

Influence of Surface Active Agents on the Interaction in Disperse Systems

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The behaviour and the properties of a dispersion are determined by the forces of interaction developing at the phase boundary due to the asymmetry of the intermolecular forces. The forces of longer ranges, the electrostatic repulsive forces, and the London dispersion forces will determine whether the dispersed particles will continue to exist as individuals or coagulate into particles aggregates (flocculation process). The behaviour of the particle networks, the question whether the individuals continue to exist in the aggregate form, separated by thin films of the dispersion medium, or flow or grow together to larger particles (coalescence), is influenced by dipole interactions, steric forces, and eventually by hydrogen bridge linkages, in addition to the electrostatic and dispersion interaction forces. To modify the interparticle forces surfactants or macromolecular compounds are used, which will both influence the long-range inter-particle forces and to a high degree, govern the interaction over short distances, especially the »steric hindrance«.

1. Influence of adsorption layers on the dispersion interaction

In considering the influence of adsorption layers on the dispersion interaction, one may start from the microscopic Hamaker theory^{1,2}. It is not possible to describe this influence from the macroscopic Lifshiz theory without difficulty.

The adsorption layer is divided into two regions, that of the polar groups and that of the non-polar groups. For nonionic surfactants as ethylen oxide adducts the thicknesses of these layers are of the same order of magnitude, but their Hamaker constants are different.

For the non-polar residues we may assume the value being valid for oils such as benzene or octane, *i. e.* $A_2 = 7 \cdot 10^{-20}$ J. For the layer of polar ethoxy groups, which are highly solvated, we shall use a value lying between that of pure water ($A_0 = 4.4 \cdot 10^{-20}$ J) and that of the oil phase, but closer to the water value ($A_3 = 5 \cdot 10^{-20}$ J). When calculating the influence of the adsorption layer, it must further be considered how the adsorbed molecules are oriented with respect to the phase boundary. If, for instance, the adsorption is effected by the interaction between a polar group and a solid particle, then the alkyl chains will be oriented towards the liquid, *i. e.* the particle is hydrophobic. If, on the other hand, the enrichment of surface active molecules is the result of the so-called hydrophobic interaction, the polar groups project into the liquid phase and the particles are hydrophilic. The results obtained by calcu-

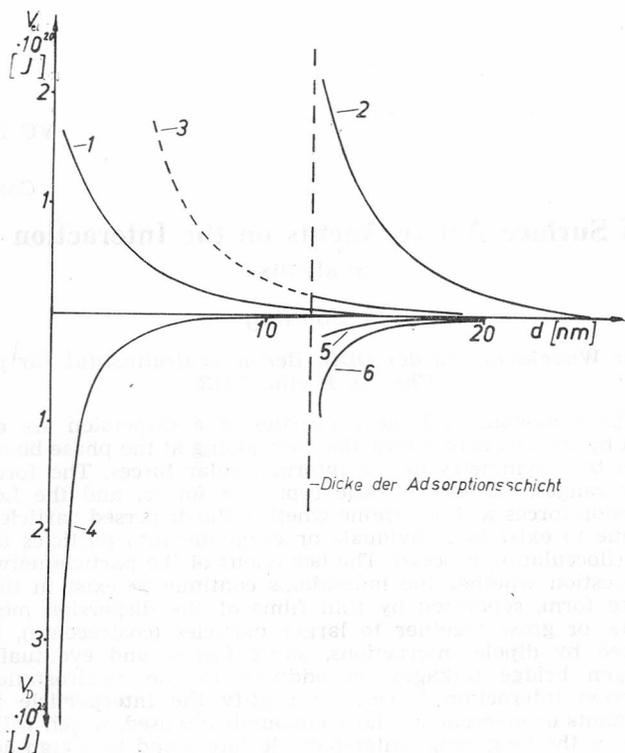


Figure 1. Dispersion energy and electrostatic repulsion energy between spherical particles (radius 10 nm) with and without an adsorbed layer, $\psi_s = 50$ mV, $C_{el} = 10^{-2}$ molar, $A_{particle} = 2 \cdot 10^{-19}$ J, hydrophobic part of the adsorbed layer thickness 2.0 nm, $A = 7 \cdot 10^{-20}$ J, hydrophilic part $\delta_2 = 4.0$ nm, $A = 5 \cdot 10^{-20}$ J, $A_{solvent} = 4.4 \cdot 10^{-20}$ J.

lating the dispersion energy for these two possible orientations of the adsorbed molecules are shown in Figure 1. Curve 4 is responsible for the dispersion energy of particles having a radius of 10 nm with a Hamaker constant $A = 2 \cdot 10^{-19}$ J, curves 5 and 6 describe the interaction in the presence of adsorbed layers with different orientation. The results clearly show that the range of dispersion energy is much increased for particles having an adsorption layer, because the effective particle radius has increased, and that with hydrophobic particles (curve 6) the interaction is about five times stronger than that with hydrophilic particles (curve 5). This difference is most apparent for distances having an order of magnitude of twice the adsorption — layer thicknesses, $d \sim 2(\delta_2 + \delta_3)$.

According to these calculations that it is not permissible to consider the adsorption layer to be a phase with a uniform Hamaker constant, a common practice in the literature.

2. Influence of adsorption layers on the electrostatic repulsion

Let us first consider how the electrostatic interaction is influenced by the adsorption of ionogenic surface active agents. It is well known that the energy of electrostatic repulsion (V_{el}) between two charged spherical particles

is the function of the potential of the diffuse electric double layer (ψ_δ), the ionic strength, expressed in terms of the reciprocal Debye-Hueckel parameter (χ), and the distance (d):

$$V_{el} = \frac{a}{z^2} f(\psi_\delta, \chi d)$$

where a means the particle radius, and z the charge of the counter ions.

Several variants of influencing the electrostatic interaction by ionic surface active agents are conceivable:

- a) The particle phase boundary gets charged only as a result of the adsorption of the surfactant molecules, *i. e.* with increasing surface concentration of the surface active agent the potential increases to a final value corresponding to the saturation limit of adsorption.
- b) The particle already carries a charge of equal sign. In this case the adsorption of the ionic surface active agent may completely fail to occur and the addition of a surface active agent will not influence the electrostatic interaction.
- c) The particle already carries a charge of the opposite sign. In this case the particle is discharged by the adsorption of the surfactant molecules, the repulsion forces decrease, and it is possible to effect a flocculation of the colloid dispersion by the addition of a surface active agent. With an excess of the surface active agent even a charge transfer can be achieved, so that again a stable dispersion is obtained, although with recharged particles.

These three mechanisms are trivial and need not be further discussed. The effects of surface active agents on the interparticle interaction are, however, not yet exhausted by this, for it is known that additions of non-ionogenic surfactants also affect the stability of colloid systems to a considerable degree.

The above consideration of the influence of adsorption layers on the electrostatic interaction assumed that the ion distribution in the diffuse double layer is not changed by the presence of the surface active agent or of the macromolecular adsorption layer. This is a boundary condition which is certainly not valid. It should be equally justified to postulate that the adsorption layer acts like a dielectric, *i. e.* that the range of electrostatic forces shifts with the thickness of the adsorption layer. If one would like to characterize these two boundary conditions, they might be considered to be the minimum and the maximum range, respectively, of electrostatic repulsion for ψ_δ being constant. For aerosil particles having a particle radius of 10 nm and a potential of 50 mV, the energy of electrostatic repulsion was calculated for 10^{-2} M 1,1 electrolyte solutions, without adsorption layer (curve 1 in Figure 1) and with an adsorption layer of a non-ionic surface active agent (NP 20), the thickness of which was $\delta = 6.0$ nm (polar group 4.0 nm, non-polar residue 2.0 nm), for hydrophobic orientation with counterions in the polar part of the adsorbed layer (curve 3) and with hydrophobic orientation (curve 2). The assumption that counterions are present only in the polar part of the adsorption layer (curve 3) may probably represent the best model.

By superposition of curve 3 and 5 results only in a very low interaction between the particles, the dispersion is stable against flocculation. The pro-

protective effect of the highly swollen macromolecular adsorption layer is mainly based on the facts that the dispersion interaction between the adsorbed layers of the two particles becomes very weak.

On the other hand superposition of curve 3 and 6 yields an interaction energy which is always negative, the particles will aggregate. Thus the sensitizing effect of the nonionic surface active agents³ finds a natural explanation, for it is known from wetting experiments that low concentrations of a non-ionic surface active agent have a hydrophobizing effect. The same holds for ionic surfactants. Thus the flocculation of dispersions by addition of oppositely charged surface active molecules is not exclusively due to the neutralization of the dispersed particles but also to the fact that the dispersion forces are increased. The flotation process or the sewage purification by additions of surface active agents can be considered to be practical examples.

Model experiments on emulsion films⁴ and unsymmetrical films⁵ clearly showed the influence of adsorbed layers on the interaction energy between two surfaces.

3. Steric interaction

If long-range repulsive forces are absent between two particles, then the particles can approach each other until their adsorption layers of the surface active agent come into contact. Depending on the properties of the adsorption layer, either coalescence may occur, or the particles continue to exist in the aggregated state, separated by a more or less highly solvated adsorption layer of the surface active agent. The possible causes of the steric stabilization of surfactant adsorption layers are shown in Figure 2. These causes may include the energies required for mutual penetration, compression, deformation or desorption into the disperse phase (this is possible only with fluid disperse particles) or into the dispersion medium.

We could show by model experiments with emulsion films and with unsymmetrical systems such as oil/water/polymer⁶ that only the resistance against vertical compression and desorption has to be considered as a stabilizing factor.

In contrast to the steric interaction of adsorbed surface active molecules, where 4 possible cases of »steric hindrance« have to be discussed the mechanism of action of macromolecular compounds reduces to penetration and vertical compression, since in many cases the adsorption is irreversible^{7,8} and, due to the larger space required by the macromolecules and the fact that several segments of a molecule are adsorbed, tangential compression is rather unlikely to occur.

In the relevant literature, both mechanisms are used in the description of the protective effect. The mutual penetration of the macromolecules was first described by Fischer⁹. The papers of Napper¹⁰ and Ottewill¹¹ are based on the same assumption. The reduction of stability to elastic deformation was first recognized by Jäckel¹². The papers of Clayfield and Lumb¹³ and Richmond and Lal¹⁴ contain similar views. A simultaneous consideration and calculation of both effects is found in the papers of Hesselinck¹⁵ and Bagchi¹⁶ and Napper¹⁷.

We studied¹⁸ the equilibrium thickness of emulsion films, stabilized by polyvinyl alcohol (PVA) as a function of various capillary pressures.

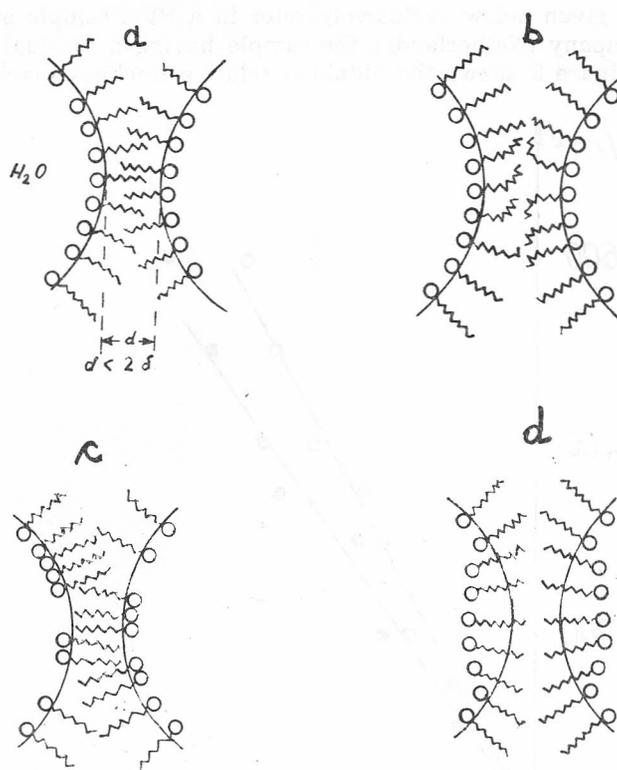


Figure 2. Schematic representation of the interaction between oriented adsorbed adsorption layers of surface active agents.

When increasing the electrolyte concentration, one observes that, unlike in the dispersions stabilized by surface active agents, in solutions of macromolecular surface active compounds the equilibrium layer thickness becomes constant beyond a certain electrolyte concentration. This is caused by the fact that the adsorbed macromolecules prevent an approach to less than twice the thickness of the adsorption layers (δ). By varying the external pressure it is now possible to compress the adsorption layers and observe the thickness variation as a function of external pressure by interference — optical methods. The model corresponds to the conditions of a dispersion if two particles collide as a result of their thermal energies, where the macromolecular adsorption layers are deformed.

By this method we investigated several polyvinyl alcohols at the cyclohexane phase boundary (aqueous solution) as a function of the concentration of the polyvinyl alcohols and of the electrolyte; at the same time we studied the influence of dioxane in mixtures with water on the mechanical properties of the PVA adsorption layers.

The individual samples of polyvinyl alcohols obtained from different producers differ in their equilibrium layer thicknesses but not in their mechanical behaviour, provided that samples of the same degree of hydrolysis are

used. The data given below exclusively refer to a PVA sample obtained from the Konam company (Netherlands), the sample having a residual acetate content of 12%. Figure 3 shows the obtained relative thickness variation plotted

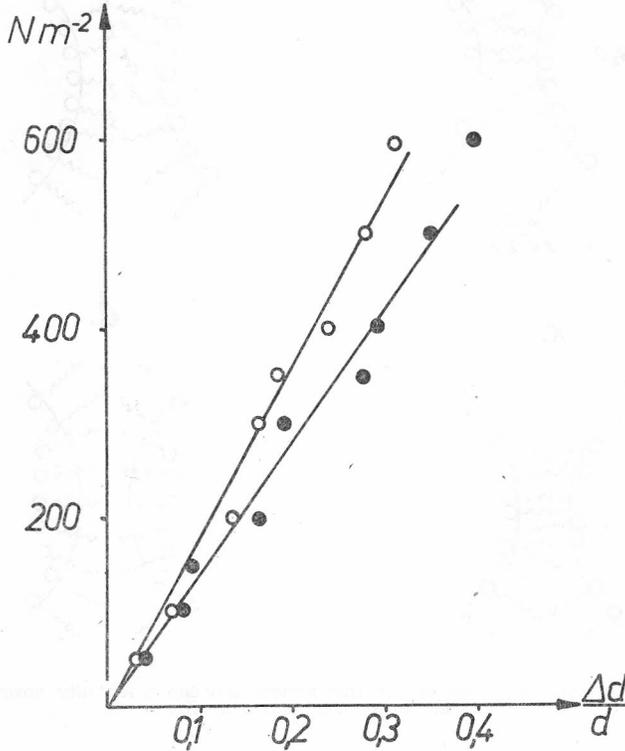


Figure 3. Relative thickness variation of the film under compressive stress. ● PVA in 10^{-3} M KCl
○ PVA in 10^{-1} M, KCl.

vs. the external pressure. This Figure shows that the relative thickness variation increases linearly over a rather wide range of pressure, *i. e.* the macromolecular adsorption layer behaves like a perfectly elastic body. The thickness variation of the adsorption layer on application of pressure is practically instantaneous and completely reversible. At higher pressures the relative thickness variation is no longer linear, but still reversible. If dioxane is added to the macromolecular solution, then the solvent character for the macromolecular phase naturally changes, and hence also the properties of the adsorption layer. This manifests itself in a different equilibrium thickness and of course in a modified elasticity (cf. Table I).

In analyzing our experimental results, let us first consider the case of mutual penetration. In the zone where the two interacting adsorption layers penetrate each other a higher concentration of polymer segments develops, and simultaneously the solvent molecules are removed from this zone.

Bagchi uses the simplifying assumption that before the onset of interaction the segment concentration is constant through the adsorption layer, and calculates the variation of free energy caused by varying the mixture

TABLE I

| Solution | d_0 /nm/ | E /N m ⁻² / |
|--------------------------------------|------------|--------------------------|
| 10 ⁻³ M KCl | 55 | 1.4 · 10 ³ |
| 10 ⁻³ M KCl + 6% dioxane | 69 | 2.0 · 10 ³ |
| 10 ⁻³ M KCl + 10% dioxane | 43.5 | 2.5 · 10 ³ |

ratio of macromolecules to solvent molecules in the region of penetration of the two adsorption layers by means of the Flory-Huggins theory. The penetration volume V (d) can be calculated if the thickness of the adsorption layer the distance (d), and the radius (a) of the particles are known.

$$V(d) = \frac{2\pi}{3} \left(\delta - \frac{d}{2} \right)^2 \left(3a + 2 + \frac{d}{2} \right) \quad (1)$$

The variation of free energy caused by the mixing process can be expressed if the concentration of macromolecules in the adsorption layer is known;

$$\frac{\Delta G_H}{kT} = N_L [(n_{H_2O} - n_M \cdot 1) \cdot \ln(\gamma_{H_2O} - \gamma_M) - 2 n_{H_2O} \ln \gamma_{H_2O} + 2 n_M \ln 2 - 2\chi \gamma_M^2 (n_{H_2O} + n_M)] \quad (2)$$

where N_L = Loschmidt number, n_{H_2O} = number of water molecules contained in the volume V , n_M = number of macromolecules contained in the volume V , l = segment length, γ_{H_2O}/γ_M = molar fraction of water to macromolecules before penetration, χ = Flory-Huggins parameter.

With the adsorbed amount of PVA measured by Lankveld and the thickness of the adsorbed layer from our experiments we obtained a concentration of PVA in the adsorbed layer with a homogenous segment distribution of about 25%.

If Bagchi's equation is used to calculate the steric repulsion of PVA adsorption layers having a segment concentration which corresponds to our experimental conditions, that a penetration of 3 nm is found sufficient to produce a V_{St} of 30 kT. This value is very high and does not agree with our measured values. From this it follows that the simple mixture setup is obviously unsuitable for the description of steric hindrance. Napper derived the following equation for the variation of free energy due to the penetration of adsorption layers:

$$\frac{\Delta G_M}{kT} = 2(\psi - \chi) \left(\frac{\bar{V}_S^2}{\bar{V}_{H_2O}^2} \right) N_L \int_V \rho dV, \quad (3)$$

where \bar{V}_S = partial molar segment volume, \bar{V}_{H_2O} = partial molar volume of H₂O, V = penetration volume, and ρ = segment density distribution at a distance $d < 2\delta$.

Depending on the values and signs of χ and ψ , Napper distinguishes three cases:

1. Entropy stabilization, if ψ and χ are positive and
2. Enthalpy stabilization, if ψ and χ are negative and
3. Combined entropy-enthalpy repulsion, if ψ is positive and χ negative.

For polyvinyl alcohol, these conditions are known in the water-dioxane system. Therefore we examined the elastic behaviour of PVA adsorption layers under vertical compression in pure water, in water + 6% dioxane, and in water + 10% dioxane. According to the author's statements, a pure enthalpy repulsion should be expected in water, an entropy-enthalpy repulsion in 6% dioxane, and an entropy repulsion in a 10% solution. The experiments have shown that the character of the repulsion energy/distance isotherms does not change in these 3 solutions. However, a change in the conformation of the macromolecules can be observed. It is manifested by the different equilibrium thickness and elasticity values (cf. Table I).

The steric repulsion caused by the deformation of the macromolecular gel skeleton without penetration of the adsorption layers has been dealt with by Jäckel². He requires of the adsorption layer that the macromolecules, which are adsorbed in loops, are similar to a crosslinked gel, that Hertz' theory of the elastic collision can be applied in calculating the deformation of the adsorption layer (*i. e.* that the mechanical deformation is purely elastic and reversible), that the modulus of elasticity remains constant, and that volume effects are negligible. This theory was supported by the rubber elasticity. As it is shown by our experiments this theory is completely confirmed with PVA adsorption layers for deformations being not too large.

The energy of repulsion for an elastic collision between spherical particles with radius a can be calculated by means of equation (4),

$$\frac{V_{st}}{kT} = \frac{E}{1.325 \cdot kT} \left(\delta - \frac{d}{2} \right)^{5/2} (a + \delta), \quad (4)$$

where E = modulus of elasticity.

For PVA-stabilized spherical particles with different radii ($E = 1.4 \cdot 10^8$ Nm⁻², $\delta = 27.5$ nm) the family of curves shown by Figure 3 is obtained. Figure 4 also shows in addition the energy of dispersion attraction for the same particle sizes without consideration of the adsorption layer.

The Hamaker constant was chosen to be $1.8 \cdot 10^{-20}$ J a value corresponding to that of polyvinyl acetate, because these polymer dispersions are frequently stabilized with PVA. As is shown in Figure 3 the protective effect is very small for particles with radii being greater than 100 nm and becomes quite impossible when $a \gg 100$ nm. For particles having a radius of about 100 nm, deformations of about 50% of the adsorption-layer thickness produce repulsion energies greater than 2 kT, which are sufficient for the stabilization. For stabilizing larger particles with PVA, products forming thicker adsorption layers are required. Very small particles are stable in spite of the low energy of repulsions, since in case of collision there is no state resulting in a flocculation.

To conclude our statements, we shall briefly refer to the paper of Hesselinck, Vrij, and Overbeek¹⁶. In contrast to the theoretical papers reported above, these authors do not start from the uniform distribution of segments in the adsorption layer, but consider the size distribution of the loops and

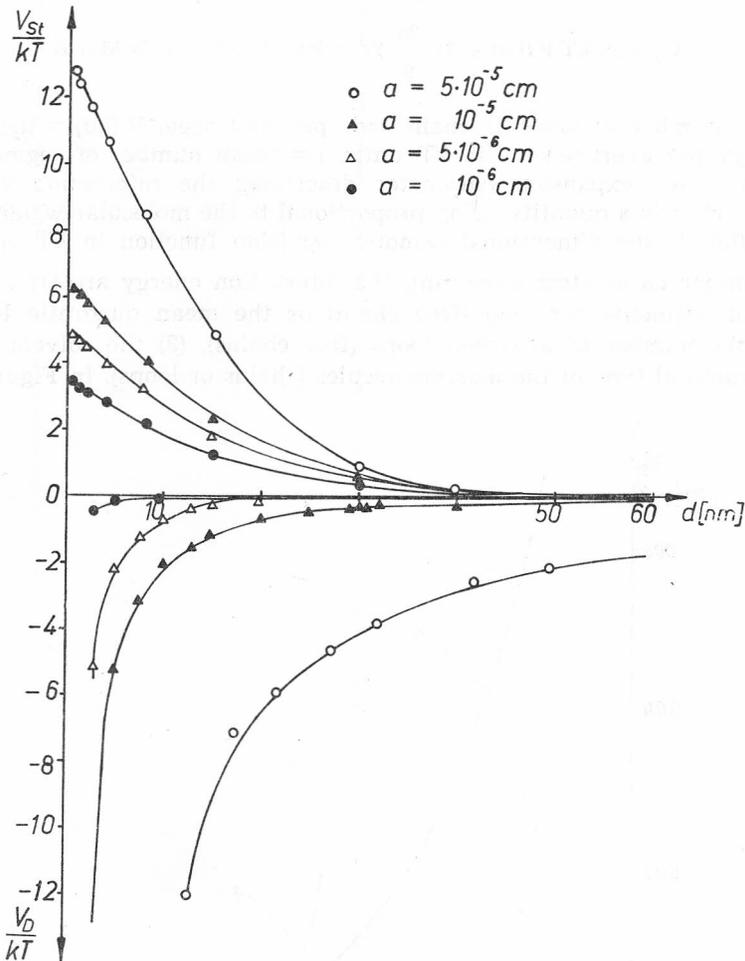


Figure 4. Steric repulsion and dispersion attraction as a function of distance for different particle radii. Modulus of elasticity — $E = 1.4 \cdot 10^8 \text{ Nm}^{-2}$, adsorption — layer thickness — 27.5 nm Hamaker constant — $1.8 \cdot 10^{-20} \text{ J}$.

free chains, respectively. They calculate an osmotic portion of repulsion when the polymer layers of the approaching particles begin to penetrate each other; there is no compression yet because the loops or free chains still do not hinder each other. The compression begins only at shorter distances. Thus the steric repulsion is the sum of both effects. Unfortunately our measurements do not reveal whether the steric repulsion is composed of two portions. This is because the equilibrium distance setting in without an external pressure being applied depends on the equilibrium between the capillary pressure and the steric repulsion. It is quite conceivable that this already compensates the osmotic portion to such a degree that both portions of steric repulsion are simultaneously covered when applying the external pressure.

The authors state the following equation for steric repulsion,

$$V_{st} = 2\nu kT V(\bar{i}, d) + 2 \left(\frac{2\pi}{9} \right)^{3/2} \nu^2 kT (\alpha^2 - 1) \langle r^2 \rangle M(\bar{i}, d) \quad (5)$$

where ν = number of loops or chain ends per unit area, $V(\bar{i}, d)$ = increase of free energy per average loop in kT units, \bar{i} = mean number of segments per loop (chain), α = expansion parameter describing the interaction with the solvent, $\langle r^2 \rangle$ is a quantity being proportional to the molecular weight of the loops, $M(\bar{i}, d)$ is the dimensional osmotic repulsion function in kT units.

The major parameters governing the interaction energy are (1) the mean number of segments per loop (free chain) or the mean quadratic loop size (\bar{i}^2), (2) the number of adsorbed loops (free chains), (3) the solvent quality, (4) the structural type of the macromolecules (chains or loops). In Figure 5, the

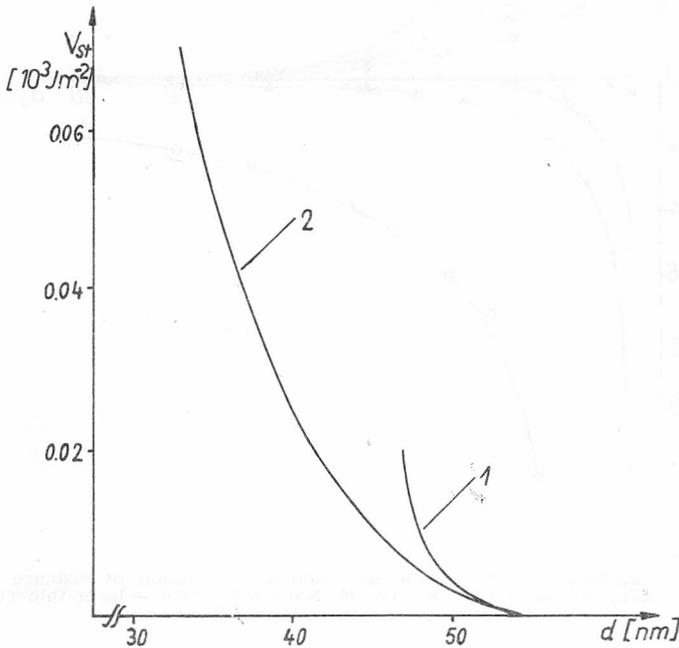


Figure 5. V_{st} as a function of distance. Curve 1 was calculated according to Hesselinck, curve 2 was obtained by experiment.

experimental values of repulsion energy obtained as a function of distance are compared with the values calculated according to Hesselinck. Although some agreement is found to exist for a shallow penetration of the adsorption layers, it should be noted that the calculations according to Hesselinck also result in much steeper curves.

In order to provide better insight into steric hindrance, additional quantitative results concerning the mechanical properties of adsorption layers are primarily required.

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SAŽETAK

Utjecaj površinski aktivnih tvari na interakcije u disperznim sistemima

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Na osnovi eksperimentalnih i teorijskih podataka pokazuje se da su svojstva suspenzija određena silama interakcija (međudjelovanja) koja se javljaju na graničama faza, kao posljedica asimetrije međumolekularnih sila. Niz sila koje djeluju na duljim razmacima kao elektrostatske odbojne sile, interakcije dipol-dipol sterički efekti i sl., određuju da li će dispergirane čestice biti stabilizirane u disperznom mediju, ili će se koagulirati u veće agregate. Nekoliko površinski aktivnih tvari ili makromolekularnih spojeva je upotrebljeno (primjenjeno) sa ciljem karakteriziranja i promjene sila koje djeluju na duljim razmacima. Pokazalo se da ta vrsta spojeva istovremeno utječe i na međudjelovanja na kraćem razmaku, osobito na steričke smetnje.

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