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On the Stabilizing Effect of Surfactants Adsorption Layers*

E. A. Amelina, A. M. Parfenova, V. V. Yaminskiy, and E. D. Shchukin

Moscow Lomonosov State University, Moscow, USSR

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Cohesion forces in contacts of discrete spherical particles (having either hydrophilic or hydrophobic surface) were measured directly in aqueous or heptane solutions. It is shown that the stabilizing action of tensides in the hydrophobic particle system was brought about by a two-dimensional pressure of the adsorbed tenside which is easily removed from the contact zone of the particle. The stabilizing action of tensides in the hydrophilic particle systems is a consequence of the formation of a mechanical barrier which has a high apparent strength due to the adsorbed layer on the solid surface.

The surface active substances (surfactants) capacity of radically influencing the interaction between solid surfaces is responsible for effects such as stabilization of disperse systems, directed alteration of their properties, washing and lubricating effects of surfactants, etc. It is thus expedient to carry out direct quantitative studies of contact interactions between different particles and the influence of surfactants on these interactions in order to establish mechanisms for the stabilizing effect of surfactants.

With this view in mind we have used the technique developed earlier^{1,2}, which is based on the use of a sensitive magnetoelectric system as a strength meter. The technique permits the measuring of cohesion forces in contacts between individual particles in a wide range from 10^{-3} to 10^2 dyn**. The experiments were performed as follows. Two particles were brought together and stayed in contact under the given compressing force (from 10^{-3} to 10^2 dyn) for a certain time t . On removal of the compressing force a steadily growing disruptive force was applied to the particles and the cohesion force N was measured, which was equal to the load making the particles separate.

B. V. Deryagin³⁻⁵ obtained strict thermodynamic relations connecting the interaction forces between molecularly smooth particles measured by their equilibrium (reversible) separation with the free energies of interaction between their solid surfaces:

$$N = \pi RF \quad (1)$$

$$F/2 = \sigma - \gamma/2 \quad (2)$$

where N is the cohesion force between elastic particles; for two spheric particles

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** Dyn = 10^{-5} N

with radii R_1 and R_2 $R = 2R_1 R_2 / R_1 + R_2$; F is the interaction energy per 1 cm^2 of two planeparallel surfaces, σ is the surface tension at the particle — medium interface, γ is the surface tension in the contact between the attached (contacting) particles.

In order to simulate the elementary acts of the surfactants stabilizing effect in aqueous dispersions of non-polar solid particles, we have used fused glass spheres about 2 mm in diameter with the surface chemically modified by dimethylchlorosilane². This surface consists of methyl groups and has paraffine-like properties. Cohesion between such spheres was studied in pure water and in solutions of surfactants. Lower alcohols of the fatty series were used as non-micelle-forming surfactants. The micelle-forming surfactants chosen were typical representatives of anionic, cationic and non-ionic surfactants, respectively sodium dodecylsulphate (SDS), cetyl pyridinium bromide (CPB) and polyoxyethylenedodecyl ether (PDDE) the average degree of oxyethylation being 20.8.

It was found that forces of cohesion between methylated glass spheres in water solutions of all the surfactants studied depend only on the nature and concentration of the surfactant and on the radii of the spheres. Variation of the compressing force from one tenth of a dyne to several dozen dynes, the time of its application from a few seconds to several dozen minutes, as well as the rate of the disruptive force growth do not affect the cohesion forces. Standard deviations of cohesion forces never exceeded 10%. The results of the measurements have shown, that the $F/2$ values, in complete agreement with Deryagin's theory, are invariant with respect to the spheres radii and can thus be used as an unambiguous parameter of the stabilizing effect of surfactants in the systems under consideration.

Figure 1. presents free interaction energy $F/2$ dependence on concentration of four lower alcohols (curves 1, 2, 3, 4) and ethylene glycol in water. As can be seen from the figure, in presence of the alcohols, $F/2$ decreases in qualitative accordance with the Traube rule for non-polar solid surfaces. In case of organic liquids freely mixing with water (the first three alcohols and ethylene glycol) the interaction energies steadily fall from $F/2 = 40 \text{ erg/cm}^2$ * in pure water to the value in the pure organic liquid. Whereas complete substitution of water by ethylene glycol results only in an approximately twofold decrease in the interaction energy, substitution by propyl alcohol decreases the interaction energies several hundred times (in pure propyl alcohol $F/2 = 0.1 \text{ erg/cm}^2$).

According to the correlation (2) the change of the interaction energy in solutions of surfactants, as compared to that in pure water, may be either due to the changing surface tension at the solid-liquid interface σ_{sl} or due to the changing surface tension in contact between the solid surfaces γ :

$$F^0/2 - F/2 = (\sigma_{sl}^0 - \sigma_{sl}) - 1/2 (\gamma^0 - \gamma) \quad (3)$$

(values with the superscript⁰ refer to pure water, those without it refer to solutions of surfactants). Using the literature⁶ on contact angles θ formed by ethyl alcohol mixtures with water on paraffine we have estimated from the Young's equation the values σ_{sl} :

* $\text{erg} = 10^{-7} \text{ J}$

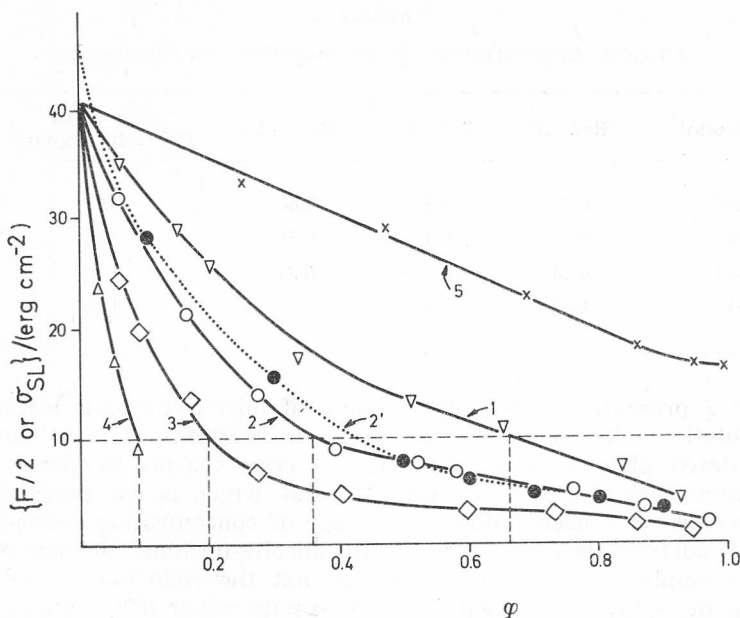


Figure 1. The free energies of interaction ($F/2$) between methylated glass surfaces in aqueous solutions of organic liquids: methanol (1), ethanol (2), *n*-butanol (4). The 2' curve describes surface tension (σ_{sl}) of ethanol aqueous solutions at the interface with solid paraffine. ϕ is the concentration of the organic liquid in water.

$$\sigma_{sl} \approx \sigma_s - \sigma_l \cos \theta$$

(curve 2' in Figure 1). The σ_s value accepted as the surface energy at the solid-gas interface was 22 erg/cm². This Figure coincides with the $F/2$ for the energy of the interaction between methylated glass spheres in air and agrees with the reported data⁷⁻⁹ on the surface energy of paraffine-like surfaces, to which methylated glass belongs. As the curves 2 and 2' in Figure 2. are very close to each other, the interaction energies are apparently equal to the surface tension at the solid-liquid interface, i. e. $F/2 \approx \sigma_{sl}$. Then, according to (2), $\gamma \approx 0$, this indicating that the dispersion medium layer is absent and that the surface forces in the contact between particles are practically completely compensated. Thus the stabilizing effect of surfactants in aqueous dispersions of non-polar solid particles is associated with the reduction of surface tension at the particle-environment interface.

This conclusion is consistent with the results of recent studies¹⁰⁻¹² on aggregative stability of coarse and fine dispersions of various non-polar solids teflon¹⁰, methylated glass¹¹, methylated aerosil¹² in water-alcohol mixtures. The increase in the alcohol concentration to a certain »critical« value (see Table I) resulted in the pronounced desaggregation of particles in the systems. Comparison of Table I with Figure 1. shows that the »critical« concentrations correspond to the reduction of free energies of interaction between non-polar solid surfaces to approximately the same level (horizontal dotted line in Figure 1). For ethylene glycol $F/2$ (Figure 1., curve 5) lies considerably above this level at all concentrations. Respectively, teflon particles are strongly aggregated even in pure ethylene glycol.

TABLE I
 »Critical« Concentrations of Alcohols (Volume Fractions)

| Alcohol | Ref. 10. | Ref. 11. | Ref. 12. | this work $F/2 = 10 \text{ erg/cm}^2$ |
|---------|----------|----------|----------|------------------------------------------|
| Methyl | 0.7 | 0.5 | 0.68 | 0.65 |
| Ethyl | 0.35 | 0.35 | 0.51 | 0.35 |
| Propyl | 0.14 | 0.185 | 0.31 | 0.19 |
| Butyl | 0.08 | 0.065 | — | 0.08 |

Figure 2 presents $F/2$ vs. concentration of micelle-forming surfactant in aqueous solutions. As seen from the figure, in solutions of these surfactants the methylated glass spheres interaction energy sharply decreases at low concentrations (below CMC) to a certain value which is not affected by the further increase in concentration. This shape of concentration dependences is typical for surface tension isotherms of micelle-forming surfactants. With SDS for example, it was directly shown that the reduction of interaction energies in the solution ($F/2$) with respect to pure water ($F^0/2$) is equal to the

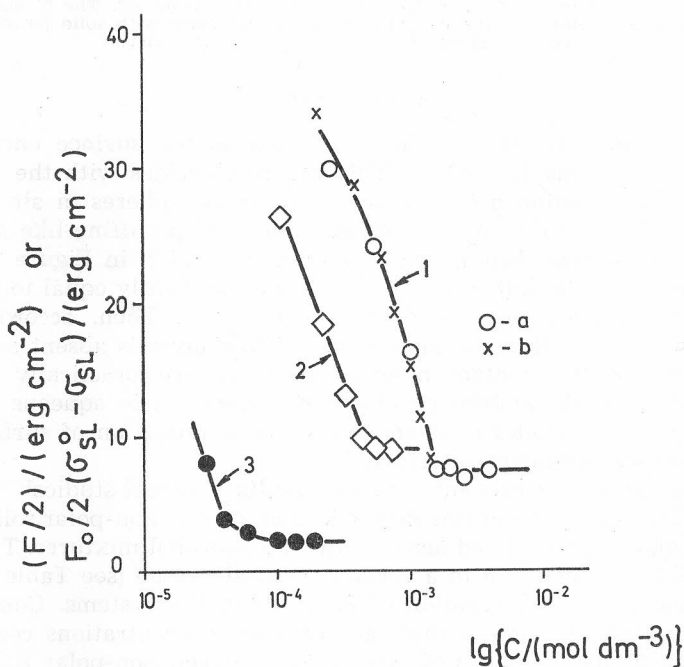


Figure 2. The free energies of interaction ($F/2$) between the methylated glass surface in aqueous solutions of micelle-forming surfactants: sodium dodecyl sulphate (1a), cetylpyridine bromide (2) and polyoxyethylene dodecyl ester (3). 1 b is the value $F^0/2 - (\sigma_{sl}^0 - \sigma_{sl})$ for methylated glass in aqueous solutions of sodium dodecylsulphate (see the text). C is the surfactant concentration in water.

reduction of surface tension, i. e. to the two-dimensional pressure $\sigma_{sl}^0 - \sigma_{sl}$ of surfactant adsorption layers at the particle solution interface.

$$F^0/2 - F/2 \approx \sigma_{sl}^0 - \sigma_{sl} \quad (4)$$

This can be confirmed by calculations of two-dimensional pressure $\sigma_{sl}^0 - \sigma_{sl}$ according to Gibbs' equation

$$\sigma_{sl}^0 - \sigma_{sl} = RT \int_0^c \frac{I'}{c} dc$$

employing results of direct measurements of SDS adsorption I' on the powder of aqueous suspension of methylated glass. Figure 2 shows (curve/1) that the difference $F^0/2 - (\sigma_{sl}^0 - \sigma_{sl})$ between the interaction energy $F^0/2$ in pure water and the two-dimensional pressure $(\sigma_{sl}^0 - \sigma_{sl})$ in the surfactant solution is practically equal to the interaction energy $F/2$ measured in the surfactant solution. From the comparison between (4) and (3) we get that $\gamma^0 \approx \gamma$. This equality of γ values in pure water and in the surfactant solution shows that all the surfactant molecules are extruded from the zone of contact between attached particles.

In order to study the stabilizing effect of oil-soluble surfactants we have measured cohesion forces between solid spheric particles with a hydrophilic surface (fused glass) in *n*-heptane with added fatty alcohols (cetyl CA and buthyl BA), fatty acids (stearic SA, myristinic MA, lauric LA, capronic CAc) and oleic OA and octadecylamine ODA. Heptane («ethalon» brand) was dried and purified from surface active admixtures by being kept in contact with ceolytes and the following fractional distillation in an apparatus made of glass only. CA, SA, MA, LA, and ODA were twice recrystallized from ethanol and from purified heptane.

In experiments with hydrophilic particles in hydrocarbon solutions of all the surfactants studied, the picture observed differs fundamentally from that in experiments with hydrophobic particles. In water solutions of surfactants the free energy of methylated particles interaction decreased no more than tenfold and was practically unaffected by the force under which the contact was formed and by the time the particles stayed in contact under this force. As for hydrocarbon solutions of surfactants, cohesion of particles there depends markedly on the compressive force applied to them, as well as on the time the particles stay in contact under the force. Particles brought together by a small compressive force f (a few hundredths of a dyne) display no cohesion: ($N \leq 10^{-3}$ dyn, $F/2 \leq 0.01$ erg/cm²). The force of interaction and its energy are in this case by several orders of magnitude lower than in the pure solvent ($N \sim 10$ dyn, $F/2 \sim 20$ erg/cm²). As the compressive force f exceeds a certain critical level f_c the particles incidentally displayed cohesion, i. e. in some cases strong contacts appeared where N and $F/2$ increased by orders of magnitude and appeared to be close to the values in the pure solvent. Further increase in the force results in the growth of the number of cases where strong contacts appear, i. e. the probability of attachment (cohesion) W increases. By the probability of attachment we mean the fraction (in %) of experimental instances w_c , where the cohesion force N was from several

dyn to about ten dyn, in the total number of contacts observed w_0 ; $W = (w_c/w_0) \cdot 100\%$.

The sharp reduction of the particles interaction energy in hydrocarbon solutions of surfactants should be regarded as the result of the protective (stabilizing) effect of surfactants adsorption layers forming at the particles surface. Finally, the extent of the stabilizing effect depends on the properties of adsorption layers, namely the degree of their formation, their resistance to destruction and removal from the contact zone when the particles approach each other.

Figure 3 presents the probability of attachment between particles vs. the time they were kept in the solution (τ) prior to being brought in contact. As seen from the figure, the probability of attachment decreases (the protective effect increases) with increasing time τ given for the adsorption layer formation. The period during which the protective effect increases is rather long. This fact can be associated with the long time necessary for the formation of the adsorption layer at hydrophilic surface and/or the possible ageing of the layer already formed¹⁴⁻¹⁷.

The value of W and its dependence on different parameters characterizes the extent of the protective effect of surfactants adsorption layers. The lower W , the greater the protective effect, if other conditions remain the same.

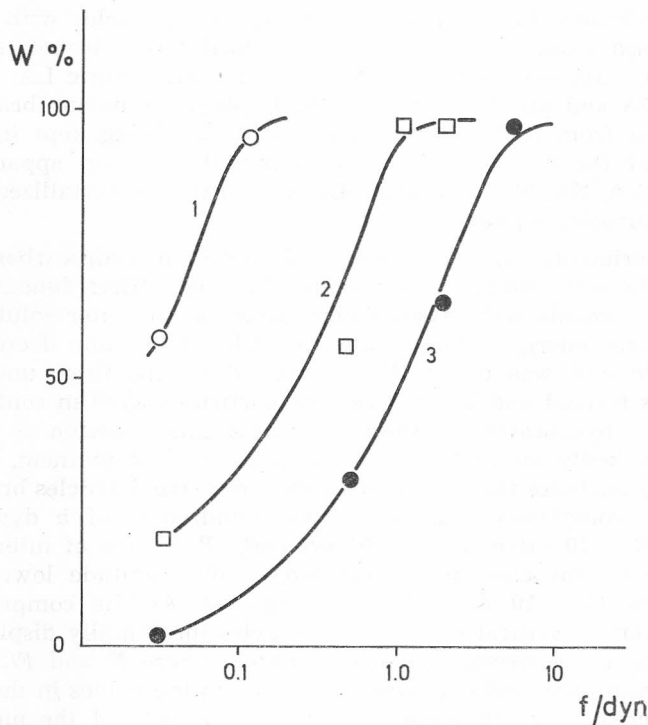


Figure 3. Probability of attachment (cohesion) of glass spheres in cetyl alcohol solution vs. the compressing force for the different times the samples are kept in the solution. 1 — 20 min, 2 — 24 h, 3 — 48 h.

Figure 4 (curve 1) presents the probability of hydrophilic particles attachment (cohesion) vs. load applied to them in stearic acid solution. At $f = 0.1$ dyn no cohesion was observed ($N \leq 0.003$ dyn). Only when $f > 0.1$ dyn strong contacts start to appear occasionally, and at $f \approx 1$ dyn only strong contacts were observed. The picture is qualitatively similar in experiments where cetyl alcohol (Figure 4, curve 2) or other surfactants were added to the solution, i. e. the probability of attachment also grows with the load. The quantitative difference is that under the same f , the probability of attachment in cetyl alcohol solutions is greater, or, in other words, the protective effect is weaker even at high concentrations.

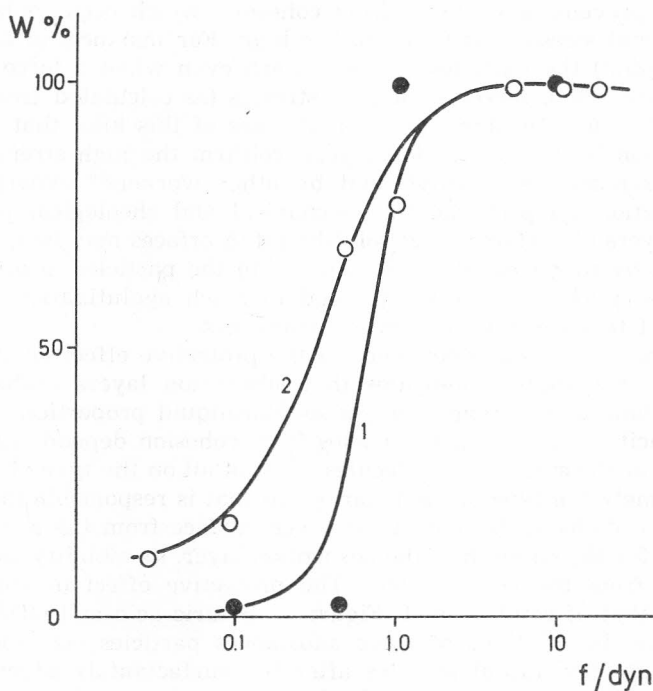


Figure 4. Probability of attachment of hydrophilic glass spheres vs. compressing force in solutions of stearic acid ($c = 10^{-5}$ mol/dm³) (1), and in solution of cetyl alcohol ($c = 10^{-3}$ mol/dm³) (2).

The probability of attachment, which characterizes the protective effect of surfactants, depends on the time of the compressive force application t other conditions being the same: the probability of attachment is greater the longer the particles were in contact under the load. As seen from Table II, the longer the particles are compressed by the force f , the weaker is the force necessary to overcome the adsorption layer resistance and to provide for cohesion.

From the above we see that the stabilizing effect of surface active additives in disperse systems with non-polar dispersion medium and hydrophilic solid disperse phase differs from that in systems »non-polar particles — water«. The free energy of interaction between particles in water solutions of surfactants decreases insignificantly if compared to the reduction in heptane

TABLE II

| f/dyn | t/s | 10 | 100 | 1000 |
|-------|------|----|-----|------|
| | 0.03 | | 20 | 60 |
| 0.1 | | 60 | 100 | 100 |

solutions. The decrease in the former case is due to the adsorption layers capacity of resisting the destruction of the contact zone, thus creating a mechanical barrier preventing particles from cohesion, which occur only under the action of normal stresses, at times rather high. For instance, in case of ODA ($c = 10^{-5}$ mol/dm³) the particles did not attach even when a force $f \approx 50$ dyn was applied for 100 s, corresponding to stresses (as calculated from the Hertz equation¹⁸), $P_c \approx 6 \times 10^8$ dyn/cm². High stresses of this kind that have withstood destruction by the adsorption layers, confirm the high strength of these layers, first reported by Hardy¹⁹ and by other workers²⁰ experimenting on boundary friction. In principle the mechanical and rheological properties of adsorption layers of surfactants at solid-liquid interfaces may be quantitatively characterized by the stress P_c , to be applied to the particles in order to overcome the adsorption layer resistance and to reach agglutination, and by the dependence of this stress on different parameters.

The above considered dependence of the protective effect on time t of the compressive force applied, indicates that adsorption layers probably have a threshold of long-term strength or possess quasiliquid properties.

The capacity of preventing particles from cohesion depends essentially on the structure of the surfactant molecules, most of all on the type of polar group, since it is namely the type of the polar group that is responsible for the nature of adsorption of the surfactant at the given surface from the non-polar environment and for the strength of the adsorption layer, its mobility and resistance to extrusion from the contact zone. The protective effect of stearic acid is greater than that of cetyl alcohol (Figure 4). Stearic acid and ODA prove still more effective. In solutions of these substances particles occasionally attach only during the few initial minutes after the surfactant is added, i. e. when the adsorption layer has not formed. However, just in an hour of staying in the ODA solution, not a single case of attachment was observed even when stresses $P_c \sim 6.8 \times 10^8$ dyn ($f \sim 50$ dyn) were applied to the particles for 1000 s.

The above results allow us to regard the stabilizing effect of surfactants in non-polar environment as a phenomenon analogous to a strong stabilization factor such as the structural-mechanical barrier.

The presence of a strongly solvated adsorption layer, as indicated by Reh binder²¹ and after him²² provides for ultimate aggregative stability of the lyophilized disperse system because the interaction energy of the particles is comparable with the energy of their heat movement²² under these conditions.

A condition necessary for reliable stabilization is the own strength of adsorption layer's own strength and its inextrudability from the contact zone. The stronger the surfactant molecules bound to hydrophilic surface, the stronger the protective effect under the same conditions, as was observed in the alcohols-acids-amines series.

The most important effect of surfactants on interaction between hydrophilic particles in heptane is thus their capacity of creating a mechanical barrier preventing particles from cohesion (attachment) and reducing the interaction energy $F/2$ to the level ≤ 0.01 erg/cm² corresponding to the interaction energy in lyophilic systems (hydrophobic particles in heptane, hydrophilic ones in water). In case the particles do attach under the action of corresponding compressive forces applied after the adsorption layer is destroyed, the absolute values of the interaction force and the interaction energy prove somewhat lower than in the pure solvent (Table III).

TABLE III

Interaction Energies of Glass Spheres in Heptane Solutions of Cetyl Alcohol
(τ — 24 h, t — 10 s)

| Concentration of CA/(mol/dm ³) | $F/2$ /(erg/cm ²) |
|-----------------------------------------------|-------------------------------|
| 0 | 30 |
| 10 ⁻⁶ | 29 |
| 10 ⁻⁵ | 18 |
| 10 ⁻⁴ | 10 |
| 10 ⁻³ | 9 |

This reduction should be analogously associated to the experiments with aqueous solutions of surfactants, with the effect of two-dimensional pressure of adsorption layers, rehabilitating when the particles are being separated. However, recalling that under these conditions the formation of adsorption layers takes a long time, we can not argue a priori that these parameters are equilibrium ones, since our experiments did not as yet involve variation of the rate of the separating (disruptive) force application.

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SAŽETAK

O stabilizacijskom utjecaju adsorbiranog sloja tenzida

E. A. Amelina, A. M. Parfenova, V. V. Yaminskiy i E. D. Shchukin

U vodenim i heptanskim otopinama tenzida izravno su mjerene sile kohezije na dodirima odvojenih kuglastih čestica s molekularno ravnim hidrofilnim i hidrofobnim površinama. Pokazano je da je stabilizacijski učinak tenzida u sistemima »hidrofobne čestice — voda« uzrokovan dvodimenzijским tlakom adsorbiranog sloja tenzida, koji se lako isključuje iz dodirne zone čestica. U sistemima »hidrofilne čestice-heptan« stabilizacijsko djelovanje tenzida prvenstveno je uzrokovano stvaranjem mehaničke ograde, prividno vrlo velike jakosti, uslijed adsorbiranog sloja na čvrstoj površini.