too concentrated. It can be seen that to reverse the charge on an emulsion, all the conditions under which charge--reversal of typical lyophobic sols proceeds must be preserved. It must be noted that the change in the $\zeta$-potential of the globules of latices, which are ideal models of emulsions, on changing the pH or adding indifferent electrolytes to the system, obeys laws characteristic for typical lyophobic colloids. A great amount of material on this question has been given in our special review[23].

Finally, the idea that the stability of emulsions stabilised by soaps is determined by the presence of an electrical double layer on the surface of the globules is favoured by the remarkable fact that the emulsifying power of soap solutions falls at fairly high concentrations[24]. In certain cases, it is absolutely impossible to prepare emulsions using highly concentrated soap solutions[25]. It has also been shown[17] that when the concentration of soap in an emulsion is increased the degree of dispersion and, consequently, the stability of emulsions of limiting concentration are reduced to a slight extent. This phenomenon is, of course, connected with the condensation of the electrical double layer in consequence of a high concentration of the stabilising electrolyte.

In a consideration of the stability of emulsions stabilised by soaps starting from the assumption that an electrical double layer is formed round the globules, a number of questions arises. These questions reduce fundamentally to the following three:

1. Why cannot stability be imparted to emulsions by low--molecular-weight inorganic electrolytes which stabilise ordinary lyophobic sols?
2. Why do the salts of the lower fatty acids not possess stabilising properties? If, in the stabilisation of emulsions, everything reduced to the formation of an electrical double layer, then an appropriate increase in the concentration of these salts, which are capable of being adsorbed at an oil–water interface, could, it would appear, produce stable emulsions.
3. Why does the concentration of emulsions (for example, by evaporation) lead to their stabilisation when such an increase in the concentration of a lyophobic sol generally causes its coagulation?

There is no difficulty in answering the first question. Inorganic polarising ions cannot be adsorbed on the non--polar surface of hydrocarbon droplets in sufficient amount for stabilisation. The low adsorption of such ions on the surface of the globules can lead only to their imparting a comparatively weak electrical charge to the latter, as was found in the well-known experiments by Ellis and Powis with dilute emulsions.

The answer to the second question is that, to attain the necessary adsorption for the stabilisation of an emulsion, the concentration of relatively low-molecular-weight soaps in the inter-globular liquid must be so high that considerable condensation of the electrical double layer and rupture of the emulsion will at once take place. According to Donnan[26], who first put forward such an explanation for the lower homologues of the series (up to sodium laurate), the absence of marked emulsifying power is connected with the predominance of the coagulating action of sodium ions, exceeding the capacity for emulsification and reduction of the surface tension. Moreover, it may be considered that the salts of the lower fatty acids, the molecules of which have short hydrocarbon radicals, are completely lacking in emulsifying power and act rather as ordinary electrolytes. The observations of Yurzhenko and Ivanchev[27] are in complete agreement with this; they made a detailed study of the influence of added salts of various fatty acids on emulsion polymerisation. While the addition to the system of salts of fatty acids with more than six carbon atoms in the chain was equivalent to an increase in the concentration of emulsifier, conversely the addition of salts of the lower fatty acids caused the sample to coagulate, leading to an increase in the mean radius of the latex globules and, at high concentrations, to a completely non--stable system.

Finally, the explanation of the possibility of concentrating emulsions leads to the fact that salts of the higher fatty acids, due to the presence of long hydrocarbon chains in their molecules, are very strongly adsorbed. Thus, for example, in rubber emulsions, soap is found almost completely in the adsorbed state on the surface of the globules[28]. Thus, comparatively small amounts of soap will be found in the dispersion medium of even concentrated emulsions, and, consequently, its ionic strength will be relatively low if, of course, saturation of the adsorbed layer is not reached.

Moreover, since the salts of fatty acids are weak electrolytes, the transition from ionised soap to molecular soap incapable of condensing the electrical double layer will take place to an ever increasing degree in the inter-globular liquid as the concentration in the emulsion is increased. Under these conditions, the increase in the concentration of emulsifier which takes place as the emulsion is concentrated cannot in any way fundamentally affect its stability.

The situation is different when the concentration of typical lyophobic sols is increased. The stabilising inorganic electrolytes in a lyophobic sol are mainly in the inter-micellar liquid. Moreover, inorganic electrolytes are generally strong electrolytes and, consequently, cannot change their degree of ionisation with an increase in the concentration of the sol. All this, of course, must lead to

coagulation of a lyophobic sol when it is concentrated excessively.

The possibility is not excluded that, although an increase in the soap concentration in the emulsion converts the electrical double layer into a non-ionised layer, the latter being sufficiently hydrated to ensure stability to aggregation in the system. This supposition is quite reasonable if one considers the outstanding polarity of the carboxyl group in which hydrogen has been replaced by an atom of an alkali metal. There are indications in the work of Deryagin[29,30] of the hydration of the electrical double layer formed by the soap molecules after the compression of this layer to the limit and of the stabilising action of the polymolecular hydrate layer arising in this way.

Of course, the papers cited answer the questions posed only in a very general, qualitative form: special investigations are necessary to establish a quantitative basis for the answers given. In recent years, the correctness of the explanation of the stability of emulsions to aggregation as being due to the presence of electrical double layers on the surface of the globules has been confirmed by an experimental test, accompanied by quantitative calculations of the forces acting between the particles.

Van den Tempel[31] has investigated the flocculation and coagulation of emulsions of the oil-in-water type as functions of the concentration of a uni-univalent electrolyte added to them. Calculation of the repulsion energy between the oil droplets of the initial emulsion showed that a potential barrier due to electrical forces must exist between approaching surfaces which exceeds the value of $kT$ by a factor of several thousand. Obviously, the energy of the Brownian motion under these conditions is insufficient to cause direct contact between the surfaces of the drops and hence their coalescence. Therefore, on adding small amounts of a uni-univalent electrolyte to the emulsion, only flocculation takes place. The globules in such a flocculated emulsion are still separated by an aqueous film and are at a distance of at least 100 Å apart. This corresponds to a second shallow minimum on the potential curve which always occurs if the attractive forces diminish more rapidly than the repulsive forces with increasing separation. This minimum is located between 100 and 200 Å for the concentrations of electrolytes used in Van den Tempel's work. More complete contact of the particles under these conditions is still prevented by a fairly high potential barrier of an electrostatic character. Coalescence of the droplets sets in only at comparatively high concentrations of electrolyte as a result of a diminution in the thickness of the aqueous film and its rupture.

In his investigation, Van den Tempel showed that a theory which included only electrostatic repulsion and van der Waal's attraction predicted a far more rapid diminution of the thickness of the aqueous film with an increase in the concentration of electrolyte than is found by experiment. Thus, the experimental results indicated the presence, in addition to the electrostatic forces, of repulsive forces of a different nature acting at distances between the surfaces of the globules of less than 125 Å. The author suggests that such forces are due to steric factors.

It is material that, even earlier, Deryagin and Titievskaya[29], studying the effect of pressure on the thickness of a soap film between two bubbles of a foam, also found evidence for repulsive forces with a small radius of action and evidently of non-electrostatic origin. As mentioned above, Deryagin and Titievskaya consider that these forces are connected with the presence of polymolecular hydrate films in the monolayers of stabiliser. Quite recently, Voropaeva, Deryagin and Kabanov[32] have detected non-electrostatic repulsive forces due to the formation of solvate layers on the surface when two crossed platinum wires are brought to contact in electrolyte solutions.

The recently published investigation of Schenkel and Kitchener[33] is of great importance for the comprehension of the reasons for the stability of emulsions. The investigation was carried out with an aqueous suspension of spherical particles of cross-linked polystyrene with a diameter of 10 $\mu$ bearing sulpho-groups on the surface. As the authors pointed out, the dimensions and shape of the particles used, the nature of the disperse phase, and the nature of the ion-forming groups make this suspension a good model of an emulsion. Of course, in this case, due to the solid nature of the dispersed phase, coalescence, which is typical of true emulsions, does not occur on coagulation. In their investigation, Schenkel and Kitchener determined the conditions which control the stability, slow aggregation, and rapid aggregation of this model suspension in solutions of $KNO_3$, $CaCl_2$, and $LaCl_3$ at various concentrations. The authors determined these states of the suspension from their sedimentation velocity and the volume and nature of the precipitate formed. The values of the zeta-potential of the particles of the disperse phase in the corresponding solutions were also determined by microelectrophoresis. Taking into account the fact that, for the given system, the $\psi_0$-potential is approximately equal to the $\zeta$-potential, Schenkel and Kitchener calculated, making all necessary corrections, the energy of repulsion of the electrical double layers and the van der Waal's attraction between the particles, and constructed the corresponding potential curves. These permitted a quantitative check on the applicability of the physical theory of coagulation to the given case. We shall not enter into the experimental details of this thorough investigation but will consider only the fundamental conclusions that follow from it.

The action of electrolytes on the model suspension proved remarkably similar to the action of electrolytes on typical colloidal systems. The transition from a stable suspension to the conditions of slow, and then rapid, aggregation had an identical character. In both cases, the valency of the counter-ion had a typically powerful influence on the system. However, the potential energy curves found showed that the particles of the suspension repelled one another extremely strongly if they approached to a distance of about 100 Å. For example, the repulsion energy of particles at this distance in $KNO_3$ solution with a concentration corresponding to the beginning of flocculation must amount to at least $1.2 \times 10^{-10}$ erg. Since the mean energy of the Brownian motion of the particles $kT$ is approximately $4 \times 10^{-14}$ erg, the energy barrier preventing contact of the particles is at least 3000 $kT$ under these conditions. Consequently, aggregation, corresponding to the first minimum of the potential curve, is completely excluded in this case.

According to the physical theory of the stability of lyophobic colloids, when an energy barrier exists between two colloid particles, a small secondary minimum must also exist in the potential curve, corresponding to greater separations. This follows from the fact that the energy of the van der Waals attraction falls with the distance according to a power law, while the energy of electrostatic repulsion diminishes exponentially. For typical colloid systems,

the minimum is very shallow compared with $kT$, except for systems containing rod-shaped or lamellar particles capable of forming tactoids and thixotropic gels. However, Verwey and Overbeek specially noted the possibility of aggregation corresponding to a second minimum in the potential curve for coarse dispersions.

The second minimum generally lies at a distance of the order of 1000–2000 Å on the potential curve. Fig. 1 shows the potential curves for different cases calculated according to the theory. Curve *a* represents the variation of the attractive energy alone; curve *b* characterises the resulting potential energy at the critical concentration; and curves *c* and *d* represent the resulting curves corresponding to the upper limit of the range of stability and lower limit of the range of rapid coagulation.

The theoretical curves enable the experimental observations to be explained extremely satisfactorily. In all regions of stability, repulsion continues to act at distances of up to 2000 Å and the secondary minimum is too low ($< 1\ kT$) to cause the combination of two particles into a single aggregate. At the critical concentration, the minimum becomes deeper and attains 4 $kT$, which is sufficient for the combination of two particles. Under these conditions, of course, there is always the possibility of the addition of a third approaching particle to the aggregate. On the other hand, dissociation of the particles, forming a pair, may also take place. This is due to the slow rate of aggregation in this region of electrolyte concentrations. Finally, at higher concentrations of $KNO_3$, there is a deep potential trough ($V \simeq -40\ kT$ at 240 Å) from which the particles cannot escape by using the energy of the thermal motion alone.

Schenkel and Kitchener put forward two qualitative observations in defence of this interpretation. In the first place, when particles which are not too coarse settle on a glass plate in $10^{-3}\ N$ $KNO_3$ solution, they keep up the Brownian motion. This indicates that the particles are not in direct contact with the glass. In a $10^{-2}\ N$ solution, the Brownian motion is no longer observed, providing a direct indication of a decrease in the distance between the particles and the glass. In the second place, a microscopic investigation of the suspension has shown that the precipitates, whether in the aggregated or non-aggregated state, can be redispersed by simple stirring. This indicates that the particles in the precipitate do not adhere firmly to one another.

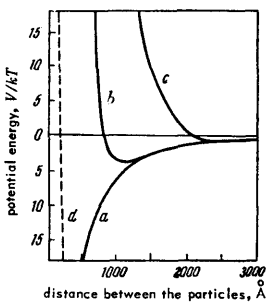



Fig. 1. Potential curves for different cases of the destabilisation of a polystyrene suspension[31].

From all that has been said, the conclusion must be drawn that the stability and aggregation of the model suspensions of polystyrene in $KNO_3$ solution is quite well explained by the theory based on the presence of a second minimum in the potential curve.

For experiments with $CaCl_2$ and $LaCl_3$ solutions, the region of critical concentration corresponds to lower electrolyte concentrations than those calculated theoretically. The authors explain this discrepancy by the complications arising on using polyvalent counter-ions for destabilising the system.

Stability of emulsions as a consequence of the structural and mechanical properties of the adsorbed layer. This theory of the stability of emulsions arises as a consequence of the viewpoint that highly stable colloidal and microheterogeneous systems can exist in a liquid medium only when the surface of the particles carries an adsorption–solvation layer possessing structural viscosity at low velocity gradients and forming a structural and mechanical barrier[34-36]. According to this theory, such layers must consist of adsorbed layers of orientated surface-active molecules which are almost saturated and form two-dimensional crystal-like structures. However, according to this theory, a particularly strong stabilising action is possessed by adsorbed colloidal layers which consist of peculiar jelly-lyogels which are strongly solvated by the dispersion medium and pass diffusely into the intermicellar liquid. Substances capable of forming such layers in hydrosols include proteins, alkali-metal soaps, and some other substances with sufficiently large organic ions.

According to Rebinder[37], the stabilising properties of structurally viscous (gel-like) absorbed layers in collisions between particles of the disperse phase is explained by the fact that the highly viscous layer between the particles cannot be squeezed out during the collision. Rebinder[38] considers that the structural and mechanical factor is the most powerful stabilising factor and has universal importance, and that its use is essential to obtain highly stable particularly concentrated disperse systems (for example, technical foams, emulsions, and suspensions).

It must be said that no direct and irrefutable proofs of the applicability of this theory to the explanation of emulsions stabilised by soaps have been given until recent times. Indications of the possibility of forming sufficiently strong, most frequently polymolecular, films of soap round the globules of an emulsion exist in many old papers of foreign workers[39-43]. However, all these lack a sufficiently conclusive experimental basis. Of Russian workers, Bromberg[44] has attempted to show the possibility of forming polymolecular layers of soap round the globules of emulsions of limiting concentrations†. However, Kremnev and Soskin[25] have pointed out a series of fundamental errors in Bromberg's calculations which make his results of doubtful validity.

The explanation of the stability of emulsions as due to the presence of a strong mechanical adsorbed layer round the globules encounters a series of insurmountable difficulties. First of all, it is now firmly established that the

† In ordinary, not too highly concentrated, emulsions, according to Bromberg, there are protective films of soap molecules which are monomolecular and have a packing density corresponding to the condensed state.

globules of emulsions stabilised with soap are covered with a layer of the emulsifier, which is generally far from saturated. Fischer and Harkins[45] were apparently the first to establish this fact. Zwicker[46] gives data from which it follows that the surface of synthetic latex globules stabilised by soaps is only 40–60% covered by the stabiliser. Maron, Elder, and Ulewitch[47], and also Voyutskii and Panich[48], who studied the adsorption of the stabiliser on synthetic latex globules, came to the same conclusion. The non-saturation of the adsorbed layers on the surface of the latex globules is shown both by the calculated area per soap molecule under these conditions, and experimentally: generally a considerable amount of soap must be added to the latex before it appears in the non-adsorbed state, as can readily be determined by the change in surface tension of the system[49].

Particularly convincing data on the incomplete coverage of globules of emulsions by soap molecules are given in the numerous and extremely thorough investigations of Kremnev and his coworkers. In his 1946 paper[24] it was shown that the area occupied by a molecule of sodium oleate on the surface of a benzene globule in an emulsion in water of limiting concentration is ~ 100 Å²‡ (as a matter of fact, the areas for one molecule of stabiliser given in the papers of Kremnev *et al.* must probably be increased still further, since they were calculated from the assumption that all the soap present in the system is adsorbed). Since this figure considerably exceeds the cross-sectional area of the carboxyl group, Kremnev quite correctly considers that highly rarefied gaseous layers of molecules of the stabiliser are present on the surface of the globules of emulsions. In the 1948 investigations[17], which were carried out with the oleates of various alkali metals, Kremnev and Kagan came to the conclusion that "the stabilising capacity of an adsorbed layer is not connected with the packing density and degree of rarefaction in it". The only exceptions are extremely rarefied coatings which no longer possess stabilising properties. In the same paper, as an example, the authors indicated that stable emulsions stabilised with an oleate can be obtained even when a molecule of the stabiliser on the surface of a globule corresponds to an area of 258 Å². In a more recent investigation (1951) Kremnev and Kuibina[50], on the basis of a large amount of experimental material, came to the conclusion that the stabilisation of emulsions by non-saturated layers of stabiliser (triethanolamine oleate or stearate) is not subject to any doubt. Finally, in a paper of 1958 on the interpretation of his experiments, Kremnev[51] again departs from the position that the stabilisation of the emulsions is brought about by adsorbed monolayers of soap. Only in one paper does Kremnev[52] consider that he has established the presence of a polymolecular layer of soap on the droplets of an emulsion of the oil–water type. However, this case relates to the system obtained by emulsifying molten paraffin wax in a hot soap solution. There is every reason to consider that dissolution of the emulsifier in the molten disperse phase takes place at elevated temperatures. As a result of this, the concentration of soap in the dispersion medium will be greatly reduced in comparison with the concentration of soap in the initial aqueous solution, which was used by Kremnev in his calculations of the thickness of the adsorbed layer. It is clear that all this makes Kremnev's conclusions concerning the polymolecularity of the adsorbed layer in the case of the paraffin-wax emulsion extremely doubtful.

‡ The Russian text gives Å as the unit of area throughout. This is given as Å² here (Ed. of Translation).

As we shall see below, Kremnev has established that, in the case of inverse emulsions and emulsions obtained with the use of a non-ionic stabiliser, the stabilising adsorbed layer is extremely far from saturation.

Further, according to generally accepted opinion[53], amphipathic molecules are arranged at an oil–water boundary in such a way that the polar or ion-forming groups are turned into the water and the hydrocarbon radicals are immersed in the droplets of the emulsion. As Kremnev and Kuibina[50] correctly remark, it is hardly possible to imagine that, in unsaturated layer, amphipathic molecules lie flat or at an acute angle to the surface, as is the case at a liquid–gas interface. In other words, the hydrocarbon radicals of the molecules present at the phase-separation boundary must be dissolved in the hydrocarbon phase. Then, thanks to the solvation of the non-polar portions of the soap molecules by the hydrocarbon of the disperse phase, the interaction between the molecules of the emulsifier must be a minimum, in contrast to the case where the soap is present at a solution–air boundary. Attention has also been drawn to this fact by Harkins[54] and subsequently by Adam[55] and by Blakey and Lawrence[56].

Taubman and coworkers[57,58] have shown quite conclusively that the soap is present in the form of a two-dimensional gas at the surface of separation of two liquid phases, irrespective of the length of its hydrocarbon chain.

On the basis of the incompleteness of the stabilising layer on the surface of the globules of an emulsion, the orientation of the amphipathic molecules at the oil–water boundary, and the gaseous nature of the two-dimensional adsorbed layer, it is very difficult to imagine the existence on the surface of the droplets of a gel-like film of emulsifier, possessing mechanical strength and responsible for the stability of emulsions to aggregations. It was just these considerations that led Langmuir, and also Harkins[53], to renounce the ideal of the interphase layer in emulsions stabilised with soaps as a strong polymolecular film and forced them to consider it as a monomolecular layer of orientated amphipathic molecules attaining continuity only under limiting conditions. These recent ideas exclude, it seems to us, the possibility of explaining the stability of emulsions by the concept of a structural and mechanical barrier. In spite of this, a number of workers adhere to this explanation.

It is particularly remarkable that Kremnev, having done so much to establish the unsaturated nature of the adsorbed layer coating the globules of emulsions, speaks in some of his papers[50,59] of "the gel-like state" of the adsorbed layers, and of "the gelatinisation of the stabiliser concentrated on the droplets (through positive adsorption) with the formation of a two-dimensional gel", and so on. His statements that the stability of an emulsion may also be promoted by a layer of a certain thickness formed under the surface of the globule from the hydrocarbon radicals of the molecules of stabiliser dissolved in it is also completely incomprehensible. In the first place, such layers cannot possess any appreciable structural and mechanical properties on account of their rarefaction and the solvation of the hydrocarbon radicals. In the second place, if such layers, located under the surface of the globule, did possess a certain strength, this could not prevent coagulation, just as the high mechanical properties of the disperse phase of typical lyophobic colloid systems with solid particles cannot prevent coagulation.

Very recently, Orr and Breitman[60], using synthetic

latices with disperse phases of different natures stabilised with various cation-active soaps, have also shown that the area covered by the stabiliser is between 44 and 70% of the total surface of the latex globules. Also, Orr's opinion that part of the surface of the globules may remain uncovered with stabiliser in the presence of excess soap[61] is extremely interesting. More recently, he has explained this by the fact that, when a stabiliser is added to a latex, the critical micelle-formation concentration is always reached before a saturated monomolecular layer of the stabiliser is formed on the surface of the globules. After the critical micelle-formation concentration has been reached in the aqueous phase, the further addition of stabiliser can lead only to an increase in the number of micelles formed and not to an increase in the amount of molecularly dissolved soap, with which the soap adsorbed on the surface is in equilibrium. According to Orr, the critical micelle--formation concentration always corresponds to the maximum stability of latices. Besides, the correctness of this position had been shown earlier for emulsions by Cockbain and McMullen[62]. It is very important that Orr came to such conclusions on the basis of experiments with latices having disperse phases of very diverse nature. This indicates the possibility of applying the ideas which he has developed to all emulsions of the oil-in-water type also.

A number of other arguments can be brought against the explanation of the stabilisation of emulsions by the formation of adsorbed layers possessing definite structural and mechanical properties on the surface of the globules.

Firstly, in contrast to previous investigations, the accurate measurements of Blakey and Lawrence[56] and a number of other workers[63,64] carried out in very recent years have shown that even saturated layers of surface--active substances (with the exception, perhaps, of saponin) on a hydrocarbon–water interphase exhibit no plasticity and, generally, no increased viscosity. This agrees completely with all that has been said above on the rarefied nature of the adsorbed interphase layers and on the solvation of their molecules. Moreover, if an adsorbed layer with definite structural and mechanical properties is present at the interphase surface, this viscosity should certainly have been detected.

Secondly, if the molecules of the emulsifier formed a strong gel-like film on the globules through the energetic interaction or mechanical interlacing of their hydrocarbon chains, the stability of the emulsions should increase with an increase in the length of these chains. However, Kremnev and Kuibina[65], using normal emulsions obtained with salts of triethanolamine and various fatty acids, showed that the emulsifying power of these stabilisers and the stability of the emulsions obtained increased with an increase in the length of the fatty acid chain only up to 12 carbon atoms (which corresponds to triethanolamine laurate). On further increasing the length of the hydrocarbon radical of the molecule of the stabiliser, its emulsifying power and the stability of the emulsions remained unchanged or even decreased slightly. Similarly, Levi and Smirnov[66] found that the optimum emulsifying power was possessed by salts of alkenylsuccinic acids containing from 10 to 16 carbon atoms in the chain or salts of alkylphosphinic acids with 7–9 carbon atoms in the alkyl radical. A decrease or an increase in the length of the hydrocarbon chains led to a reduction in, or the complete loss of, their emulsifying action.

This relationship is, of course, an argument against the explanation of the stability of emulsions by the formation of a strong adsorbed layer on the surface of the globules, since the mechanical properties of this layer should increase extremely sharply at longer chain lengths, when the interaction between the hydrocarbon radicals increases and the possibility of forming a strong two-dimensional gel becomes greater.

On the other hand, such a relationship is very readily comprehensible if it is assumed that the stability of emulsions depends on the action of the electrical double layer. The rise in the emulsifying power of the emulsifier and the stability of the emulsions observed with an increase in the length of the hydrocarbon chain up to a definite limit is naturally explained in this case by a reduction in the solubility of the emulsifier and, hence, an increase in its adsorbability. As Donnan[26] has shown, an appreciable absorption of soap at an aqueous solution–paraffin oil boundary commences with sodium caprylate and rises sharply on passing to the laurate. The diminution in the stability of the emulsion after the hydrocarbon part of the molecule of soap has reached its optimum dimensions can readily be explained by the increase in the solubility of the soap in the hydrocarbon phase and the decrease in the electrical charge on the surface of the globule.

Thirdly, as experiment has shown, stable emulsions can be obtained using emulsifiers known to be incapable of giving mechanically strong adsorbed films. Here are included the crystalline nekals (alkali metal salts of alkylnaphthalene sulphonic acids), triethanolamine, and other quite widely-used stabilisers.

Fourthly and finally, the effect of electrolytes on emulsions stabilised with soaps also conflicts with the idea of a mechanical protective action of the adsorbed layers. If a gel-like layer is present on the surface of the globules, the addition of electrolytes which usually favour gel-formation, should increase the thickness and density of the surface film and thereby increase the stability of the emulsion. In actual fact, the addition of electrolytes leads to the coagulation of the emulsion; this coagulation, as we have seen, generally follows the Schultze–Hardy rule.

It has been shown in a number of papers that it is possible to increase the stability of concentrated emulsions to aggregation by imparting thixotropic structural properties to the dispersion medium[67–70]. For example, Kremnev[70] observed a marked increase in the stability of benzene emulsions whose aqueous phase contained cetyl alcohol in addition to sodium oleate. However, it would be incorrect to suppose that this phenomenon has anything in common with the effect of a structural and mechanical factor in the sense in which this is understood in the explanation of the stability of emulsions. In the investigations cited, the stability of the emulsions was determined by the transition of the whole system to the state of a thixotropic gel and not by the formation of a gel-like adsorbed layer on the surface of the globules changing diffusely to the dispersion medium. This point of view is confirmed both by the increase in the sedimentation stability of such emulsions and by the fact that measurement of the area occupied by a molecule of the emulsifier on the surface of the globule under these conditions, as Kremnev himself indicates, does not leave any doubt of the monomolecularity and even considerable incompleteness of the adsorbed layers.

## II. STABILITY OF INVERSE EMULSIONS

Long ago the opinion was already widespread that emulsions of the water-in-oil type can be stabilised only by the

strength of an interphase film. The existence of an electrical double layer on the surface of the globules was not considered, since the hydrocarbon phase possesses a low dielectric constant and therefore prevents ionisation[71,72].

However, the idea of the presence of a strong adsorbed film on the surface of the globules of inverse emulsions was shaken by a study of the properties of this layer. Kremnev and Kuibina[50], using water-in-benzene emulsions obtained with triethanolamine oleate as the emulsifier, showed that inverse emulsions are also stabilised by a highly unsaturated adsorbed layer. These authors also consider that the degree of rarefaction of the adsorbed layer is even far higher in inverse emulsions than in normal emulsions. According to their results, the area occupied by a molecule of triethanolamine oleate on the surface of the benzene droplets is from 130 to 210 Å$^2$, depending on the concentration of the stabiliser. Kremnev and Kuibina[65] came to the same conclusions in another investigation in which they prepared emulsions of water in benzene by stabilising them with alkali-metal oleates in the presence of electrolytes.

On the other hand, Fuoss and Krauss[73] showed that slight polarisation may take place even in non-polar oils. Salts of polyvalent metals and organic acids generally exhibit a degree of ionisation of the order of $10^{-8}$ in hydrocarbon media. Consequently, for a solution of such a salt in benzene with a concentration in the mM range, the ionic concentration will have a value of the order of $10^{-10}$ $N$. Under such conditions, the electrical double layer will, of course, be very diffuse — calculations indicate that the value of $1/\kappa$ must be a few microns. Hence, as Koelmans and Overbeek[74] indicate, the capacity of the double layer in such a non-polar liquid is extremely small and a very small charge is necessary to cause the presence of a considerable surface potential.

Koelmans and Overbeek carried out an analysis of whether the free energy of the electrical double layer in a hydrocarbon medium can provide the potential barrier of about 15 $kT$ required, according to Verwey and Overbeek[75] to impart stability to the system. They assumed that, at low ionic concentrations, the change in the repulsive energy with distance can be represented approximately by Coulomb's law and that — in contrast to hydrosols, where, as a result of the screening effect of the counter-ions, the fall in the repulsive energy takes place far more abruptly — the repulsive potential falls relatively slowly with the distance in hydrocarbon media. Combining the energies of electrostatic repulsion and van der Waals attraction by Hamaker's method, they obtained a potential curve having a maximum, $v_{max}$. The height of this maximum was not very sensitive to changes in the van der Waals constant $a$ used in the calculation. This explained the comparatively slow decrease in the repulsive energy with distance. The values for $v_{max}$ calculated for $a = 10^{-12}$ erg and expressed in units of $kT$ at room temperature ($4 \times 10^{-14}$ erg) are given in Table 3.

TABLE 3. Maximum repulsion as a function of the dimensions of the particles $r$ and the surface potential $\zeta$.

| $\zeta$ mV | $\frac{v_{max}}{kT}$ | | |
|---|---|---|---|
| | $r=10^{-4}$ cm | $r=10^{-5}$ cm | $r=10^{-6}$ cm |
| 25 | 13 | — | — |
| 35 | 26 | 1 | — |
| 50 | 62 | 4 | — |
| 75 | 152 | 11 | — |
| 100 | 256 | 20 | 1 |
| 150 | 662 | 54 | 4 |

In spite of the low $\zeta$-potentials, systems with a hydrocarbon medium and with particles with a size of 1 $\mu$ and above may be stabilised as a result of the action of the electrical double layer. This may be ascribed to the fact that repulsion begins to play its role at distances where attraction is quite inappreciable. At the same time, the low value of the repulsive energy characteristic of particles with $r < 10^{-6}$ cm completely excludes the possibility of stabilising highly dispersed oleosols using an electrical double layer.

Van der Minne and Hermanie[75], studying the electrophoresis of suspensions in benzene, found a good correlation between the stability and the results of electrophoretic measurements, and showed by direct experiments that stabilisation of suspensions in hydrocarbons can be explained by the presence of an electrical double layer on the surface of the particles.

Quite recently this question was again subjected to detailed investigation by Albers and Overbeek[11]. Experiments with emulsions of water in benzene, stabilised with oleates and sulphonaphthenates of various multivalent metals, which are capable of ionising in a hydrocarbon medium, showed that, in such emulsions, there was no correlation between stability and flocculation, on the one hand, and the $\zeta$-potential of the drops of water in benzene, on the other hand. Although the energy barrier for emulsions with particles having a radius greater than 1 $\mu$ and a $\zeta$-potential greater than 25 mV is calculated to be higher than 15 $kT$, this barrier is not capable of preventing the separation of the system into the dispersion medium and a cream, and does not exclude subsequent flocculation and coalescence of the globules. Thus, the observations made in this work appear to contradict the work of Koelmans and Overbeek[74] cited. Albers and Overbeek explain this contradiction by the fact that the case developed by Koelmans and Overbeek[74] is true for extremely dilute suspensions and emulsions, but is inapplicable to the more concentrated emulsion with which they worked and, in any case, to a layer of cream. In both the latter cases, the attractive forces between the droplets of water causing them to draw together are so high that when the globules approach one another, the highly mobile solvated negative ions on their surface are readily pushed apart, thus permitting coalescence.

Albers and Overbeek did not only find that a rise in the $\zeta$-potential of the globules does not increase the stability to aggregation of emulsions of the water-in-oil type, but they even found a clear inverse correlation between the $\zeta$-potential and the coalescence. They explained the existence of this relationship as follows. The molecules of soap, on their adsorption on the interphase surface, are naturally orientated in such a way that their non-polar part is in the benzene and the ion-forming head is turned into the aqueous phase. Under these conditions, partial hydrolysis takes place, the degree of this hydrolysis depending on the nature of the soap. The hydrolysis products (being insoluble in water and in benzene) accumulate at the interphase boundary in the form of fine particles. Thanks to their generally hydrocarbon character, they are more readily wetted by

benzene than by water and therefore their greater part is located in the external hydrocarbon medium, thereby stabilising the water-in-oil emulsion by purely mechanical means (for the stabilisation of the emulsions by protective layers of granules, see below). The greater the degree of hydrolysis which has taken place the lower, naturally, the $\zeta$-potential at the interphase boundary. Hence the inverse correlation between the magnitude of the $\zeta$-potential and the stability of the emulsion found in Albers and Overbeek's investigation is comprehensible.

In their next paper, Albers and Overbeek[11] made a detailed investigation of the reason why the presence of a fairly high energy barrier (greater than 15 $kT$) of electrostatic origin round the droplets of water-in-oil emulsions did not prevent the flocculation of these systems. The authors showed that, in consequence of the long-range action of the electrical forces in systems with an external hydrocarbon medium, it was necessary to omit the repulsive force between only two adjacent particles from the calculations. The behaviour of water-in-oil type emulsions can be understood only by taking the interaction between a large number of particles into consideration. Albers and Overbeek formulated their discussion in the following way. In a system in which the continuous phase is water, the thickness of the electrical double layer is only $\sim 10^{-3}$–$10^{-2}\,\mu$, so that electrostatic interactions can be observed only at extremely small distances between the particles. The potential energy of charged particles at particle separations greater than $10^{-2}\,\mu$ is thus practically zero.

The case is different in a system with a continuous hydrocarbon phase. In this case, the thickness of the electrical double layer is generally several microns. This thickness is of the same order as the distance between the globules in a moderately concentrated emulsion. Therefore, the globules of such emulsions already possess a certain amount of potential energy in comparison with that which they would have if they were at an infinitely great distance from one another. Consequently, the energy barrier is reduced in this case and the stability with respect to flocculation must also be reduced. This effect was shown earlier by Verwey[77].

A further reduction of the energy barrier in a system with an external hydrocarbon phase takes place in consequence of the combination interaction of more than two particles, as can be seen from Fig. 2, which shows the reduction in the energy barrier for particle *2* under the influence of two neighbouring particles — *1* and *3*. The broken lines represent the change in the energy of interaction with the distance between particles *1* and *2* in the absence of particle *3* and between particles *3* and *2* in the absence of particle *1*. The symbol $E_1$ denotes the energy barrier which must be overcome for particle *2* to approach particle *1* from infinity. This barrier diminishes to $E_2$ if particle *2* begins its movement from the position shown. It is reduced still more, to $E_3$, if its interaction with particle *3* is taken into consideration. The continuous line in the figure represents the resulting potential curve.

Since in systems with an external hydrocarbon phase, as previously mentioned, each globule of the water-in-oil type emulsion possesses a greater potential energy than if it were present at an infinitely great distance from the other particles, the flocculation of a certain number of globules to the bottom of the vessel causes the remaining globules to act like a compressed spring accelerating their movement downwards. Further, according to the authors, each

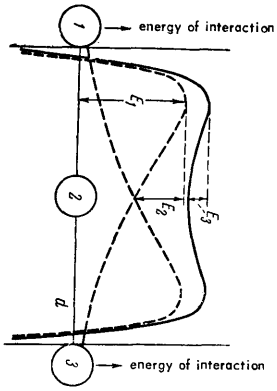



Fig. 2. Sketch explaining the decrease in the energy barrier between the particles of an emulsion of the water-in-oil type[11].

globule tends to move downwards under the influence of the cumulative weight of all the globules present above it.

Thus, the sedimentation rate of a charged globule under these conditions will be some orders of magnitude higher than the rate of settling of a globule under the action of its own weight. Consequently, extremely rapid flocculation takes place and lasts until the concentration of the disperse phase above the precipitate is very low, that is, until the distance between the globules is greater than the thickness of the electrical double layer.

To confirm the correctness of their considerations, Albers and Overbeek carried out extremely thorough calculations and pointed out that a flocculated state is characteristic of water-in-oil type emulsions, or, as Pink[72] formulated it, the difference between emulsions of the normal and inverse types consists in the more rapid formation of creams in emulsions of the water-in-oil type.

As a result of all that has been said above, a number of investigators now adhere to the opinion that the stability of inverse emulsions may be due to the presence of an electrical double layer on the surface of the globules. However, it is still difficult to resolve finally whether inverse emulsions can be stabilised by electrostatic forces, since far fewer data have been accumulated for these systems than for oil-in-water emulsions.

In conclusion, we must dwell upon two further possible causes for the stability of inverse emulsions.

The first possibility consists in the adsorption on the surface of the water droplets of fairly long and flexible hydrocarbon chains, possessing polar end groups, dissolved in the external non-polar phase of the emulsion and capable of performing a micro-Brownian motion[74,79]. In this case, the stability is obviously determined by the thermal motion and the mutual repulsion of the hydrocarbon radicals having only one end attached to the globules of the emulsion, that is, with a factor having the character purely of entropy[9].

Repulsion in consequence of thermal motion of chains adsorbed in this way can, of course, only be observed where chains which are connected to two neighbouring particles interact. This means that van der Waals attraction will take place only at distances greater than twice the

TABLE 4. Van der Waal's attraction between spheres at a distance of 40 Å from one surface to the other.

| $a$ | $\frac{v_{min}}{kT}$ | | |
|---|---|---|---|
| | $r=10^{-4}$ cm | $r=10^{-5}$ cm | $r=10^{-6}$ cm |
| $10^{-12}$ | 510.0 | 42.0 | 1.2 |
| $10^{-13}$ | 51.0 | 4.2 | 0.1 |
| $10^{-14}$ | 5.1 | 0.4 | 0.01 |

length of the chain of the stabiliser. Table 4 gives the values of the minimum total interaction $v_{min}$ calculated by Koelmans and Overbeek[74] for the conditions of an inter-particle distance of 40 Å and various values of $r$ and $a$. Since there is no reason to consider that the van der Waals constant in xylene differs appreciably from the constant in water ($a = 10^{-12}$), the values given in Table 4 show that the adsorbed chains cannot prevent coagulation if the length of the stabiliser molecule is not commensurate with the size of the particles.

In agreement with the considerations expressed, experiments have shown that suspensions with large particles and non-ionic stabilisers are never stable. The weak stabilisation observed increased with an increase in the length of the chain. The longer chains obviously keep the particles at greater distances and thus make the potential trough shallower. However, these results do not contradict the possibility of stabilising emulsions having a low degree of dispersion using the entropy factor by adding stabilisers with sufficiently long molecules (for example, high-molecular-weight stabilisers) to them.

The second possible cause of the stability of inverse emulsions consists in stabilising the droplets of water with a protective layer of granules formed from insoluble alkaline-earth metal soaps[11,50,80] or of the product of their hydrolysis[11]. In this case, the mechanism of stabilisation is completely analogous to the mechanism of the stabilisation of emulsions using powder emulsifiers.

## III. STABILISATION OF EMULSIONS BY SUBSTANCES OTHER THAN SOAPS

Experimental data on the stability of emulsions stabilised by substances not having the nature of soaps are extremely sparse. The information given on this question in recent monographs devoted to emulsions is completely inadequate for the causes of the stability of these emulsions to aggregation to be deduced. Only in the last few years has there been a series of investigations enabling some conclusions to be drawn in this respect.

Let us turn first of all to investigations on emulsions stabilised by the so-called protective colloids. Kremnev and Soskin[25], who studied gelatine-stabilised emulsions of benzene-in-water of limiting concentration, showed that the thickness δ of the critical layer was ~800 Å in this case, *i.e.* eight times greater than the thickness of the corresponding layer when sodium oleate was used as the stabiliser. However, if the thickness of the adsorbed layer of gelatine in the dry state is calculated and the minimum thickness of a monolayer of gelatine is taken as 7–9 Å,[81-83] it is found that emulsions of limiting concentration are stabilised by extremely unsaturated gelatine films ($\delta_{gel}$ amounts to only 2.7–5.2 Å).

Kremnev and Soskin's conclusion that the adsorbed layer of protein at an oil–water interphase surface is not polymolecular was confirmed by Cockbain[84]. Cockbain investigated the distribution of blood albumin and sodium dodecyl sulphate between the interphase surface and the aqueous phase of an emulsion of n-decane; he showed that, in the absence of dodecyl sulphate the adsorbed layer of albumin was monomolecular. In the presence of dodecyl sulphate, its complex with the albumin was formed at the interphase surface and in the aqueous phase.

Saunders and Saunders[85], studying the action of methylcellulose on dilute latices, also observed that stabilisation of the system took place when the globules were covered with a monomolecular layer of the protective colloid. In the latter case, the system is far less sensitive to small additions of electrolytes.

Addition to dilute latices of amounts of methylcellulose insufficient to form a monomolecular layer, on the other hand, caused sensitisation of the system — reduction of the ζ-potential, the formation of aggregates, and a fall in the stability to electrolytes.

When considerable amounts of ionic emulsifying agents were present in the latices, the protective action of methylcellulose began at lower concentrations. When the interphase surface was completely covered by the emulsifier, the methylcellulose was not adsorbed and the stability of the latex was then, in the opinion of the authors, entirely determined by the electrical double layer due to the adsorbed emulsifier.

Nielsen *et al.*[86] investigated the influence of various protective colloids on the interphase viscosity at a water–styrene boundary and determined the stability of the hydrocarbon droplets to coalescence at this boundary. The experiments showed that the presence of protective colloids increases the life of the droplets to the greatest extent under conditions corresponding to a low solubility of a high-molecular-weight stabiliser. This was also shown in experiments with poly-(methacrylic acid) and its salts. The lower the pH of the solution, the lower was the solubility of the polymer and the greater the life of the droplets. Stabilisation by gelatine may serve as another example. Gelatine exhibited the greatest stabilising action at the isoelectric point. This is probably due to the increased adsorbability of the protective colloid under conditions where it is sparingly soluble.

As far as the results of viscosity measurements are concerned, an appreciable interphase viscosity was shown only by a solution of poly-(methacrylic acid) at low pH values. In the other cases, the interphase viscosity was small or completely absent. Very frequently, an increased interphase viscosity corresponded to a longer life of the droplets and, consequently, to better stabilisation. However, cases were also observed in which interphase viscosity was completely absent and the droplets possessed high stability to coalescence. In his paper, Nielson gives no indication of the nature of the adsorbed layer in the cases investigated, *i.e.* whether it was monomolecular or polymolecular.

For inverse emulsions of water in toluene stabilised with ethylcellulose, Kremnev and Shadrin[87], using a method of calculation similar to that used earlier[25], established

that the adsorbed layer of emulsifier was not monomolecular but consisted of several layers of polymer molecules. However, this conclusion cannot be used as a confirmation that the stability of these emulsions is determined by a structural and mechanical factor. In view of what has been said on the stability of inverse emulsions, it is unlikely that the stability of systems containing protective colloids is determined by the entropy factor[9].

Here it is convenient to mention that, in connection with the action of the entropy factor, it is pointless to speak of the polymolecularity of the adsorbed layer and to establish its thickness from the amount of emulsifier adsorbed by unit interphase surface and the diameter of the molecular chain for, as Simha, Eirich, and Frisch have shown in a series of papers[88-92], chain molecules are generally adsorbed on the surface at one or more points, while the greater part of the chain continues to be in the dispersion medium and is capable of performing micro-Brownian motion.

It is interesting that similar views on the causes of the stability of gelatine-stabilised emulsions to aggregation were developed by Bromberg[93] as early as 1946. According to Bromberg, adsorbed films cannot possess a high mechanical strength even if the specific orientating influence of the boundary is taken into consideration and, therefore, the stability of emulsions cannot be determined by the structural and mechanical properties of the adsorbed layers. On the other hand, according to Bromberg, attempts to reduce the protective effect to the presence of diffuse hydrate layers are also unsatisfactory. Bromberg considers that the sole cause of the stability of emulsions in the presence of protective colloids is the osmotic swelling forces of the intermediate gel-like layers of gelatine. It is just these forces which prevent the free escape of water, and consequently, the approach of particles of the disperse phase to one another.

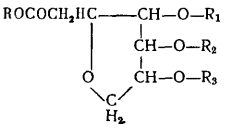
However, in the case of normal emulsions stabilised with protective colloids having molecules containing ion-forming groups, it can be fully admitted that the emulsions are stabilised by the formation of an electrical double layer on the surface of the globules as a result of the ionisation of these groups.

Recently, there has been a wide use in the production of emulsions of the so-called non-ionic emulsifiers, whose molecules consist of a fairly large hydrocarbon radical with several polar groups, generally hydroxyl groups, located at its end. When such emulsifiers are used, it is not very likely that stabilisation of the emulsions occurs as the result of the formation of an electrical double layer on the surface of the globules.

However, just as in the case of emulsions stabilised by ion-forming substances, there are no grounds for assuming the formation of a strong adsorbed layer or a two-dimensional gel on the interfaces of such emulsions. The stability of oil-in-water type emulsions stabilised with non-ionic substances is most simply explained by the orientation of the amphipathic stabiliser molecules at the interphase boundary in such a way that the hydrocarbon chain of the molecules is dissolved in the oil and the polar hydrated groups project into the water and form a fairly strong hydrate layer round the globule. It may be assumed that, to obtain a hydrate layer sufficient to stabilise an emulsion, the concentration of the polar groups at the hydrocarbon–water surface must be very great. This is indicated by some observations of Levy and Smirnov[66] who showed that monoglycerides acquire emulsifying properties only when a sufficient number of polar hydroxyl groups are present at the end of the chain.

It must be noted that, according to the same observations of Levy and Smirnov, the introduction of one or two ion-forming carboxylic groups into the molecule of a non-ionic stabiliser already containing a relatively large number of hydroxyl groups greatly increases its emulsifying properties. This indicates that ion-forming groups exert a far higher influence on emulsifying action than polar non-ionic groups.

In a recently published paper, Sata and Harisaki[94] investigated the stability of the drops of oil in water and of water in oil in the presence of the stabiliser Emasol, the molecules of which have the structure



where R is a hydrocarbon radical, and $R_1$, $R_2$, and $R_3$ are poly-(ethylene oxide) chains of different lengths. The authors showed that Emasol protects drops of oil in water from coalescence well, but is ineffective for drops of water in oil. They explain these properties of Emasol in the following way.

In the case of droplets of oil in an aqueous medium, the three hydrated poly-(ethylene oxide) chains of each molecule of stabiliser are directed into the aqueous phase forming a strong hydrate layer on the surface of the drops which does not break when the drops come into contact and prevents coalescence. In the case of droplets of water in an oleaginous medium, only the one hydrocarbon radical is directed into the external phase, and the droplets are insufficiently protected and therefore readily coalesce. Unfortunately, it is impossible to deduce from Sata and Harisaki's paper the state of the poly-(ethylene oxide) chains of the stabiliser in the aqueous medium on the surface of the oil droplets, and, in this case, the protective action may be ascribed both to the hydration of the chains and to the fact that they maintain their thermal motion (entropy factor).

In Orr and Breitman's investigations[60,61], which we have touched on above, they made attempts to determine the geometry of the molecules of a non-ionic stabiliser present on the surface of latex globules. The authors worked with non-ionic stabilisers in which the hydrophilic part of the molecule consisted of a single poly-(ethylene oxide) chain. In Orr and Breitman's opinion, at ordinary temperatures the hydrophobic part of the molecule of such a stabiliser is immersed in the particle of latex and the poly-(ethylene oxide) chain is turned into the water and arranged on the surface of the globule like a caterpillar, as is shown in Fig. 3. The correctness of this viewpoint is confirmed by the observations of Rosch[95], who considers it quite possible that such a shrinkage of the poly-(ethylene oxide) chain is due to the electrostatic attraction of the dipoles which form the individual links of the chain. Orr and Breitman, using a Fischer–Hirschfelder model, calculated the dimensions of an individual fold of the chain in the non-hydrated state and found that each fold was 16 Å high and contained nine ethylene oxide residues. At higher temperatures, the hydrophilic part of the molecule of the stabiliser straightens out and the stabiliser becomes more oil-soluble, as a result of which its stabilising action

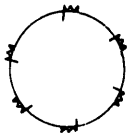


Fig. 3. Configuration of the molecules of a non-ionic stabiliser on the surface of a globule.

in oil-in-water systems falls sharply. The fact that heating aqueous solutions of non-ionic stabilisers leads to their precipitation agrees well with the assumption that dehydration of these stabilisers takes place at elevated temperatures.

The observation of Orr and Breitman that the addition of a non-ionic stabiliser increases the efficacy of ordinary ionic soaps is extremely interesting. These authors explain this by a decrease in the electrostatic repulsion of the soap ions due to the presence of molecules of the non-ionic stabiliser between them in the adsorbed layer and, consequently, a contraction of the area occupied by a soap ion. The observations of Orr and Breitman agree well with the results of a series of well-known investigations by Cockbain in which it was established that the use of mixtures of two stabilisers gives a positive effect only where a mixture of an ionic and a non-ionic stabiliser is used.

A particular case of the stability of emulsions takes place in stabilisation by solid emulsifiers. However, in view of the special mechanism of this stabilisation, this case requires special consideration. We shall mention only that in the case of emulsions of the water-in-oil type, for example, the presence on the surface of the globules of a protective layer, consisting of granules of a relatively hydrophobic solid emulsifier is still insufficient to ensure the stability of the system to aggregation. The globules of such an emulsion should adhere to one another when they collide for the same reasons which cause the unstabilised particles of the hydrophobic powder to adhere in water. Hence, the obvious conclusion that the stability of such emulsions may be due to the mosaic structure of the granules of the solid emulsifier. This ensures, on the one hand, adhesion of the granules to the internal phase and, on the other hand, formation on the surface of the granules turned towards the external phase of a sufficiently strong solvated layer or electrical double layer[3,9].


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