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# Stabilisation of Disperse Systems by Water-soluble Polymers

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The stabilisation of disperse systems by the addition of uncharged and partly charged water-soluble polymers is considered. The influence of the adsorbed non-ionic polymers on various components of the interaction energy of the colloidal particles as well as the results of direct measurements of the repulsion forces between the adsorbed macromolecules are analysed. The mechanism of the stabilisation of real dispersions by adsorbed layers of uncharged macromolecular substances is discussed. The bibliography includes 141 references.

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## I. INTRODUCTION

High-molecular weight compounds (HMC) are effective stabilisers of disperse systems and extremely small amounts of these substances can radically increase the stability of colloidal solutions as regards sedimentation and aggregation. This is used widely in various branches of modern technology: for the stabilisation of emulsions in the food, pharmaceutical, and cosmetic industries, in the manufacture of varnishes, dyes, paper, and photographic emulsions, in medicine, etc.

As early as the beginning of the 20th century, a study was made of the stabilising (protective) effect of the addition of hydrophilic substances (gelatine, starch, albumen, haemoglobin, etc.) on the hydrophobic sols of gold, silver, sulphur, and other colloids. Such substances are characterised by "gold", "silver", and other numbers.[1] Since the 1950s, synthetic polymers have been used on an increasingly wide scale for the stabilisation of dispersions, which led to an appreciable increase of the number of publications in this field during the last 15–20 years. Although many aspects of the influence of added HMC on the stability of colloidal solutions have been thoroughly investigated, the mechanism of the stabilising effect of polymers has not been finally elucidated and the theoretical principles of their selection for such purposes are in the initial stage of development. This is caused by the great complexity of the polymer-containing disperse systems and the multiplicity of factors responsible for their stability.

The stabilising effect of polymers in colloidal systems is directly related to their adsorption on the surface of the disperse phase. As a result of the adsorption of macromolecules or their aggregates,[2] the properties (including rheological properties[3]) of the interface and the intensity of the interaction between the surface and the intermicellar liquid are radically altered. This leads to a modification of the previous factors or to the appearance of new factors governing the stabilisation of the disperse systems; both effects are usually manifested. For a correct understanding of the mechanism of the action of HMC on the stability of colloidal solutions, it is necessary to have data on the adsorption of polymers by the disperse phase and the parameters of the adsorbed layers formed on the surface and on the influence of the adsorption of high-molecular-weight substances on the structure of the electrical double layer and on the hydration condition of the particles. Examination of the rules governing the adsorption of HMC by disperse particles and the structure of the electrical double layer is outside the framework of the present review; a discussion of these questions can be found, for example, in Refs. 4 and 5. Detailed information about the influence of the adsorption of HMC on the double layer and about the electro-surface methods for the determination of the parameters of the polymeric adsorption layers has been published.[6]

This review surveys the results of experimental and theoretical studies devoted to the elucidation of the rules and mechanism of the stabilisation of disperse systems by the addition of uncharged and partly charged water-soluble polymers, which have been published mainly during the last ten years. In particular, the methods for the measurement and for the theoretical calculation of the forces which determine the interaction of the polymer-containing particles have been examined.

## II. RULES GOVERNING THE STABILISATION OF DISPERSE SYSTEMS BY WATER-SOLUBLE POLYMERS

As already mentioned, the influence of HMC on the stability of colloidal solutions is due to the characteristic features of the adsorption on the particles of the disperse phase and of the structure of the adsorbed layers formed under these conditions. However, the relation between the adsorption of the polymer and its influence on the stability was not considered in the vast majority of investigations, particularly in the earlier ones. The dependence of the stabilising effect of HMC on the nature and amount of the added reactant, its

molecular weight, the conditions in its introduction, the presence of electrolytes in the system, and other factors has been mainly investigated. We shall analyse briefly the influence of the above factors on the stabilisation of dispersions by high-molecular-weight substances.

## 1. The Nature of the Stabiliser

High-molecular-weight compounds, which, on the one hand, are adsorbed by the particles, and, on the other, readily dissolve in the dispersion medium, serve as stabilisers of dispersions. These are frequently copolymers, one of the components (A) of which is bound to the surface via chemical interactions, hydrogen bonds, etc., while the second component (B) exhibits a high affinity for the intermicellar liquid. For example, two polymers in which the role of component A is assumed by the substance which forms the disperse phase exhibit an effective stabilising activity towards latex dispersions. The inclusion in the composition of A of ionogenic groups bearing a charge opposite to that of the particles or highly polar functional groups significantly improves the bond between component A and the surface.[7] A polymer readily soluble in the dispersion medium and exhibiting a weak affinity for the surface is selected as component B. For aqueous media, such polymers are, for example, poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), etc., while for aliphatic hydrocarbons polyisobutylene, poly(lauryl methacrylate), etc. are used.[8]

In the systems considered component B forms a steric energy barrier necessary for stabilisation, while substance A ensures a bond with the surface. The ratio of the molecular weights of components A and B ($M_A$ and $M_B$) is important for copolymers. As an approximation, one can assume that $M_A \cong nM_B$, where $n$ is the number of polymer chains of B linked to the skeleton of A.[9] As a rule, $M_A$ is in the range $10^4$–$10^5$ and $M_B$ is in the range $10^3$–$10^4$.[8] The higher the adsorption energy of an elementary unit, the lower the value of $M_A$ necessary to attain a satisfactory stabilising effect. $M_B$ must be sufficiently large to ensure steric hindrance over distances ranging from several to several tens of nanometers from the surface; it depends on the size and chemical nature of the particles.

Substances with comparatively low molecular weights were used initially as stabilisers, namely carboxylic acids, alkylbenzenes, etc.—they were employed to obtain stable suspensions of carbon black, titanium oxides, iron, and other substances in organic solvents which are of practical importance.[8] High-molecular-weight compounds such as, for example, poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), methylcellulose (MC), non-hydrolysed and hydrolysed polyacrylamide (PAA and PAA-H), poly(acrylic acid) (PAAC), poly(methacrylic acid) (PMAAC) and its salts, polyethyleneimine (PEI), salts of carboxymethylcellulose (CMC) and polyvinylpyrrolidinone (PVP) and copolymers based on them, gelatine, and many others have been used recently to stabilise hydrodispersions. Table 1 lists examples of the employment of water-soluble polymers for the stabilisation of many model practically important dispersions.

As yet, it is difficult to formulate unambiguous criteria which would make it possible to decide which particular HMC would be the most effective stabilisers of a particular colloidal system. On the basis of theoretical considerations (see Section III) and the available experimental data, one can assume that, among non-ionic polymers, high-molecular-weight specimens which form fairly thick or fairly dense adsorbed layers on the surface of the particles will exhibit an effective stabilising activity. In the case of charged HMC, polyelectrolytes bearing like charges and having a high charge density on the macrochain would be more effective. The influence of the nature of the polymer on the stabilisation is to a large extent determined by the structure of the adsorbed layers formed on the surface, which depends on interactions of different types in the complex polymer-containing systems polymer–surface, polymer–solvent, polymer–polymer, and surface–solvent.[5,9] The stabilising effect of HMC depends not only on the degree of their polymerisation and the type and number of functional groups in the macromolecule but also on the character of the distribution of the latter along the polymer chain. Copolymers are as a rule more effective regulators of stability than homopolymers.[8]

Table 1. Water-soluble polymers used to stabilise disperse systems.

| Polymer | Dispersion | |
|---|---|---|
| | of negatively charged particles | of positively charged particles |
| **Non-ionic polymers** | | |
| Poly(ethylene oxide) | Au [10—13], AgI [14, 15], $Sb_2S_3$ [16] | AgI [14], $Fe_2O_3$ [12] |
| Poly(vinyl alcohol) | AgI [17, 18], AgBr [19], $Sb_2S_3$ [20], o/w [21, 22] | — |
| Poly(vinyl acetate) | AgBr [19] | — |
| Gelatine | AgI [23, 24], AgBr [19, 25], Au [1], $SiO_2$ [26] | AgBr [25, 27] |
| Methylcellulose | AgI [28], AgBr [25], $Sb_2S_3$ [28], latex [29], carbon black [30] | AgBr [25] |
| Unhydrolysed polyacrylamide | $Ca_3(PO_4)_2$ [31], $SiO_2$ [32]; kaolinite [32], $MnO_2$ [33] | $CaF_2$ [34] |
| **Anionic polyelectrolytes** | | |
| Hydrolysed polyacrylamide | AgBr [35], $MnO_2$ [33], $SiO_2$ [36], latexes [37] | — |
| Sodium polystyrenesulphonate | Au [12], AgBr [35], latexes [39], montmorillonite [38] | $Fe_2O_3$ [12] |
| Poly(acrylic acid) and its salts | AgI [40], AgBr [35], $SiO_2$ [41], ZnS [43, 44], kaolin [45] | AgI [40], $Al_2O_3$ [41] |
| Sodium salt of carboxymethylcellulose | AgI [46], $Sb_2S_3$ [46], montmorillonite [47] | $Fe_2O_3$ [48] |
| **Cationic polyelectrolytes** | | |
| Polyethyleneimine | $SiO_2$ [37], latexes [49] | — |
| Polyamines | $SiO_2$ [37], latexes [37] | — |
| Vinylpyridine-butyl methacrylate copolymers | AgI [50], latexes [51] | — |
| Poly[dimethyl aminoethylmethacrylate (methyl acrylate)] | Latexes [39, 52] | — |

Note. The numbers in square brackets denote refences (Ed. of Translation).

## 2. Methods of Investigation

The stabilising effect of polymers can be inferred by various methods: from the change in the coagulation thresholds of the sols under the influence of electrolytes determined by measurements of the optical density or light scattering in the system[11,14–20,24,28,33,43,48] or on the basis of direct ultramicroscopic determinations of the number of particles per unit volume,[13,50,51] from the change in the rate of sedimentation of suspensions and of the volume of the deposits,[31,32,34,44,52,53–56] or from the change in the rheological characteristics of the dispersion.[47] Measurements of the dielectric parameters[57] and of the relative electrical conductivities of the dispersions,[58] measurements of light scattering at low angles (below 1°),[59] and laser Doppler spectroscopy[49,60] are promising but as yet little used methods for the study of

the degree of aggregation of particles in disperse systems. A more detailed analysis of the methods for the study of the stability of disperse systems is described in other communications.[8,53]

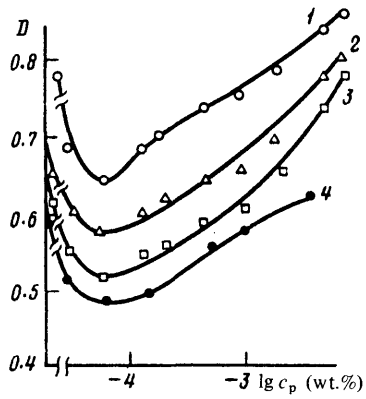



**Figure 1.** Dependence of the optical density $D$ of a manganite suspension on the concentration $c_p$ of the unhydrolysed (curves *1–3*) and hydrolysed (curve *4*) PAA dispersed in it. Time from onset of precipitation of the dispersion (min): 1) 10; 2) 20; 3) and 4) 30; concentration of the disperse phase $c_{d.p.}$ = 1 g dm$^{-3}$.[33]

### 3. The Stabiliser Dose

The processes involving the stabilisation or coagulation of dispersions by high-molecular-weight substances are interrelated. Usually, with increase of the content of the polymer in the system its stability initially falls (flocculation) and the increases (stabilisation). This is illustrated by the variation of the optical density of suspensions of manganite as a function of their content of different polyacrylamide specimens (Fig.1)[33] or by the dependence of the thresholds in the coagulation of silver iodide sol by sodium ions on the concentration of the added poly(ethylene oxide) (Fig.2).[61] Analogous changes in stability have been observed after the addition of poly(vinyl alcohol),[17–20] poly(ethylene oxide),[14–16] and methylcellulose[28] to Au, AgBr, AgI, and $Sb_2S_3$ sols, of poly(ethylene oxide)[8] and a number of cationic polyelectrolytes[51,52] to a polystyrene latex, of poly(methacrylic acid) to dispersions of a zinc sulphide phosphor,[43,44] etc.

The width of the stabilisation and destabilisation regions depends on a large number of a wide variety of factors: the chemical composition and molecular weight ($M$) of the reactant, the degree of ionisation of the polyelectrolyte macromolecules, the concentration of the solid phase, the electrolyte content of the system, the duration of contact between the macromolecules and the particles of the disperse phase, and also the method used to estimate the stabilising activity of the HMC. The latter is due to the fact that the vast majority of procedures used to measure the stability are indirect methods sensitive not only to the degree of aggregation of the particles but also to experimental factors, for example, to the wavelength in optical measurements, to the shape of the particles in conductimetric and rheological methods, to the density and type of packing of the particles in the deposits in filtration methods, etc. With the exception of the rapid coagulation thresholds found with the aid of direct ultramicroscopic studies of coagulation kinetics, the threshold in the coagulation of sols by an electrolyte is also a conventional quantity which depends on the duration of the observation and on the composition of the added electrolyte (the thresholds for coagulation by different electrolytes can characterise different degrees of aggregation). In the study of the stabilisation of dispersions by polyelectrolytes one must take into account the influence of the possible chemical interactions of multicharged ions with the functional groups of the stabiliser,[46,62] which alters the coagulation thresholds. It is believed[8] that the "pseudostability" zone observed by Levi and Stepanova[19] before the region of the flocculation of AgBr sols in the presence of PVA and poly(vinyl acetate) is a result of the employment of an unsuitable method for the measurement of the degree of aggregation.

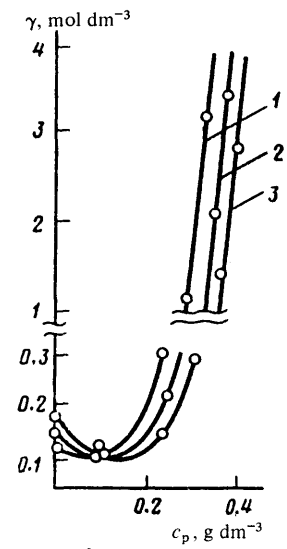



**Figure 2.** Dependence of the coagulating concentration $\gamma$ of NaCl for a silver iodide sol on its content of PEO with $M = 1.7 \times 10^4$ and in the presence of different concentrations of KI in the system (mol dm$^{-3}$): 1) $10^{-2}$; 2) $10^{-3}$; 3) $10^{-4}$; $c_{d.p.}$ = 0.42 g dm$^{-3}$.[61]

Studies of the influence of the addition of non-ionic polymers (PEO, PVA, and MC) on the stability of hydrophobic gold, silver iodide, antimony sulphide, and polystyrene sols, which was measured in terms of the coagulating concentrations of the counterions, indicate the rules governing the stabilisation of colloidal solutions by uncharged HMC and have much in common:[14–16,18,20,28,61,63] after the attainment of a specific HMC concentration, the dispersion obtains its limiting stability and does not coagulate in the presence of any realistically attainable electrolyte contents in the system: a sharp increase of stability takes place over a narrow range of polymer contents in solution; the thresholds in coagulation by counterions of different charge are gradually levelled out as the concentration of the polymer in the colloidal solution increases; there is a linear relation between the concentration of the solid phase in the sol and the minimum amount of stabiliser necessary for the attainment of a given stability.

Some of these relations are illustrated in Fig.3. The results of adsorption experiments have shown that, in the region of polymer additives corresponding to an abrupt increase of stability, the HMC introduced into the system is wholly absorbed by the disperse phase.[17,28,63-65]

In the studies mentioned above, it has also been shown that small amounts of added non-ionic polymers lower the stability of sols relative to singly charged counterions but not multicharged counterions (see Fig.3); stabilisation takes place only after a fairly broad destabilisation zone. We believe that the appearance of the latter is due to the sensitisation of the system as a result of the interaction of dipolar units of the macromolecule involved in an arrangement of the same type on the opposite walls of the particles. It has been shown theoretically[66] that such interaction leads to the appearance in the system of a negative wedging pressure, i.e. to an additional attraction between the particles. Clearly this mechanism can operate only for low degrees of adsorption of the HMC when the polymer is distributed on the surfaces of the particles in a monomolecular layer and for low values of the "critical gap" between the particles in the coagulation of the sol by singly charged counterions.

When PEO and PVA were added to a sol made up of positively charged AgI particles, an unusual phenomenon was observed—a change in the charge on the particles manifested both by a change in the sign of the electrokinetic potential[67] and by the appearance of a sensitivity of the protected sol to cations,[14] as can be seen from the data in Fig.4. We explained this effect by the occurrence in the oriented layer of adsorbed dipolar segments of the macrmolecules with appreciable "adsorption potential jumps" $\psi_a$, which are superimposed on the ionic potential of the double layer $\psi_i$ (for $\psi_a > \psi_i$) and can alter the sign of the surface charge of the particle (see also below).

The addition of polyelectrolytes to dispersions sometimes leads to dependences of the stability on the concentration of the reactant more complex than those described above. For example, it has been shown[43,44] that the dependences of the rate of sedimentation and of the optical density of suspensions of the zinc sulphide phosphor on the amount of added poly(methacrylic acid) exhibit a series of minima and maxima (Fig.5); the authors explained this by the simultaneous alteration of the electrokinetic potential of the particles and of the thickness of the adsorption layer with increased degree of adsorption of the stabiliser macromolecules.

## 4. The Influence of the Molecular Weight

As a rule the stabilising effect of the HMC increases with increase of *M*. In other words, a sharp increase of stability is attained at a lower concentration of the polymer in the system the higher the degree of its polymerisation. This dependence can be clearly traced after the addition of PEO to gold[11-13] and silver iodide[14,15] sols and to polystyrene latex,[8,63] of PVA to silver iodide[17,18] and antimony sulphide[20] sols and an o/w (oil in water) emulsion,[21] of CMC and MC to colloidal AgI and $Sb_2S_3$ solutions,[28,46] of PAA to kaolinite suspensions,[8] etc.

It has been shown[11,14] that low-molecular-weight specimens of poly(ethylene glycols) ($M < 2 \times 10^3$) do not alter the thresholds in the coagulation of gold and silver iodide sols by an electrolyte. At the same time it has been observed that the variations of the stabilising and flocculating effects of PEO on calcium carbonate suspensions[68] and of the effect of PAA on calcium phosphate dispersions[69] with the molecular weight of the HMC pass through a maximum. After the addition of non-ionic polymers to hydrophobic sols by the "double addition" method (the reactant is added to half the volume of the dispersion and after a time this solution is mixed with a second portion of the initial colloidal solution[12,13,17]), the optimum dose of the flocculant and stabiliser depends little on its molecular weight, which was explained by the weak dependence of the equilibrium thickness of the adsorbed layer of flexible-chain polymers on the degree of their polymerisation. We believe[53] that the different dependences of the flocculating and stabilising effects of polymers on *M* are determined by a series of factors: the degree of approach to the HMC adsorption equilibrium, the dependence of the thickness of the adsorbed polymer layer and of the character of

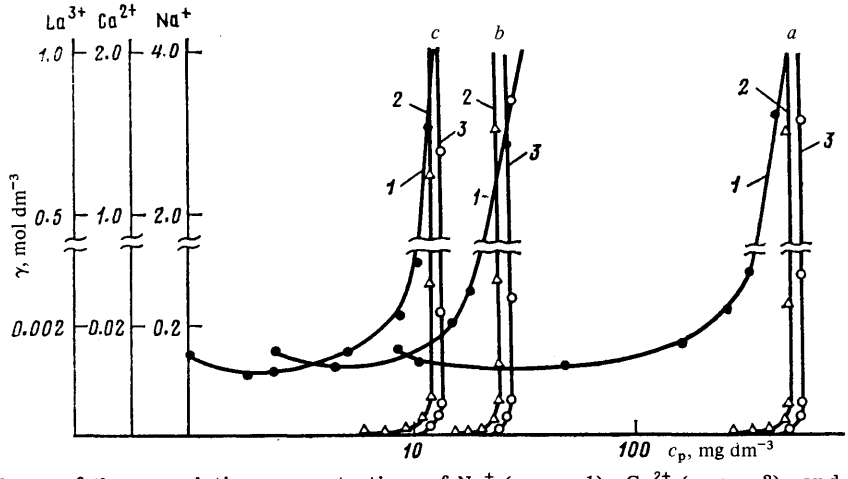



**Figure 3.** Dependence of the coagulating concentrations of $Na^+$ (curve *1*), $Ca^{2+}$ (curve *2*), and $La^{3+}$ (curve *3*) ions for an antimony sulphide sol on the content in the system of PEO having different molecular weights: *a*) $2.3 \times 10^5$; *b*) $1.3 \times 10^6$; *c*) $2.6 \times 10^6$.[16]

the distribution in the latter of the macromolecular segments on the degree of polymerisation, and also the mechanism of the stabilisation or flocculation processes.

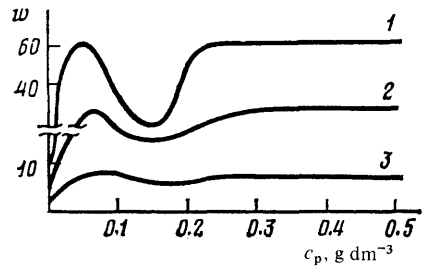



**Figure 5.** Dependence of the coagulation retardation coefficient $w$ for a suspension of the zinc sulphide phosphor on the content of added poly(methacrylic acid) for different $c_{d.p.}$ (g dm$^{-3}$): 1) 0.1; 2) 0.25; 3) 2.0.[44]

## 5. The Influence of the Concentration of the Solid Phase

In most cases it has been observed that the higher the content of the solid phase in the system the higher the HMC concentration at which the same stabilisation effect is attained. For dilute sols, there is a linear relation between the concentration of the disperse phase and the minimum amount of the polymer necessary to attain a specified stability (i.e. approximately equal thresholds in coagulation by an electrolyte).[14-16,18,20,28,62] A similar dependence for the coagulation of AgI and $Sb_2S_3$ salts containing added poly(ethylene oxide), proportional to the concentration of the solid phase, is illustrated by the data in Table 2..

The above dependence indicates indirectly the complete adsorption of the polymer in the experimental concentration range and shows that, in order to attain a given degree of stabilisation, the same surface coverage of the particles by the high-molecular-weight substance is required. Within the framework of these ideas, the increased stability of AgI sols containing the same amount of added PEO with increase of their age, which we have observed,[61] can be explained by the decrease in the area of the adsorbing surface and by the accompanying increase of the amount of HMC corresponding to a unit surface area.

Table 2. Dependence of the thresholds in the coagulation of AgI and $Sb_2S_3$ sols by sodium chloride ($\gamma_{NaCl}$) on the content of the solid phase in the presence of added poly(ethylene oxide).[16]

| $c_{d.p.}$, g dm$^{-3}$ | $c_{PEO}$, mg dm$^{-3}$ ($M = 1.7 \times 10^4$) | $\gamma_{NaCl}$, mmol dm$^{-3}$ | $c_{PEO}$, mg dm$^{-3}$ ($M = 1.3 \times 10^6$) | $\gamma_{NaCl}$, mmol dm$^{-3}$ |
|---|---|---|---|---|
| | | AgI sol | | |
| 0.5 | 3.2 | 140 | 1.7 | 240 |
| 1.0 | 6.4 | 145 | 3.4 | 250 |
| 2.0 | 9.6 | 140 | 5.1 | 250 |
| | | $Sb_2S_3$ sol | | |
| 0.2 | 12.8 | 60 | 1.7 | 350 |
| 0.4 | 25.6 | 65 | 3.4 | 325 |
| 0.6 | 36.4 | 65 | 5.1 | 340 |

## 6. The Influence of Particle Size

There are few literatue data concerning the influence of this factor on the conditions in the stabilisation of dispersions by polymers. It has been shown[56] that the form of the influence of the same amounts of added PEO on the rate of sedimentation of silica suspensions (for a constant $c_{d.p.}$) depends on the size of their particles: a gradual stabilisation of the systems has been observed for the coarsest fractions with increase of the HMC concentration, whereas flocculation has been noted for the fine fractions before stabilisation. It has been observed[70] that the flocculating (and stabilising) concentration of polyelectrolytes for fine-particle silica suspensions (particle diameter < 40 mn) is proportional to the specific surface of the particles, i.e. is inversely proportional to their diameter, whereas for large particles it varies

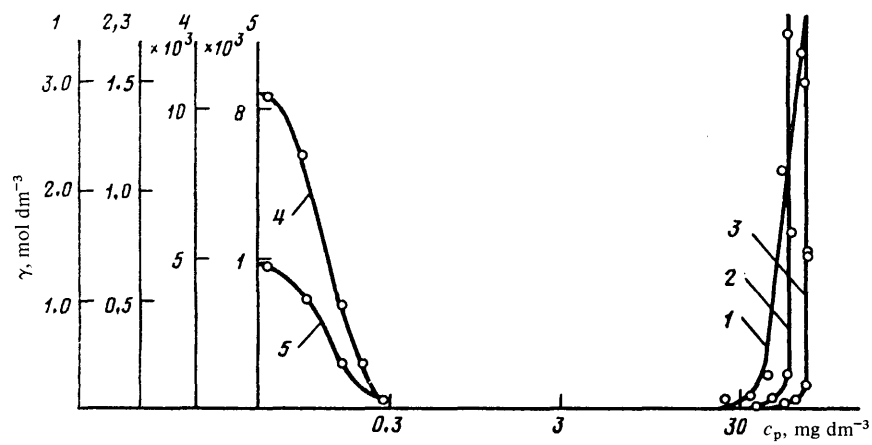



**Figure 4.** Dependence of the coagulating concentrations of $Na^+$ (curve 1), $Ca^{2+}$ (curve 2), $La^{3+}$ (curve 3), $NO_3^-$ (curve 4), and $SO_4^{2-}$ (curve 5) ions for a positively charged silver iodide sol on its content of PEO with $M = 2.6 \times 10^6$.[14]

in proportion to the square of the particle diameter. Thus the influence of the particle size on the stabilisation is associated with the variation of the adsorption surface area of the disperse phase. However, here one must also bear in mind the possible influence of the variation of the thickness of the adsorbed polymer layers, for a given specific adsorption, with increasing radius of curvature of the particles.[71]

### 7. The Influence of Temperature

It has been shown[72,73] that the critical concentrations of the counterions for the Au, AgI, $As_2S_3$, and $Sb_2S_3$ sols containing small amounts of added PEO, PEA, CMC, and gelatine diminish significantly with increase of temperature, while in the range 32–40° abrupt changes appear in the $\gamma-T$ curves (Fig.6). For the same sols without polymer additives, anomalous changes in stability with increasing temperature have not been discovered.[74] Therefore the above features of the influence of temperature on the stability can be naturally attributed in the first case to a change in the nature of the surface of the particles as a consequence of the adsorption of hydrophilic substances on the latter. The overall decrease of $\gamma$ with increase of temperature is caused by the gradual dehydration of the particles and the decrease of the thickness of the lyosphere surrounding them.

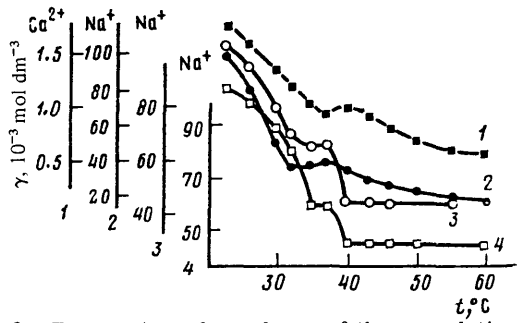



Figure 6. Temperature dependence of the coagulating concentration of the counterions for an antimony sulphide sol when the system contains 9.6 mg $dm^{-3}$ of PEO with $M = 1.7 \times 10^4$ (curve *1*), 20.6 mg $dm^{-3}$ of PEO with $M = 1.1 \times 10^5$ (curve *2*), 7.2 mg $dm^{-3}$ of PEO with $M = 2.6 \times 10^6$ (curve *3*), and 14 mg $dm^{-3}$ of PEO with $M = 1.3 \times 10^6$ (curve *4*).[72]

### 8. The Influence of the Degree of Surface Coverage

Measurements of the degree of adsorption and of stability carried out on the same object revealed a dependence of the stabilising effect of the HMC on the amount of polymer adsorbed by a unit surface. It has been shown[15,17,18,20,28,56,63] that for each polymer there exists a definite "critical" degree of adsorption $\Gamma_{cr}$, the abrupt increase of the stability of the sol being caused by the attainment of this degree of adsorption or its being exceeded (Fig.7); the above degree of absorption usually varies in the range 0.4–1.0 mg $m^{-2}$. $\Gamma_{cr}$ depends on the nature and the molecular weight of the polymer, on the charge of the polyelectrolyte macromolecules, and ultimately on the structure of the adsorbed polymer layer on a given surface (see below). For example, it has been shown[15] that an increase of the molecular weight of PEO from $2.3 \times 10^5$ to $2.6 \times 10^6$ results in a diminution of $\Gamma_{cr}$ for silver iodide sol particles from 1.0 to 0.5 mg $m^{-2}$. The increase of the fraction of non-hydrolysed acetate groups in the poly(vinyl alcohol) molecule from 2 to 18% gives rise to a decrease of the degree of surface coverage of the AgI particles, corresponding to a sharp increase of the stability of the sol, from ~0.8 to 0.4 mg $m^{-2}$ (Fig.7).

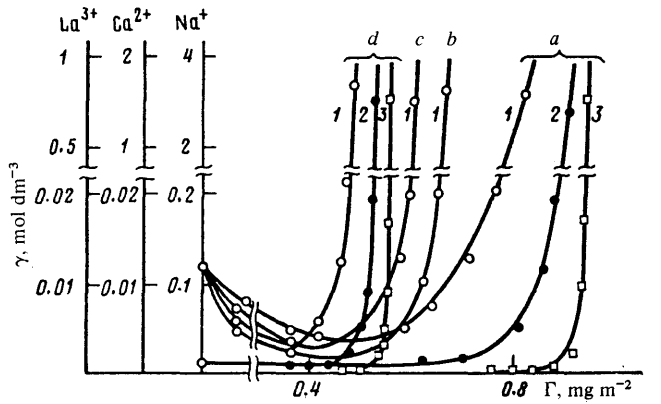



Figure 7. Dependence of the coagulating concentrations of $Na^+$ (curve *1*), $Ca^{2+}$ (curve *2*), and $La^{3+}$ (curve *3*) ions for a AgI sol on the degree of adsorption of PVA; *a*) $M = 2.2 \times 10^4$, 12% of acetate groups; *b*) $M = 4.1 \times 10^4$, 2% of acetate groups; *c*) $M = 5.9 \times 10^4$, 12% of acetate groups; *d*) $M = 6.5 \times$ *d*) $M = 6.5 \times 10^4$, 18% of acetate groups.[18]

One must note that in a system as complex as a hydrophobic sol–polymer solution–electrolyte solution system an increase of temperature not only disrupts the boundary solvation layers but also alters the solid phase–HMC solution adsorption equilibrium and the conformation of the adsorbed macromolecules and causes a rearrangement of the water structure in the surface hydrate layers. On the basis of general theoretical considerations and the experimental data obtained,[72,73] one can assume that none of the factors enumerated, except the last, can undergo abrupt changes over a narrow temperature range. This is also indicated by numerous data concerning the anomalous changes in many properties of adsorbed water precisely in the temperature range indicated.[75]

However, comparison of the results of the adsorption and coagulation measurements requires caution. This is because measurements of the degree of adsorption of HMC are carried out on colloidal deposits (sol coagulates) and those of stability are performed on "live" dispersions. It may be expected that a smaller surface area is available for the adsorption of macromolecules in the coagulates than in the sols and suspensions owing to the possible aggregation of particles on coagulation. According to Koopal and Lyklema,[76] ~35% of the surface of the particles in silver iodide suspensions and deposits is inaccessible to the adsorption of PVA. As a result of the aggregation of the particles in the presence of the polymer (partial flocculation), the specific adsorption of HMC at a given equilibrium concentration becomes a function of the content of the solid phase in the dispersion, as has been

shown for the adsorption of poly(vinyl alcohol) in suspensions of montmorillonite,[77] silver iodide,[76] and other systems.[78] This is reflected in its turn in the stability of the sol.

It has been observed in a number of studies that the addition of electrolytes decreases the degree of adsorption of non-ionic polymers by the disperse particles[64,65] and increases the degree of adsorption of polyelectrolytes.[79,80] This complicating effect must also be taken into account in devising a relation between the stability and the degree of adsorption of HMC on the basis of the determination of the concentrations of the electrolytes at the coagulation point.

## III. THEORETICAL IDEAS CONCERNING THE STABILISATION OF COLLOIDAL SOLUTIONS BY ADSORBED LAYERS OF NON-IONIC POLYMERS

According to modern ideas, the stability of disperse systems is determined by the balance of the attraction and repulsion forces between the particles. In ion-stabilised dispersions, these are van der Waals attraction and repulsion forces in electrical double layers.[1,4] The adsorption of water-soluble polymers by charged particles alters the above forces by changing simultaneously the effective Hamaker constant and the structure of the electrical double layers of the particles. Moreover, the adsorption gives rise to the appearance of additional repulsion forces during the interaction of the adsorbed macromolcules and the appearance (or the enhancement of the role) of the solvation stability factor—the so-called structural component of the wedging pressure.[81] In real disperse systems the above factors are manifested simultaneously, i.e. the stability is determined by the joint action of several of these. Hence it is evident that the theoretical interpretation of the mechanism of the stabilisation of dispersions by high-molecular-weight substances and the search for theoretically well-founded criteria governing the application of a particular HMC for this purpose are complex.

In considering the contribution of the above components to the overall interaction energy of polymer-containing particles ($\Delta F$), it is necessary to bear in mind that the influence of the adsorption of the HMC on $\Delta F$ is determined not only by the degree of adsorption of the polymer but also by the structure of the adsorbed layers formed on the surface of the particles—their thickness, the form of the distribution of the density of the segments along the normal to the surface $\rho(x)$, and the number and length of the "tails" and "loops" bound to a unit surface. The determination of these characteristics requires the application of special research techniques[5,6,8,17,63] and some of these, for example, the character of the functions $\rho(x)$, can be estimated only theoretically.[17,82,83]

In this review we are unable to consider the modern ideas about the adsorption of HMC on a solid surface and about the structure of the adsorbed polymer layer; these questions have been discussed in a number of communications.[2,5,6,8,17,82,83] We shall only mention the principal features necessary for the understanding of the problem under consideration.

The structure of the polymer shell on a solid surface depends on many factors—on the amount of the adsorbed substance and its molecular weight, the adsorption energy of an elementary unity, the quality of the solvent, the flexibility of the polymer chain, and, for polyelectrolytes, also the density of the electric charges on the latter. Various models of the adsorbed HMC layers have been discussed and justified: in the form of a thin layer with a large number of contacts between the macromolecule and the surface[84]—this obtains when the affinity of the polymer for the surface is high, i.e. in the presence of chemisorption interactions between the HMC and the adsorbent; in the form of an undeformed polymer coil (when the interaction between the rigid macromolecule and the surface is relatively weak);[28,85] in the form of supermolecular formations transferred to the surface from concentrated HMC solutions;[2,5] in the form of loops and tails of equal or different sizes[6,15,17,18,63–65,76] and (for polyelectrolytes) in the form of ellipsoids of rotation for different degrees of deformation.[79,80]

At the present time the stabilisation of hydrophobic dispersions by the addition of non-ionic flexible-chain water-soluble polymers is most readily susceptible to theoretical interpretation. The adsorption layer is in this case usually described in terms of the Bulas–Hoeve–Hesselink model,[82,86] according to which the polymer shell on the surface consists of a denser first layer (with a relatively large number of contacts between the macromolecule and the surface) and a loose layer made up of unequal tails and loops turned towards the liquid whose distribution with respect to size is described by an exponential relation.[17,82] The density of the segments changes abruptly at the boundary between the first and second layers.[86] Depending on the conditions, linear, power, or most frequently, exponential $\rho(x)$ relations have been postulated for the peripheral part of the adsorbed layer.

We shall consider the influence of the adsorption of polymers on various components of the interaction energy of disperse particles.

### 1. The van der Waals Attraction

The presence of a surfactant or a polymer around part of the layer can diminish the attraction energy $\Delta F_A$ between them both as a result of steric considerations (owing to the increase of the minimum distance to which the particles can approach one another) and because the adsorbed layers alter the effective Hamaker constant $A$. In the expressions describing the relation between $\Delta F_A$ and $A$ (see, for example, Fridrikhsberg[4] and Sonntag and Strenge[88]) the attraction energy is a function not only of the interaction constant of the disperse phase ($A_1$) and the dispersion medium ($A_2$) and the constant for the interaction of the disperse phase with the medium ($A_{12}$) but also of the Hamaker constant of the adsorbed layer ($A_3$).

The influence of the parameters of the adsorption layers of the polymers on the molecular attraction of the disperse particles has been considered theoretically in a study[89] where the following expression for $\Delta F_A$ was obtained in the case of unretarded London forces in terms of the microscopic approximation:

$$\Delta F_A = -\frac{1}{12}\left[(A_2^{1/2} - A_3^{1/2})\frac{a+h}{a-2h} + (A_3^{1/2} - A_1^{1/2})\frac{a}{d} + 4(A_2^{1/2} - A_3^{1/2})(A_3^{1/2} - A_1^{1/2})\frac{a+h}{(d-h)(2+h/a)}\right] \quad (1)$$

where $a$ is the radius of the particles, $d$ the distance between them, and $h$ the thickness of the adsorbed HMC layer.

Vincent[90] derived the corresponding equations for retarded London forces and also examined the case of the interaction between plates and a sphere containing a homogeneous adsorbed layer on the surface. Some of his results are illustrated in Fig.8. Deryagin and Churaev[81] and Ninham and Parsegian[92] obtained an analytical expression for the London–van der Waals forces in the case of three-layer films in air and in water on the basis of the macroscopic Lifshits theory of interactions between condensed bodies.

The complex expressions obtained for $\Delta F_A$ can be simplified under certain conditions. For example, for emulsions of the water/oil type stabilised by hydrocarbons, one can assume that $A_2 \cong A_3$, since the molecular interaction forces between hydrocarbon chains and between the latter and the oil are similar.[88] In the general case the adsorption of polymers can both diminish and increase the attraction between the particles. Its influence is determined by the results of the combination of Hamaker constants: when a dense particle ($A_1 > A_2$) is "clad" in a light adsorbed layer ($A_3 < A_2$), the effective Hamaker constant for the particle plus adsorbed layer system decreases. Conversely, a heavy coat with a low density diminishes the attraction. However, it has been shown[89] that the change in $A$ owing to the appearance of adsorbed polymer layers never converts attraction into repulsion.

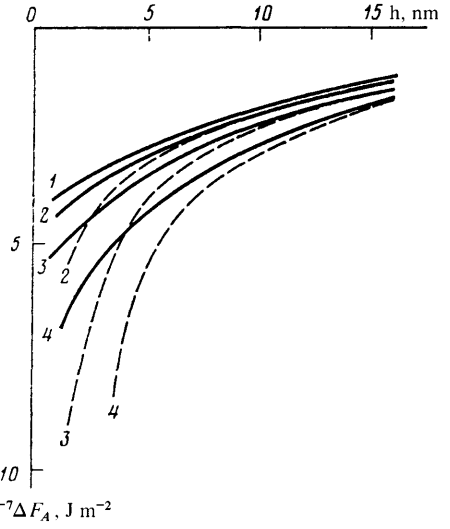



Figure 8. Theoretical variation of the influence of the adsorbed homopolymer on the van der Waals attraction of two plane-parallel plates on the assumption of an exponential (continuous lines) or uniform (dashed lines) distribution of the density of units in the adsorption layer. Average volume fraction of units in the layer: *1*) 0; *2*) 0.03; *3*) 0.1; *4*) 0.2. The Hamaker constant is $20kT$ for the particles, $17.5kT$ for the polymer, and $10kT$ for the solvent; the thickness of the layer is 10 nm.[90]

The influence of the Hamaker constant for the adsorbed layer $A_3$ on the particle attraction force has been examined[93] and it has been shown that, under the conditions where $A_1 > A_2$, the plot of $\Delta F_A$ against $A_3$ passes through a minimum. In discussing the influence of the adsorption of water-soluble polymers on $A$, one must bear in mind that the adsorbed layer contains polymer units plus water molecules. According to Fleer and Lyklema[55] and Sonntag and Strenge,[88] when the polymer is strongly hydrated one can assume that $A_2 \cong A_3$, i.e. that the molecular attraction of the particles with the adsorbed layer is the same as the attraction in the pure dispersion medium. In this case the expression for the attraction energy becomes

$$\Delta F_A = -\frac{1}{12}(A_2^{1/2} - A_1^{1/2})^2 \frac{a}{d}. \qquad (2)$$

The character of the distribution of the density of the units in the adsorbed layer influences significantly the $\Delta F_A(A)$ relation, primarily over short interparticle distances.[90,93]

New possibilities for a more exact calculation of the influence of the adsorption of HMC on the molecular attraction of the particles have been provided by Lifshit's macroscopic theory. Without going into the description of this theory here (see, for example, Dzyaloshinskii et al.[94]), we may note that the results of the calculation of $\Delta F_A$ by the Lifshits method, particularly for aqueous media, can differ markedly from those based on the London theory,[8,95] because the high polarity of water leads to a greater contribution to $A$ by polarisation interactions at infrared and microwave frequencies than at ultraviolet frequencies (in Hamaker's procedure only the ultraviolet frequencies of the dispersion are used in the calculations of $A$). Furthermore, allowance for the low-frequency components of the distortion forces in the macroscopic theory leads to a dependence of $A$ on temperature[91,92] and on the presence of salts in the system. All these factors must be considered in discussing the influence of the adsorption of HMC on the molecular attraction of the particles.

## 2. The Repulsion of Electrical Double Layers

The adsorption of non-ionic polymer macromolecules can alter the parameters of the electrical double layer, which is reflected in its turn in the contribution of the electrical component $\Delta F_R$ to the particle interaction energy. These changes reduce mainly to the following.

(a) The accumulation of polymer units in the Stern layer can alter the density of the electrical charges on the surface—either as a result of a change in the dielectric constant and hence of the capacity of the double layer or as a result of the appearance of "adsorption potential jumps" $\psi_a$ in the oriented layer of dipolar segments on the surface. The appearance of $\psi_a$ having the same sign as the ionic potential jump $\psi_i$, under the conditions of a constant interphase potential jump ($\psi_0 = \psi_i + \psi_a$), inevitably entails a decrease of $\psi_i$ (subject to the condition $\psi_a < \psi_i$) or even alters its sign (when $\psi_a > \psi_i$), which is manifested experimentally as a change in the charge on the particles in the presence of the added non-ionic polymer.[14,63,67]

(b) The adsorbed macromolecules can displace from the Stern layer some of the specifically adsorbed counterions, which increases the $\psi_1$ potential and hence the stability of the colloidal solution. This explains, for example, the initial increase in the electrokinetic potential of AgI particles in the presence of small amounts of added poly(ethylene oxide)[67] or poly(ethylene glycol).[96]

(c) The formation on the surface of a fairly dense adsorbed polymer layer with a high density of units, in which water loses its solvent power, leads to an increase in the thickness of the Stern layer and to the separation of the components of the double layer, which is again responsible for the growth of the $\psi_1$ and $\zeta$ potentials,[97] i.e. for the stabilisation of the dispersion. These ideas have been evoked to account for the increased stability of hydrophobic sols as a result of the adsorption of diphilic molecules of organic substances[98,99] and can also be used to interpret a wide variety of changes in the stability of disperse systems in the presence of polymeric additives.[8,44]

(d) The formation on the surface of fairly thick hydrodynamically impermeable layers of non-ionic polymers shifts the slip planes into the bulk of the liquid phase, which entails a decrease in the $\zeta$ potential and in the contribution of the electrical forces to the repulsion of the polymer-containing particles. These ideas have served as a basis for calculating the effective thickness of the adsorbed layers of non-ionic HMC (for a more detailed description, see Refs.6, 9, and 17).

The addition of oppositely charged polyelectrolytes to a colloidal solution usually leads to a significant decrease in the $\zeta$ potential and to a change in the charge of the particles,[48,50-52] which is accompanied by the destabilisation (flocculation) of the system. As a rule, the stability minimum and the isoelectric point of the particles of the dispersion do not coincide.[48,50-53,100] The adsorption of polyelectrolytes bearing charges of the same kind as the particles is in many cases responsible for the increase in the electrokinetic potential and for the stability of the dispersion.[44,46,62,63]

### 3. Interaction of the Adsorbed Macromolecules

The adsorbed macromolecules are hardly ever located in a planar position on the surface: some of the macrochains in the form of loops and tails are immersed in the surrounding liquid. The interpenetration of two such adsorbed layers gives rise to repulsion forces of two types:[8,101] (1) as a consequence of the decreased number of possible conformations of the polymer chain, which leads to the loss (decrease) of the configurational entropy and hence to an increase in the free energy of the system and (2) owing to a change in the polymer–solvent interaction in the overlap zone and the appearance of a local osmotic pressure under these conditions. In a details study it is possible to differentiate two limiting cases of the "entropic repulsion".[8,101] The first arises when the decrease of the entropy of the system in the interaction of adsorbed molecules entails desorption of the latter. This increases the interfacial free energy, i.e. leads to the repulsion of the particles. This model has been considered theoretically[102,103] in relation to short weakly adsorbable rod-like molecules, which have sufficient time for desorption during the elementary particle collision step. It explains, for example, the stabilisation of dispersions of carbon black in hydrocarbons by alkylbenzenes,[104] the extremum in the dependence of the stabilising effect on the degree of surface coverage by the polymer,[103] etc. For slowly desorbable or altogether non-desorbable high-molecular-weight polymers (i.e. when the simultaneous rupture of a large number of contacts with the surface is unlikely), another mechanism is more suitable, in which it is assumed that, in the course of particle collisions, the polymer–particle adsorption equilibrium does not change and the increased free energy of the system is due to the decrease of its entropy following the redistribution or compression of the adsorbed segments in the overlap zone.

In this constant adsorption model one distinguishes in its turn two limiting cases: the mutual interpenetration of the adsorbed layers without the compression of the adsorbed polymer chains (the "mixing" effect) and compression of the adsorbed layers without their mutual overlapping (the "volume restriction" effect). Naturally both these cases are idealised and there are always difficulties in selecting a model of the interaction in quantitative calculations, because the two contributions mentioned above cannot be separated in real systems. On the basis of general considerations, one can only assume that at a high concentration of units on the surface, in the adsorption of substances with not unduly high molecular weight and when the interacting surfaces have approached one another very closely, the "volume restriction effect" will predominate, while for low degrees of surface coverage, for low degrees of adsorption of low-molecular-weight polymers, and for large interparticle distances, the "mixing" effect is the dominant one.[8,15] Difficulties also arise in the selection of a model of the adsorbed layer in the form of tails or loops. The distribution of the density of units in the loop and in the tail, which determines the interaction between the macromolecules, changes in different ways with increasing distance.[105-107] It has been shown theoretically that in the case of a long-chain homopolymer it is possible to neglect the concentration of the tails compared with that of the loops,[82] but for not an unduly long macromolecule the adsorption in the form of tails is energetically more favourable.

A number of attempts have been made at a quantitative calculation of the repulsion energy of hypothetical particles (plates) with a polymer coating, caused by the "volume restriction" effect ($\Delta F_{VR}$) and the "mixing" effect ($\Delta F_M$). $\Delta F_{VR}$ has been calculated[102] for short rigid rodlike molecules on the hypothesis that the increase in the free energy of the system is determined by the decrease of the configurational entropy $S$ as the second surface approaches: $S = k \ln N$ (where $N$ is assumed to be proportional to the area occupied by the free ends of the rods). Mackor's model has been extended[108] to the interaction of a sphere with another sphere, the lateral interaction of the adsorbed chains being considered simultaneously. Using the same concentration, an increase in the entropic repulsion with increasing length of the macromolecular chain, the impossibility of stabilisation of unduly small particles by macromolecules having the specified lengths, etc. have been predicted theoretically.[109] The earlier attempts to calculate $\Delta F_{VR}$ are not considered here, since they were based, as shown by Hesselink,[106] on an incorrectly selected distribution of the densities of the adsorbed units as a function of the distance from the surface; furthermore, they have been considered in fair detail in another review.[8]

The "mixing" or osmotic effect was first considered by Fischer.[110] In the derivation of an expression for the calculation of the contribution $\Delta F_M$, arising when two spherical polymer-containing particles approach one another, he suggested that (1) the concentration of the segments in the adsorbed layer is identical throughout, (2) the concentration of the segments in the overlap region is equal to the sum of the concentrations in both interacting adsorbed layers, and (3) that the Flory–Krigbaum theory of dilute solution is applicable to the calculations of $\Delta F_M$. In this theory the free energy of mixing of the polymer units and solvent molecules in a small volume element is expressed as:[111]

$$\delta(\Delta F_M) = kT(\delta n_1 \ln \Phi_1 + \chi \delta n_1 \Phi_2), \qquad (3)$$

where $\delta n_1$ is the number of solvent molecules in the volume element $\delta V$, $\Phi_1$ and $\Phi_2$ are the volume fractions of the solvent and the polymer respectively, and $\chi$ is the Flory–Huggins interaction parameter. The change in the free energy of mixing in the volume $V$ is calculated as the sum of the changes in all the volume elements. Thus an expression has been obtained[110] for calculating the repulsion energy between two particles with an adsorbed layer of a non-ionic polymer:

$$\Delta F_M = \frac{4\pi k T c^2}{3 V_1 \rho^2} (\Psi - \chi)\left(h - \frac{d}{2}\right)^2 \left(3a + 2h + \frac{d}{2}\right) \qquad (4)$$

where $c$ is the concentration of the polymer segments per unit volume of the adsorbed layer, $\rho$ the density of the adsorbed

substance, $h$ the thickness of the layer, $V_1$ the partial molar volume of the solvent, and $\psi$ the entropic parameter of the interaction.

For small overlaps, the hypothesis (2) is entirely reasonable, but for larger overlaps it is not very suitable. It follows from the work of Hesselink[106] that the first assumption also has little justification in this theory. An advantage of Meier's theory[109] is the use in the expression for $\Delta F_M$ of the familiar Flory parameter $\chi$ in an explicit form, which makes it possible to take into account the contribution of the nature of the solvent to the repulsion. On the other hand, the expression for $\rho(x)$ used by the same investigator is apparently erroneous.[8,106]

The latest advances in this field are associated with the development of statistical methods for the calculation of the number of conformations of adsorbed macromolecules by Hesselink[82,106] and other workers.[112,113] Hesselink[106] quotes an expression for the calculation of the number of conformations of a single loop and a single tail lost following the approach of a second surface, subject to an exponential distribution of the density of units along the normal to the surface. On this basis, Hesselink et al.[114] derived relations suitable for the calculation of the increase in the free energy of the system resulting from the restriction of the volume of the adsorbed polymer chains and their mixing (calculated per unit area of the surface):

$$\Delta F_{VR}=2\nu kTV(\bar{i}, d); \quad (5)$$

$$\Delta F_M=2(2\pi/9)^{3/2}(\alpha^2-1)kT\nu^2\langle r^2\rangle M(\bar{i}, d). \quad (6)$$

In these expressions the terms $V(\bar{i}, d)$ and $M(\bar{i}, d)$ describe the increase in the free energy as a function of the distance $d$ between the surfaces for the average loop; they depend on the mechanism of binding of the macromolecule to the surface and on the average number of units in the loop $\bar{i}$; $\nu$ is the number of loops (tails) per unit area, $\alpha$ the swelling coefficient, and $\langle r^2\rangle^{1/2}$ the mean square distance between the ends of the polymer chain.

Relations for the calculation of $V(\bar{i}, d)$ and $M(\bar{i}, d)$ have been published.[114] Various cases of the binding of macromolecules to the surface were then considered, namely adsorption in the form of tails and loops of equal size, in the form of a macromolecule with an exponential distribution of tails and loops with respect to size, or in the form of a homopolymer all the segments of which have equal chances of binding to the surface.

The values of $V(i, d)$ and $M(i, d)$ for a simplified model, frequently used in practice, of the adsorption of a polymer in the form of identical loops and subject to the conditions $d/(il^2)^{1/2} \geq 1$ can be calculated from the following relations with an error up to 2%:[114]

$$V(i, d)=-2(1-12d^2/il^2)\exp(-6d^2/il^2), \quad (7)$$

$$M(i, d)=(3\pi)^{1/2}\{6d^2/il^2-1\}\exp(-3d^2/il^2), \quad (8)$$

where $i$ is the number of units in the loop.

Although the Hesselink–Vrij–Overbeek (HVO) theory yields reasonable values for $\Delta F_{VR}$ and $\Delta F_M$ and can, as will be shown below, predict many experimental relations, it has a series of weak points. Since it uses the exponential distribution $\rho(x)$, it assumes the existence of the "volume restriction" effect over any interparticle distances, which is naturally incorrect. Nor is the hypothesis that the values of $\alpha$ for macromolecules in the bulk phase and in the adsorbed layer are identical fully justified in the HVO theory. In addition, it suffers from the limitations of the Flory–Krigbaum theory, which constitutes the basis of the calculation of $\Delta F_M$.

The Napper–Evans steric stabilisation theory[115–119] constitutes an expansion and development of the Fischer theory. The main factor determining the stabilisation of HMC dispersions is believed by these authors to be the polymer–solvent interaction, which influences decisively the conformation of the stabiliser in the surface layer of particles. A satisfactory stabilisation is attained when the solvent used is better than a θ-solvent; under these conditions, the polymer–solvent interaction predominates over the polymer–polymer and solvent–solvent interactions. Near the θ-point a transition should be observed from a stable to an unstable state, as follows from Eqn.(4), according to which $\Delta F_M = 0$ under θ-conditions, where $\chi = 0.5$. On passing to solvents inferior to the θ-solvent, the medium–medium and polymer–polymer interactions become energetically more favourable ($\Delta F_M < 0$), which leads to flocculation in the system. Conversely, positive values of $\Delta F_M$ ensure the stabilisation of the system.

Numerous experiments whereby Napper and co-workers[115–119] did indeed demonstrate convincingly that, after the attainment of θ-conditions (by altering the temperature or solvent composition), there is an abrupt change in the stability of polymer dispersions stabilised by various block copolymers of type AB. Analysis of stabilisation conditions[118] for ~40 systems has shown that the θ-point is close to the limit of stability of a sterically protected dispersion and that the θ-point and the critical point for flocculation are clearly correlated in both aqueous and non-aqueous media.

Napper introduced the concept of the enthalpic, entropic, and mixed entropic-enthalpic stabilisations. This classification is best examined by dividing the free energy change occurring on mutual interpenetration of the macromolecular chains (the energy of mixing) into the enthalpic ($\Delta H_M$) and entropy ($\Delta S_M$) components:

$$\Delta F_M=\Delta H_M-T\Delta S_M. \quad (9)$$

The generalised Flory–Huggins interaction parameter, characterising the thermodynamics of the polymer–solvent interaction, can be represented in its turn by the sum

$$\chi=\chi_h+\chi_s,$$

where $\chi_h$ is the parameter of the enthalpy of mixing (measured calorimetrically) and $\chi_S$ is the entropic parameter, which characterises the volume effects of mixing, a change in the structure, dissociation and formation of hydrogen bonds, etc. At infinite dilution, $\Delta H_M \to (-q)$ and $\Delta H_S \to (-\psi)$, where $q = \chi_h$ and $\psi = 1/2 - \chi_S$. On the basis of the above considerations, Napper[120] established the conditions under which a particular type of steric stabilisation predominates (Table 3).

Table 3. Comparison of different types of steric stabilisation (according to Napper).

| $q$ | $\psi$ | $\Delta H_M$ | $\Delta S_M$ | $\Delta H_M/\Delta S_M$ | $\Delta F_M$ | Type of stabilisation |
|---|---|---|---|---|---|---|
| $<0$ | $<0$ | $>0$ | $>0$ | $>1$ | $>0$ | Enthalpic |
| $>0$ | $>0$ | $<0$ | $<0$ | $<1$ | $>0$ | Entropic |
| $>0$ | $<0$ | $<0$ | $>0$ | $\lesssim 1$ | $>0$ | Mixed |

The majority of solutions of polymers in non-polar media are characterised by positive values of $q$ and $\psi$ and therefore entropic stabilisation is to be expected for them. Negative

values of $q$ and $\psi$, caused by the rupture of the hydrogen bonds with increased HMC concentration in the system, correspond to many polymers in non-aqueous solutions (for example, a solution of PEO in water). The addition of dioxan to aqueous solutions of surfactants decreases the negative (increases the positive) values of $q$ and $\psi$, which is accompanied by a transition from the enthalpic to the entropic mechanism of stabilisation.[120]

The type of steric stabilisation can be established from the form of the change in the disperse system with increase of temperature. Napper and co-workers showed[117-119] that colloidal systems, which flocculate on aggregation, undergo enthalpic stabilisation at least below the critical flocculation temperature (c.f.t.), while systems which flocculate on cooling are stabilised entropically at least above the c.f.t. In other words, systems with enthalpic stabilisation tend to lose stability on heating, while entropically stabilised systems flocculate on cooling. According to Napper,[117] the c.f.t. is the minimum temperature causing the flocculation of dispersions stabilised enthalpically or the maximum temperature at which dispersions stabilised entropically flocculate.

A new approach to the problem of the stabilisation of colloids by non-ionic polymers has been developed recently in a study[121] whose authors attribute the appearance of repulsion forces to the presence in the solution of free non-adsorbable HMC. Such a situation can obtain for an inert surface or a surface which repels the polymer and also when all the adsorption centres on the surface have been occupied. The average density of units is assumed to be lower on the surface than in the bulk phase. The appearance of repulsion forces as the surfaces approach one another to distances less than twice the distance between the centres of mass of the macromolecules is attributed to the differences between the free energies of mixing of the polymer with the solvent (calculated by the Flory–Krigbaum procedure) in the initial and final states of the system.

### 4. Solvation of the Disperse Phase

The adsorption by colloidal particles of water-soluble polymers containing a large number of hydrophilic groups must lead to the hydrophilisation of the surface of the disperse phase and hence to an increased contribution by the solvation stability factors. However, among various aspects of the influence of HMC on the stability of colloidal solutions, this effect has not so far been examined.

Here one should note that the concept of the solvation of the disperse phase as an aggregative stability factor for colloidal systems has been firmly and for a long time incorporated in the literature,[122,123] although neither the structure of the surface solvate layers nor the physical nature of the corresponding repulsion forces have so far been unambiguously established.[124-128] It is believed that the solvation stability factor is determined by the presence on the surface of polymolecular layers of the solvent with an unusual structure (differing from that in the bulk phase) and properties.[124,126-128] The interaction of these layers induces the appearance between them of repulsion forces whose nature has not been finally elucidated. It is most likely that they are caused by a change in the statistical distribution of the water molecules in the overlap zone (by an increase of the degree of their order).[72] The present state of the theory of the liquid state does not permit the calculation of the above forces; they can be estimated only indirectly by subtracting from the experimental force of the interaction of the disperse phases the sums of the theoretically calculated repulsion forces of the double layer and molecular attraction forces.[81] Such estimates have so far been made only for a small number of model systems.[81,129]

The solvation of the disperse phase has been regarded as an important or dominant factor in the stabilisation of not only hydrophilic sols[122,130,131] but also of hydrophobic systems stabilised (hydrophilised) by adsorption layers of low-molecular-weight surfactants.[132,133]

The important role of the structural component of the wedging pressure in the mechanism of the stabilisation of colloidal solutions with a polymer additive is also indicated by data concerning the hydrophilic properties of the stabilised macromolecules as well as the temperature dependence of the stability of polymer-containing dispersions (see Section II). It has been shown[134-136] with the aid of high-resolution NMR and the spin-echo method that three forms of water exist in the PEO–water, PVA–water, and CMC–water systems: the hydration sphere bound firmly to macromolecules and consisting of 2–3 $H_2O$ molecules per unit at the boundary of which there is an abrupt change in many properties of water, the polymolecular hydration layer made up of 16–20 water molecules per unit in which the mobility of water molecules still differs from that in the pure liquid with a gradual transition to the properties of the latter in the bulk phase, and finally water corresponding to the usual liquid in all its properties. Thus, like hydrophilic solid surfaces,[124-128] water-soluble polymers exert a structure-forming effect on several molecular layers of water.

The observed[72,73] abrupt changes in the coagulation thresholds of hydrophobic sols containing water-soluble polymers with increasing temperature can be explained by the influence on the stability by the structural component of the wedging pressure, in particular the structure of water itself in the polymolecular hydrate layers formed on the surface (see Section II). The contribution of this stabilisation factor depends on the degree of adsorption of the HMC by the particles, the degree of hydration of the stabiliser macromolecule, and other factors (see below).

## IV. THE MECHANISM OF THE STABILISATION OF REAL DISPERSIONS BY NON-IONIC POLYMERS

It is possible to use two procedures to carry out an experimental test of the theories of the interaction of adsorbed macromolecules and to discover the mechanism of the stabilisation of real HMC dispersions. The first more direct method involves the direct measurement of the repulsion forces of the adsorbed polymer chains and their comparison with the corresponding values calculated theoretically. The second method consists in comparing the experimental characteristics of the stabilisation of dispersions by polymers [the influence on the latter of the degree of adsorption and the molecular weight (MW) of the stabiliser, the ionic strength of the solution, and other factors] with the characteristics predicted on the basis of the analysis of the potential curves for the interaction of polymer-containing particles constructed using the parameters of the electrical double layer and the adsorbed polymer layer, which have been determined by an independent method and which enter into the equations of a particular theory.

### 1. The Energies of the Interaction of the Particles with the Adsorbed HMC

It follows from the foregoing features described in the previous Section that the overall free energy of the polymer-containing particles is in the general case given by

$$\Delta F = \Delta F_A + \Delta F_R + \Delta F_P + \Delta F_{st} \quad (10)$$

where $F_{st}$ is the contribution of the structural component of the wedging pressure, which cannot be determined quantitatively but which can be neglected, as will be shown below, for high degrees of adsorption of the polymer and $\Delta F_P = \Delta F_{VR} + \Delta F_M$.

Our previous communications[15,16,18,20,22,28,63] present the results of calculation of the component (and their sum) of the interaction energies of silver iodide, antimony sulphide, and styrene particles as well as oil drops in water containing adsorbed PVA, PEO, and MC, using the parameters of the electrical double layer and the adsorbed polymer layer found by independent methods.

The contributions $\Delta F_{VR}$ and $\Delta F_M$ were calculated from the formulae of the Hesselink–Vrij–Overbeek theory [Eqns.(5) and (6)] for models of the binding of macromolecules to the surface which were most appropriate for a given system: for undeformed statistical coils, i.e. $\langle r^2 \rangle = \bar{l}l^2$ and $\nu = \Gamma N_A/M$, where $\Gamma$ is the degree of adsorption in g $m^{-2}$ and $N_A$ the Avogadro number (this model is suitable for the adsorption of PVA on the surface of oil in water and of MC on AgI and $Sb_2S_3$ particles), for loops of equal size, i.e. under conditions where Eqns.(7) and (8) are valid, and, finally, for an adsorbed layer with an exponential distribution of loops with respect to size (the model of adsorbed layers of PVA and PEO on the surface of hydrophobic $Sb_2S_3$ and AgI particles). For the last two models, the number of loops was found from the relations $\nu = n/\bar{l}$, where $n$ is the number of units in the form of loops bound per unit surface, calculated as the difference between the total degree of adsorption and the degree of adsorption in the first layer. The quantity $\langle r^2 \rangle$ for adsorbed chains was found as $\langle r^2 \rangle = \alpha \bar{l} l^2$, using the quantities $\bar{l}$, $l$, and $\alpha$ found previously.[6,28,63-65] In conformity with Hesselink's procedure,[82] the concentration of tails compared with that of the loops was neglected for the high-molecular-weight polymers employed.

The attraction energy was found in terms of the microscopic approximation for the model of plane-parallel plates:[88]

$$\Delta F_A = -\frac{A_{12}}{12\pi d^2}. \quad (11)$$

The repulsion energy of the double layer of plates was found from the formula valid when $\kappa d > 1$:[1]

$$\Delta F_R = \frac{\varkappa}{z^2} f(Z); \quad Z = ze\psi_1/kT \quad (12)$$

where $z$ is the charge of the counterion and $\kappa^{-1}$ the Debye radius.

The Stern potentials $\psi_1$ for silver iodide and polystyrene particles were determined from the results of dielectric and conductimetric measurements[63] and the surface potential $\psi_0$, calculated from the charge densities on the surface,[63] was adopted as the effective potential of the $Sb_2S_3$ particles. The values of the functions $f(Z)$ were taken from the Tables quoted in Kruyt's monograph.[1]

Analysis of the character of the variation of $\Delta F_{VR}$ and $\Delta F_M$ as a function of the interparticle distance for AgI, $Sb_2S_3$, or polystyrene containing different amounts of an adsorbed HMC (for example, see Fig.9) leads to the following conclusions.[15,16,18,20,22] Repulsion owing to the overlap and mixing of the adsorbed macrochains is manifested over longer distances than the repulsion induced by the restriction of their volume. This is due to the fact that the former effect arises as soon as the interpenetration of the segments located on the opposite walls begins, while the manifestation of the latter effect (the compression of the flexible polymer chain) requires an adequate approach to the second (restricting) surface.

$\Delta F_{VR}$ and $\Delta F_M$ increase both with increasing degree of adsorption of the polymer (as a consequence of the lengthening of the adsorbed tails and loops) and as the surfaces approach one another (owing to the involvement in the interaction both of an increasing number of units of the given loop and also of shorter loops). The contribution of osmotic effects is greater in the adsorption of methylcellulose and poly(ethylene oxide) than in the adsorption of poly(vinyl alcohol), because water is a better solvent for the former polymers ($\Delta F_M \propto \alpha^2$). Calculations have also shown that the repulsion of the adsorbed macromolecules increases with increasing molecular weight of the polymer for the same degree of adsorption and the same ionic strength of the solution, despite the fact that the area of the polymer shell is the same under these condition. This is caused by the unequal concentrations of the loops in the adsorbed layer for specimens having different molecular weights. Thus the HVO theory explains the experimentally observed increase of the stabilising effect of polymers with increase of their molecular weight.

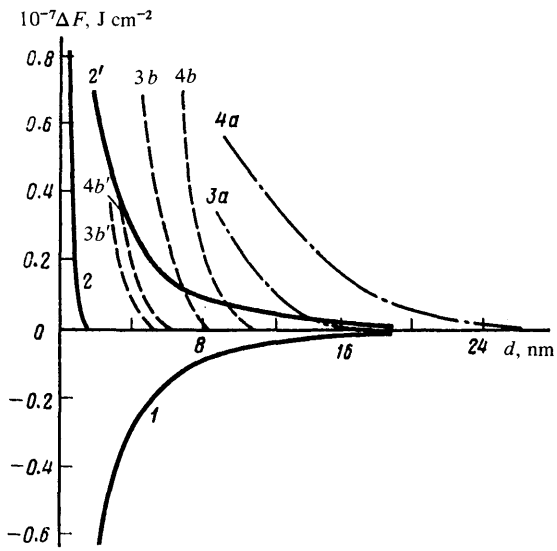



Figure 9. Different components of the interaction energy of $Sb_2S_3$ particles which have adsorbed 0.4 mg $m^{-2}$ ($b'$) and 1.0 mg $m^{-2}$ ($a$ and $b$) of PVA with $M = 2.2 \times 10^4$: 1) $\Delta F_A$; 2) $\Delta F_R$ in 1 M KCl solution; 2′) $\Delta F_R$ in $10^{-3}$ M KCl solution; 3) $\Delta F_{VR}$; 4) $\Delta F_M$ for the model involving adsorption in the form of undeformed coils (a) and with an exponential distribution of loops with respect to size ($b$).[20]

Comparison of the values of $\Delta F_R$ and $\Delta F_P$ made it also possible to estimate the contributions of different forces to the repulsion of real particles containing adsorbed HMC. Fig.9 shows that in a concentrated electrolyte solution the stabilisation of the sol is determined in all cases soley by the polymer component, because the double layer is in this case "hidden" within the polymer shell. On the other hand, in the case of dilute electrolyte solutions the contributions $\Delta F_R$ and $\Delta F_P$ to the repulsion of particles depend on the degree of adsorption of the HMC: with decrease in the salt concentration (with increased thickness of the double layer) and

with decrease of Γ (with a decrease in the length of the loops), the contribution of the repulsion also increases (Fig. 10).

Thus the interaction between particles coated by an adsorbed layer of a HMC is not determined solely by the balance of the van der Waals attraction and repulsion forces of the polymer chbins, as has been frequently suggested.[8,107-110,114,121] As a special case, this obtains only in concentrated electrolyte solutions when the thickness of the electrical double layer is much smaller than the effective thickness of the polymer coating; when $\kappa^{-1} > h$, the opposite picture is observed.

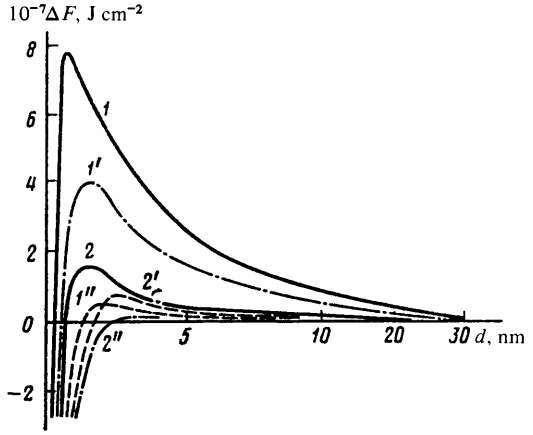



Figure 10. Potential curves for the interaction of $Sb_2S_3$ particles which have adsorbed 0.4 mg m$^{-2}$ (curves *2*, *2′*, and *2″*) and 1.0 mg m$^{-2}$ (curves *1*, *1′*, and *1″*) of PVA with $M = 2.2 \times 10^4$: 1) and 2) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_{VR} + \Delta F_M$; 1′) and 2′) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_M$; 1″) and 2″) $\Delta F = \Delta F_A + \Delta F_R + \Delta F_{VR}$.[20]

The potential curves for the interaction of the particles with the adsorbed non-ionic polymer have been constructed by adding together $\Delta F_A$, $\Delta F_R$, and $\Delta F_P$.[15,16,18,20,28,63] It has been shown (Fig. 10) that, with increase in the degree of adsorption of the HMC, the interaction energy between the particles increases significantly, reaching values amounting to several and several tends of erg cm$^{-2}$, which explains the formation of highly stable sols in the presence of the PVA, PEO, and MC polymers. Comparison of the results of theoretical calculations by the HVO method with the experimental stabilisation data (see Section II) has shown that the abrupt increase in the stability of the sols occurs for approximately the same degrees of adsorption ($\gtrsim$0.5–0.7 mg m$^{-2}$) as in the case where there is an appreciable barrier preventing the mutual approach of the particles, sufficient for the stabilisation of the colloidal solution. The HVO theory also predicts correctly the dependence of the stabilising effect of polymers on their molecular weight. At the same time this theory in its pure form is unsuitable for the description of the stabilisation of dispersions by the addition of HMC in dilute electrolyte solutions; it does not take into account the change in the interaction of the polymer with the solvent following adsorption and does not allow the separation of the contributions to the interaction caused by the volume restriction and osmotic effects.

Thus, on the basis of the general approach of the physical Deryagin–Landau–Verwey–Overbeek theory of stability (involving the allowance for the balance of the attraction and repulsion forces between the particles) and resorting to the HVO theory, it is possible to interpret many experimental relations obtained in the study of the stabilisation of dispersions by the addition of non-ionic water-soluble polymers and also to determine the contributions of different factors to the stabilisation of these systems.

As already stated, the contribution of the solvation of the particles to the mechanism of the stabilisation of polymer-containing dispersions cannot as yet be estimated quantitatively. However, the set of experimental stabilisation data and their comparison with the results of adsorption measurements permit qualitative estimations. Apparently, in the case of dispersions with a small amount of added polymer, i.e. for small thicknesses of the adsorbed HMC layer, the contribution of the structural component of the wedging pressure is comparable to that of the other stabilisation factors. This is indicated particularly by the results of the study of the temperature dependence of the stability of polymer-containing hydrophobic sols (see Section II). At the same time, in the presence of large amounts of the high-molecular-weight substance in the system, whereupon there is a sharp increase of its stability, the solvation of the disperse phase is a weaker stabilisation factor than the steric repulsion. This is indicated, for example, by the insensitivity to the temperature factor of highly stable polymer-containing sols and the impossibility of achieving their coagulation by adding concentrated salt solutions. This constitutes the radical difference between colloidal solutions protected by low-molecular-weight surfactants, on the one hand, and those protected by water-soluble polymers, on the other. In the former case, the breakdown of the boundary solvate layers (by the addition of dehydrating agents, by an increase of temperature, etc.) leads to the coagulation of the sol[132,133] while in the latter case the same result is not attained.

### 2. Direct Measurements of the Repulsion Forces Between Adsorbed HMC

The small number of publications on the direct measurement of the repulsion forces between adsorbed macromolecules reflects the difficulty of the experimental study of these systems. Thin aqueous films stabilised by the adsorbed layer of HMC, whose thickness can be measured fairly accurately by optical methods, are convenient objects for study. Furthermore, by altering the hydrostatic pressure, it is possible to determine the dependence of the interaction force between the surfaces (and of its individual components when the remaining components are either constant or small) on the thickness of the gaps separating them. Here it is appropraite to mention that the dependence on interparticle distance of the ionic-electrostatic forces, arising following the overlap of the double layers, was established for the first time precisely in relation to liquid films and the principal conclusions of the DLVO theory were subjected to a quantitative test.[88,137]

The condition for equilibrium in the liquid film is defined thus:[88]

$$P_A + P_R + P_P + P_h = 0 \qquad (13)$$

where $P_A$ is the van der Waals attraction force, $P_R$ the repulsion force of the double layers, $P_P$ the repulsion force of the adsorbed macromolecules, and $P_h$ the hydrostatic force.

The results of the measurement of the equilibrium thicknesses of water films between oil drops stabilised by adsorbed layers of poly(vinyl alcohol) have been published.[21,129,138,139] The thickness of the films $h$ was determined by the light interference method.[88,137] The values of $h$ obtained in relatively concentrated electrolyte solutions (where the thickness of the adsorbed layer is much greater than the effective thickness of the double layer) proved to be much greater than twice the radius of inertia or twice the effective hydrodynamic radius $R_h$ of the spherical macromolecular coils in solution calculated from viscosity measurements. The high thicknesses of the PVA film (up to 80–90 nm) have been explained[138] by the presence in the adsorbed layer of long tails, which produce little change in the hydrodynamic radius of the coil but are strongly manifested as a second surface approaches.

In order to account for the finding that $h > 2R_h$, the author of the present review[129] suggested that the equilibrium thickness of the films is determined not only by the thickness of the adsorbed macromolecules but also by the thickness of the polymolecular hydrate layers bound to them, which can reach several nanometers.[136] It has also been shown[21] that the thickness of the adsorbed PVA layers in emulsion films depends little on the molecular weight of the polymer (for different PVA specimens stabilising emulsions of cyclohexane in water, it amounts to 31–35 nm), but change appreciably when the nature of the non-aqueous phase is altered.

Lyklema and van Vliet[138] measured the hydrostatic force which must be applied to horizontal films stabilised by PVA in order to compensate for the steric repulstion of the adsorbed macromolecules as the surfaces approach one another, subject to the condition that the $P_A$ and $P_R$ contributions are small, i.e. when $P_P = P_h$. The experimental dependences of the equilibrium thickness on the wedging pressure (steric repulsion) (see the dashed curve in Fig.11) show that, with increase in the molecular weight of the polymer, a sharp rise of $P_P$ begins with increasing interparticle distances. The experimental $P_P(d)$ curves for a series of stabiliser specimens are close to the corresponding theoretical relations calculated by the Hesselink–Vrij–Overbeek method on the assumption that (1) the interaction of the adsorbed macromolecules is via long tails and (2) that the distribution of the tails with respect to size is the same in the adsorbed state as in the bulk phase. Hence it was concluded[138] that the long tails extending into the bulk phase play a decisive role in the steric repulsion of adsorbed poly(vinyl alcohol).

Analogous $P_P(d)$ relations have been found also for other PVA specimens stabilising aqueous films in symmetrical emulsions of oil in water.[129,139,140] The sharper increase of $P_P$ observed[129] as the surfaces approach one another compared with the theoretical calculation in terms of the HVO theory was explained by the authors on the grounds that the theory does not take into account the energy consumed in the "expulsion" (at least partial) of water molecules from the gap between the film walls as its thickness decreases, i.e. does not take into account the possible contribution of the structural component of the wedging pressure.

Having expressed the relative change in the film thickness as a function of pressure, Sonntag et al.[139] obtained a linear relation between $h/h_0$ and $P$ up to $h/h_0 \cong 0.3$. It has also been shown that this relation is relatively insensitive to the molecular weight of the stabiliser (PVA). On further interpenetration of the adsorbed macrmolecules, the repulsion energy rapidly rises. Both in this region and in the linear region, the deformation of the adsorbed layers is reversible and is independent of its duration, i.e. during deformation there is no intertwining of the macromolecules into a coil or their desorption. The linear character of the relation between the pressure and deformation in the initial stage of the interpenetration shows that in the outer regions of the adsorbed layer there are no large segment (unit) concentration gradients, which agrees with Hoeve's model[86] for the distribution of the density of units as a function of distance for macromolecules with a high adsorption energy. In this case there is an appreciable gradient of the density of segments near the interface and a slow decrease in the direction of the bulk solution.

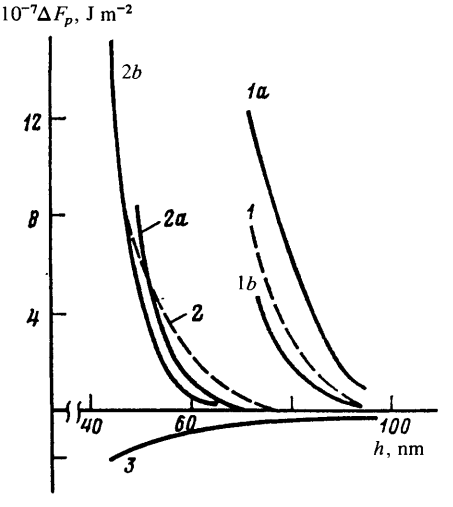



Figure 11. Variation of the steric repulsion of the tails of PVA bound to the oil/water interface and having $M = 1.43 \times 10^5$ (curves *1*) and $4.25 \times 10^4$ (curves *2*); dashed curves—experimental data; continuous curves—data calculated by the HVO method for 0.30/1 (curve *1a*), 0.40/2 (curve *1b*), 0.40/1 (curve *2a*), and 0.60/2 (curve *2b*) specimens, where the numerator represents the fraction of units in the form of tails and the denominator the number of tails per polymer molecule; 3) $\Delta F_A$.[138]

It has also been shown[139] that, as the surfaces approach one another, the experimental $P_P$ increases more slowly than would follow from the Hesselink–Vrij–Overbeek theory. This can be attributed to the fact that the real concentration of units in the outer component of the adsorbed HMC layer is higher than is assumed in the theory.

Sonntag et al.[140] measured the steric repulsion of various specimens of poly(vinyl alcohol) adsorbed at the oil/water interface and on quartz filaments as a function of the specific adsorption of the polymer, the molecular weight of the specimen, and the nature and concentration of the added electrolytes. It was concluded that only a small proportion of the tails of the macromolecule (one tail on 30 nm$^2$ for an average number of units in the tail ($\bar{n} = 500$) or one tail on 20 nm$^2$ for $\bar{n} = 800$) are responsible for the steric repulsion. With decrease of the number of unhydrolysed acetate groups in the molecule, the thickness of the adsorbed layer also rises, but the steric repulsion diminishes. It has likewise

been observed that, with increase of the KCl concentration in solution from $10^{-3}$ to 2 M, a sharp rise of $P_P$ begins for increasingly shorter interparticle distances. In conformity with the HVO theory,[114] this shows that the contribution of the osmotic effect to the steric repulsion diminishes with increasing content of the electrolyte in the system. The transition in the lyotropic series from rubidium chloride to lithium chloride leads to the same effect for an unaltered concentration of the added salt.

Cairns et al.[141] developed another approach to the study of the steric repulsion between adsorbed macromolecules; it is based on the idea that this interaction can be characterised as an excess osmotic pressure ($\Pi$) in the isotropic disperse system. In other words, the potential energy of the interaction between the particles is expressed in terms of $\Pi = P$. It has been shown that the experimental dependence of $\Pi$ on the volume fraction $\Phi_C$ of poly(methyl methacrylate) particles, stabilised by poly-1,2-stearic acid in dodecane, is close, in the region where $\Phi_C = 0.5-0.6$, to the relation evaluated theoretically from the formula $P = P_A + P_P$, where $P_A$ was calculated by Hamaker's method and $P_P$ was calculated by the statistical Flory–Krigbaum theory [see Eqn.(4)]. For higher values of $\Phi_C$, the experimental $\Pi$ increase more sharply than the theoretical values, i.e. under these conditions the adsorbed layer is less compressible than predicted by the theory, which assumes a uniform distribution of segments in the adsorbed layer. Hence it is concluded that in fact the concentration of segments in the outer part of the polymer shell is lower than in the inner part.

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Thus direct measurements of the repulsion forces between the adsorbed macromolecules make it possible, firstly, to infer the character of the distribution of the polymer segments in the section of the adsorbed HMC layer, secondly, permit the determination of the mechanism of the stabilisation of polymer-containing dispersions under various conditions, and, thirdly, serve as an instrument for the experimental test of the validity of the theories of the interaction of adsorbed polymer chains.

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