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BASIC PRINCIPLES IN THE FORMATION
OF
HIGH-STABILITY CONCENTRATED EMULSIONS

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One of the fundamental problems in the physical chemistry of dis-
perse systems is that of stability, the latter being necessary for a
long-lasting uniform distribution of finely divided matter in the
dispersion medium. In the case of highly concentrated emulsions, stability
is achieved by making the drops of one of the liquids as small as pos-
sible in the presence of a good surface active stabiliser. Separation
is prevented by the small size of the drops and stability depends on the
capacity of these drops to execute Brownian movement. However, the
so-called homogenisation requires complicated equipment and often in-
volves a considerable expenditure of mechanical energy. We shall
not deal here with spontaneous emulsification, which is unusually in-
teresting, and which was discussed not long ago by Rehbinder [1].

Two other means of obtaining high-stability concentrated emulsions
have practical value.

1. Systematic studies in our laboratory of the necessary stabi-
lising conditions and of the properties of highly concentrated (gela-
tinised) emulsions [2] has shown that, when most of the drops have a
diameter of 1 micron, high stability depends on the structure of the
system as a whole which structure is produced by the close proximity
of greatly deformed drops. Non-flowing gel-like emulsions with very
high concentrations of the dispersed phase (for example, 265 cm^3
of benzol in 1 cm^3 of a 8% solution of sodium oleate) will maintain
their stability for many months because of the ~~toughness~~ stability of the film
framework. Disturbance of the structural elements (cell walls, honey-
combs) leads to a breakdown of the emulsion, which is especially found
in systems of maximum concentration. The latter are stabilised by
protecting the layers with a critical thickness of 0.01 micron in the case of sodium
oleate solutions, which have low resistance to breakdown. Therefore
emulsions of maximum concentration easily begin to break down on
shaking ~~because of~~ with an excess of organic liquid. However, shaking a

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system with 2 - 3 drops of water not only stops the breakdown ~~of the~~
~~breakdown~~ of the emulsion but also reestablished the emulsion because
of the ~~reinforcement~~ (thickening of the layer) or water between the drops. If a greater amount
of water is added to an emulsion of maximum concentration or of generally
high concentration, the water (or an addition of a weak solution of the
stabilizer) ~~expands~~ moves the cells apart and separates them from each other. The
free drops which assume the usual spherical shape, remain suspended
in the dispersion medium with an early formation of protective layers
on them; i.e. a thin ~~concentrated~~ dilute emulsion is obtained whose stability
is basically determined by the dispersion of the original system.

2. According to the generally accepted views of Rebinder (3), the
necessary stability conditions of concentrated emulsions are: suf-
ficient surface activity (soluble emulsifiers) relative to the
liquid-liquid interphase boundary and toughness of the stabilizer in
the adsorption layer. These conditions ensure kinetic stability of
emulsions when highly dispersed or when formed from two liquids of
equal specific weights. But if in the system there is found a signi-
ficant number of large drops not having Brownian movement, then the
uniform distribution is disturbed and interphase layers appear, which
point to insufficient kinetic stability of the original emulsion. The
interphase layers here are stable with concentrations of the dispersed
phase of about 80% (the upper limit of filling the volume by isodia-
metrical spheres because of the poly-dispersion of the system), because
of the presence of strong hardened layers of the stabilizer on the
drops.

Kinetic instability of the original emulsion can be compensated
for even with a small concentration of the dispersed phase; i.e.
with large intervals between the drops. For this purpose, the pro-
tective layers encircling the drops must be fortified so that a spatial
network be formed whose walls are strong enough to maintain the

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suspension of the drops. Stating the problem in this way is not accidental since in 1934 Talmud and Bresler proposed/4/ that "From our point of view all stabilizing adsorption layers and surface films of emulsions appear to be 'spumoid'".

The present state of colloidal chemistry makes it possible to construct such structures in ~~thin concentrated~~ dilute emulsions, ~~which would~~ so that appear to ~~impede~~ the movement of the drops. is impeded; ~~The matter concerns~~ This is achieved by ~~the possibility of~~ using, for a sudden increase in stability of concentrated emulsions, thixotropic colloidal solutions of surface-active stabilizers, which are easily reformed after cessation of mechanical action.

The stabilizer should have for this point a) surface activity relative to the interphase boundary of water and oil and sufficient surface strength in a fine layer of the solution and b) the ability suddenly to form the thixotropic systems with a sufficiently rapid restoration of the spatial structures destroyed in emulsification.

The surface activity of the stabilizer, as is known, ensures the formation of a protective layer on the oil drops. Therefore not all thixotropic solutions can be used for our purposes. Colloidal solutions of materials which do not have a noticeable surface activity (for example, thixotropic solutions of iron hydroxide or vanadium pentoxide) are not effective stabilizers of emulsions. The use of/such substances usually leads to the formation of quasi-emulsions in which the drops are mechanically enclosed within the spaces of the cells. Shaking of the quasi-emulsion leads to coalescence of the drops, which are freed when the cells are disturbed. Only thixotropic solutions of surface-active substances can ensure the covering of the drops with a protective layer even in the case where the spatial structure network in the free solution between the drops is disrupted by shaking the prepared emulsion or in forming the emulsion.

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Since emulsions are obtained as the result of the mechanical processing of two fluids, ~~then~~ the process of emulsification should involve a disruption of the spatial structures in the stabilizing solution. ~~Therefore~~ *Consequences* it is essential in ~~preventing~~ *order to prevent* the system from ~~separa~~ting into layers to have a simultaneous and sufficiently rapid restoration of the disrupted spatial structures after cessation of emulsification. The emulsion will ~~appear~~ *be* kinetically stable for a long period, if the adsorption layers on ~~the~~ drops of the dispersed phase, as a part of the structural elements of the system, are rapidly ~~secured~~ *interconnected* *and attached* to each other ~~by~~ *during repeated ~~ ~~* structural fragments in a free solution, ~~during re-~~ ~~peated ~~. The structures should be disturbed relatively *easily* ~~easy~~ by mechanical action to avoid using large energies in overcoming these resistances during emulsification. It is ~~natural~~ *obvious* that the properties of these systems should be studied and characterized by measuring the viscosity of the solutions for variable pressures (velocities of flow).

That very stable emulsions could be obtained by this relatively easy method of using thixotropic solutions was proved in a series of cases.

In connection with this, we will now examine the stabilizing properties of mixtures of sodium oleate with aliphatic alcohols in the formation of concentrated emulsions.

Experimental Section

The sodium oleate was prepared from oleic acid which had been freshly distilled in vacuum and a caustic soda solution. The alcohols were chemically pure. Carefully purified and distilled benzol served as the dispersed phase. The alcohol was mixed with either the benzol or a 1% soap solution. The viscosity was measured by Ostwald's viscosimeter in Kroyt's apparatus. The surface tension was measured by Rebinder's maximum-drop and bubble-pressure method.

The emulsions were prepared by stirring stabilizer solutions with the benzol in various proportions by means of a 400-rpm agitator for 5 minutes and making two 30-second interruptions after the first and third minutes of dispersion.

The stability was determined by the emulsion's rate of separation into layers which was observed in graduated cylinders.

The influence of alcohols on the stability of an emulsion.

Investigations showed that the introduction of alcohols into benzol or into the soap solution generally leads to an increase in the stability of an emulsion of the oil-water type which may have various volumetric phase relationships. The stability increases higher as 1) more alcohol of any chain length is introduced into the system and 2) with the length of the chain for equal concentrations of alcohol. This is shown by the curves of figures 1 and 2 for emulsions with a 60% (volumetric) concentration of benzol.

The study of viscosity, carried on earlier in our laboratory

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/5/, showed that the middle members of a homologous series of aliphatic alcohols bring about in sodium-oleate solutions the development of struc- tures of a coagulative nature. Although the spatial structures are sufficiently fragile, the stability of the emulsion is significantly increased. However, as is seen from figures 1 and 2, an exceptionally sharp increase in sta- bility is produced by octyl alcohol in benzol or in a soap solution.

It is very important to notice that the presence of small amounts of octyl alcohol, about 0.1%, in a 1% solution of sodium oleate is sufficient to form an emulsion which is practically non-separating for a long period.

With increase in alcohol content, the emulsion becomes stable practically without limit and non-separating for a year and longer if stored in tightly-closed containers.

The statements of Shulman and Cookbain on the very poor stability of emul- sions prepared with sodium oleate and containing octyl alcohol in the oil phase together with their attempt of/a̲ theoretical proof of this seem strange.

Viscosity of water mixtures of sodium oleate with octyl alcohol.

1% sodium-oleate solutions were boiled under a reflux for 10 minutes with various amounts of octyl alcohol. In 2 hours after preparation, the solu- tions were measured with the viscosimeter.

We estimated the solutions' capacity of thixotropic restoration in the following way. After finishing the measurement under the highest pressure, the "zero point" was repeatedly determined; i.e. the time of flow of the solution under the first pressure at which the test was started. If the zero point was reproduced, then the restoration of the spatial structure could be considered complete.

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In other cases, the degree of thixotropic restoration of structures was
established in this way.

The viscosimetric ~~results of~~ ^(measurements on) soap solutions as a function of cetyl
alcohol content are represented in figure 3. The general pressure P,
including the average hydrostatic difference $\frac{Hcp \cdot d}{?}$, is the abscissa, and
the ordinate is the relative viscosity η / η_o , where η and η_o corre-
spond respectively to the density of the solution and water. The measure-
ments were conducted at 20^oC.

The obtained data show that ~~the diffusion of~~ ^(dissolving of) cetyl alcohol in a
sodium-oleate solution leads to a structure-forming system which is
stronger, the higher the alcohol concentration. ~~The matter concerns~~ This refers to
the spatial structures developed in solutions, which are partly
disturbed during increased rates of flow, but which are rapidly re-
established when in a state of rest. Actually, repeated measure-
ments at zero pressure show in all cases the reestablishment of abnormal
(structural) viscosity ~~and~~ the restoration being more complete,
the lower ~~is~~ the alcohol content. This is verified by table 1.

It could be established
√ ~~Actually~~, for alcohol concentrations up to 1%, that the structures
are practically fully restored in a short time after their disruption
as the result of drawing the solution through capillaries, with a gradual
increase in pressure to P = 1800 mm of water.

Apparently the structures are restored as rather loose non-dense
formations ~~made of~~ ^(resulting from) soap and alcohol in the gelatinization process. ~~In~~ With
alcohol concentrations of less than 0.1%, structure-formation is not
found in soap solutions. At the same time, these solutions do not ~~show~~ bring about
a noticeable increase in stability of the emulsion.

A similar change in viscosity is shown ~~in actually concentrated~~

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solutions of oleate and cetyl alcohol (as ~~such evidence~~ of equal concentration) can be seen from Table 2.

Solutions weaker than 0.06% practically do not ~~structurize~~ form structures and do not exert any influence upon the stability of emulsions prepared with their aid.

The temperature of the mixture significantly influences the ~~structurizing~~ structure forming process (figure 4).

Corresponding with the known data on the gel~~atinizing~~ ation of other colloidal systems, there is found in the present case an increase in ~~structurization~~ structure formation with decrease in temperature.

The abnormal viscosity of the dispersion medium and its dependence upon temperature are fully revealed by the emulsion viscosity; this is clear from the curves of Figure 5, which represent one of many conducted Experimental ~~tests~~. Thixotropic viscosity also appears in emulsions and is expressed by the fact that the zero point in repeated measurements more ~~and more~~ closely approaches the ~~minimum~~ values of the initial measurements ~~with smaller and smaller~~ at the lowest pressures. These points on the curves are indicated by dotted lines.

The temperature dependence of viscosity is unusually characteristic. If the abnormal emulsion viscosity in the presence of cetyl alcohol in our tests had been chiefly due to the deformation of the particles, then we could not have explained by this means the ~~curves sudden increase~~ sharp rise of the curves denoting structure with decrease in temperature. Thus the abnormal emulsion viscosity at ~~small~~ low pressures depends upon the structure formation of the dispersive medium and stabilizer solution; but the presence of benzol drops apparently increases the capacity of soap-alcohol mixtures to gelatinize in the water layers between the drops.

In conclusion we will ~~stop at~~ briefly consider the surface activity of sodium-oleate and cetyl alcohol mixtures. By the maximum bubble pressure

method we measured the surface tension on the/boundary of separation.

However, the measurements on the surface of benzol-water separation did

not lead to ~~obtaining~~ uniform results because of the formation of a viscous

film of alcohol and soap which made the work very difficult. In any

case, the curves of figure 6 show the increase in surface activity of

the mixture in weak equally-concentrated solutions. However, the sur-

face tension of the mixture becomes higher than that of the original

soap solution. This is due to the formation of heavy micelles which

have lower adsorption on the surface.

In summarizing, we come to the conclusion that, with sufficient activity of the stabilizer and strength of the adsorption films, the unusually high stability of the studied emulsions is dependent upon the ability of the stabilizer solutions to restore the structures thixotropically in the emulsifying process, which impedes the system's layers formation.

Conclusions

1. For a sudden rise in stability of concentrated emulsions, it is proposed to use thixotropic solutions of surface-active stabilizers which can restore sufficiently rapidly the structures disrupted in the process of emulsification.

2. It was shown that the use of thixotropic solutions of a mixture of sodium oleate and cetyl alcohol leads to an unusually sudden increase in stability of concentrated emulsions which do not separate for a very long time.

3. The following were studied: the viscosity of mixtures of sodium oleate and cetyl alcohol for various combinations, the viscosity of the emulsions obtained with their aid, and the influence of temperature variations upon structurisation.

4. The influence of aliphatic alcohols (homologous series) upon the stability of concentrated emulsions was studied.

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/ p.21/ Figure 1. Influence of alcohols in benzol upon the stability of an

emulsion. I - butyl; II - amyl; III - octyl; IV - cetyl alcohols;

Ψ - volume in % of the 1% sodium-oleate solution separating; N -

Normality of the alcohol in benzol.

/ p.21 Figure 2. The influence of alcohols in a 1% sodium-oleate solution

upon the stability of an emulsion: I- butyl; II - amyl; III - octyl;

IV - cetyl alcohols; v - volume in % of the sodium-oleate solution

separating: N - normality of the alcohol in sodium-oleate solution.

/ p.22/ Figure 3. (a graph) Relative viscosity η/η_o of 1% sodium-oleate

solution for various pressures and cetyl-alcohol concentrations.

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Figure 4 (a graph)
(p. 24)

p 24 The influence of temperature upon the viscosity of a 1% sodium-oleate solution in the presence of cetyl alcohol.

Figure 5 (p. 24) Viscosity of an emulsion having 60% (volumetric) by volume of benzol in a 1% sodium-oleate solution. The normality of the cetyl concentration alcohol in the benzol is 0.2N

Figure 6((p. 24) Influence of cetyl alcohol upon the surface tension: 1-sodium-oleate solution; 2-equally concentrated solutions of sodium oleate and cetyl alcohol.

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Table 1

Thixotropy of the viscosity of mixtures of sodium oleate and cetyl alcohol; relative viscosity η / η_0 of the mixtures.

P mm of water	Concentration of Cetyl Alcohol in %										
	0.1	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
	Initial Measurements										
106	1.19	1.27	1.40	2.03	3.48	5.66	—	—	—	—	—
270	—	—	—	—	—	—	10.1	13.5	54.1	94.7	—
	Repeated Measurements										
106	1.19	1.26	1.39	2.01	3.12	4.95	—	—	—	—	—
270	—	—	—	—	—	—	6.08	6.91	29.1	47.3	—

Table 2

Relative Viscosity of Equally Concentrated Solutions of Soap and Cetyl Alcohol.

P mm of water	Concentration of Soap and Alcohol in %				
	0.062	0.0125	0.25	0.50	1.0
106	1.28	1.50	1.93	3.54	5.66
154	1.23	1.43	1.85	3.35	5.00
270	1.16	1.30	1.62	2.97	3.45
530	1.14	1.28	1.61	2.54	2.61
742	1.14	1.28	1.61	2.28	2.38
968	1.14	1.28	1.61	2.24	2.35
1300	1.14	1.28	1.61	2.22	2.33
106 (repeated)	1.20	1.42	1.84	3.32	4.95

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