

Theoretical Views on the Interaction of Polymers with Disperse Particles in Drilling Muds

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Abstract: *The work is a theoretical overview of the processes of interaction of polymers with dispersed particles in drilling muds. The development and creation of new drilling mud systems, which contains polymer reagents, is a priority of the exploration industry. Such muds provide not only the desired properties, but also provide a mutually induced improvement of technological properties drilling mud. In order to understand the nature and mechanism of physicochemical processes, careful theoretical studies of physicochemical phenomena occurring in the drilling system are required. They allow to develop recommendations on correlation between physicochemical and technological parameters of drilling muds and their influence on processes of deformation and destruction of rocks. They also make it possible to predict the composition and properties of drilling muds that ensure the stability of the well walls and optimal conditions for rock destruction at the bottom well, as well as the preservation of reservoir properties of productive formations.*

Keywords: *Drilling mud, polymers, disperse system, adsorption of macromolecules, theory of stability, colloidal system, technological parameters, destruction of rocks.*

1. Introduction

The problems of aggregative and kinetic stability of colloidal systems have always been one of the central ones in colloid chemistry. The successful development of research in the field of physical and colloidal chemistry of polymers has created fundamentally new opportunities for stabilization of disperse systems, which are achieved as a result of adsorption of macromolecules on the surfaces of colloidal particles. This possibility based on theoretical and experimental studies of polymers adsorption made polymer-containing disperse systems of great practical importance. While investigations into the conditions of stabilization and flocculation of colloid solutions by high-molecular weight compounds (HMC) resulted in the development of a new vast section of colloid chemistry in general and colloid chemistry of polymers in particular that was devoted to the interrelation of the structure of polymers adsorption layers on the

surface of colloidal particles and stability of disperse systems.

The stabilizing effect of polymers on colloidal solutions is directly related to their adsorption on the surface of the dispersed phase. Adsorption of macromolecules (ions) and their aggregates radically changes properties, including rheological ones, of the interface and intensity of interaction between the surface and intermicrocellular fluid [1-3]. It leads to appearance of new factors of disperse system stabilization or modification of existed earlier ones. Most often we deal with the manifestation of both effects. For a proper understanding of the effect of the HMC on the stability it is necessary to have data on the adsorption of polymers by the dispersed phase and the parameters of the adsorption layers formed on the surface, the effect of HMC adsorption on the double electric layer (DEL) and the conditions of hydration of particles.

Naturally, the adsorption of polymers will have a great influence on the structure of the solvate shell of the dispersed phase, and, consequently, on the structural-mechanical properties of drilling muds. The study of the interphase phenomena in such systems is complicated by the lack of a unified theory of polymers adsorption from concentrated solutions and limited possibilities of using traditional methods of colloid chemistry for such purposes.

A. A. Tager has shown [4] that such parameters as concentration, quality of the solvent, etc., have a great influence on the structure of the polymer solutions. So, for example, in some cases the formation of polymer associates is observed already at a concentration of only 0.1 wt. %. Naturally, these factors will have a significant impact on the processes of sorption of the HMC on the surface of the solid phase particles and further processes of structure formation of the disperse system.

The simplest assumption about the structure of the polymer adsorption layer is that the molecule lies on the surface of the solid phase particle and forms many Van der Waals bonds with it. Such an arrangement of molecules is in principle possible in the early stages of adsorption when the surface filling is low or when adsorbing solutions that are not very dilute. Therefore,

a number of models of the adsorption layer structure have been proposed in which it is assumed that the polymer molecule adsorbed by the surface unfolds to form a kind of "bristle". However, this requires evidence of such specific adsorption [5].

The notions on the structure of the adsorption layer of HMC were developed in the works of Y.S. Lipatov and coworkers [1, 6] and in the works of A. Silberberg [7, 8]. They indicate that mutual entanglement of polymer macromolecules in the adsorption layer, as well as adsorption of associates, is possible. In the latter case, not only polymer molecules bound to the surface of a solid particle are in direct contact with the surface. In addition, solvent molecules may also be present in the adsorbed layer.

The lack of a unified theory of the interaction in the solid phase – solution of HMC system has led to the fact that up to now, the selection of polymer additives is carried out empirically.

2. Discussion

Virtually all information about the formulations is present in the patent literature with no data on the physicochemical processes, occurring during the formation of coagulation structures with polymer additives [9-13].

However, for a better understanding of such processes, let us consider the mechanism of interaction of vinyl copolymer consisting of sodium salt of polyacrylate and acrylamide with clay particles in solution.

Clay particles are known to consist of thin sheets about 50 Å thick, but some particles in section have a thickness of 1000 to 10000 Å. On the other side vinyl polymer molecules do not have constant sizes and shapes: they are very variable. In the solution they are rather in a compressed state with constantly changing size and shape. However, their average dimensions can be calculated by the formula:

$$R = 2nL \quad (1)$$

where R – the root means square distance from one end of a polymer chain to the other, n – the number of bonds in the chain and L – is the distance between carbon atoms in the chain. R does not express the actual diameter of the particle, but only an approximate and most useful size criterion.

Using this equation we find that acrylic type polymer with molecular weight 200000 will have $R=150$ Å (total distance between carbon bonds in the main skeleton of the polymer is ~ 700 Å).

In vinyl polymers containing ionizable groups, two important factors act to change their size.

1. The electric field of repulsion of equal charges located along the polymer chain. In alkaline solution these polymers, being ionized, cause the increase of size due to mutual repulsion of negative charges of carboxyl ions. The degree of expansion depends on the number of carboxyl groups in the molecule and on the pH of the solution (concentration of hydrogen ions). Under these conditions the size of molecules can be calculated by the formula proposed by Flory [14]:

$$R = \sqrt{M \eta / 2.1 \cdot 10^{21}} \quad (2)$$

where M – is the molecular weight, η – is the intrinsic viscosity at a given pH, $2.1 \cdot 10^{21}$ – is the constant established for polymethacrylic acid and accepted as a fairly approximate constant for the acrylic system. Applying these formulas to an acrylic polymer ($M = 200000$) containing 68% acidic and 32% amide groups, we obtain $R = 2000$ Å at pH = 9.5.

2. The screening effect of other electrolytes, which reduces the electrostatic repulsion field in solution and causes structure compression.

As known bentonite clay molecule has negative charge on the whole; this explains ionic exchange properties and colloidal state of the solution. On the destroyed edges of clay leaves also have positively charged areas where anions are attracted from the solution. The action of diluting additives is explained, in particular, by neutralization of positive sites and elimination of possibility of joining to negatively charged sites on the surfaces of other leaves. This will prevent aggregation of clay particles.

The polymer added to the solution, usually concentrated on the edges of the clay plates, has the following effect:

- 1) as a dispersant, it neutralizes positively charged areas, which could contribute to the binding of some clay plates with others;
- 2) reduces water loss filtration due to blocking effect of polymer particles attached to clay plates;
- 3) increases the viscosity of the liquid phase and correspondingly reduces the filtration rate;
- 4) binds clay leaves; however, this can happen only under certain concentration conditions and only with some polymers.

It has been found, for example, that a slight addition of polymers to the drilling mud causes change in its viscosity and yield point, which pass through the maximums on the curves when the polymer concentration decreases. Mud viscosity decreases as the polymer concentration increases. At very low polymer concentration the interaction between clay particles and polymer is obviously insufficient to

prevent structure formation in the solution. However, at a certain critical polymer concentration, a network of bonds can be formed, which is confirmed by the increase in viscosity and gel strength. With further increase concentration of the polymer in the solution, its amount begins to exceed the amount required to saturate the existing bond sites on the clay surface, and every extra polymer molecule is not used. Acrylic polymers can also influence on the value electrical charge of clay particles.

When the influence of polymer molecular weight (180000; 250000; 390000) and the ratio of carboxyl to amide groups (58:42, 68:32, and 72:27) was studied, it was found [15] that:

- 1) mainly the influence of the increased molecular weight of the additive is to reduce the water loss filtration, viscosity and yield point of the drilling muds;
- 2) the influence of the ratio of carboxyl and amide groups is not manifested so definitely and one can suppose that the character of ions in the drilling mud plays a significant role in it.

The influence of hydrolyzed PAA on drilling muds is somewhat different from that of PAA-type polymers and it has been found out that it reaches optimum value when the ratio of carboxyl and amide groups is somewhat lower.

The results shown in Figs. 1 and 2[15] were obtained for five PAA-type polymers, which had almost the same molecular weight (about 250000), but different ratios of carboxyl and amide groups. These polymers were used in concentrations up to 2.86 kg/m³ and were added to a red mud (with the addition of quebracho) containing a large amount of solids and having a low pH.

This solution was chosen to better reveal the effect of the additive on the viscosity and gel strength mud.

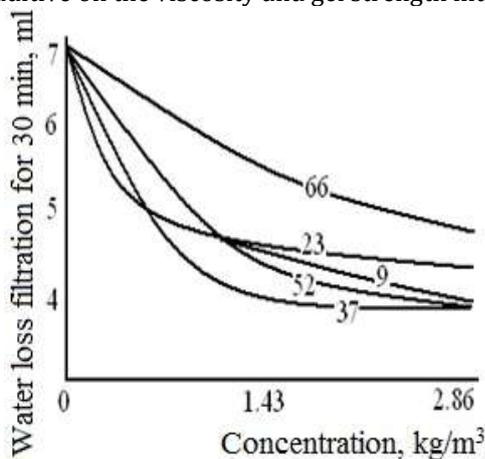


Fig. 1 - Change in water loss filtration in depending on the % content of the carboxyl group in the polymer and its concentration.

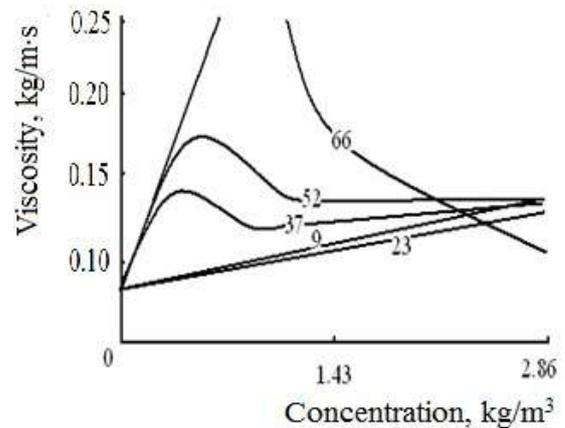


Fig. 2 - Change in viscosity depending on the % content of the carboxyl group in the polymer of the added and its concentration.

When the content of carboxyl groups is less than 50 %, the water loss filtration of the mud decreases to a minimum and the values of viscosity and yield point reach a minimum at about 23 % of carboxyl groups. If in the polymer contains between 52 and 66% carboxyl groups, the peaks in the viscosity and yield point curves are observed when the polymer is added at a concentration of about 0.849 kg/m³.

The composition of the polymers shown in the figures 1 and 2 is characterized by the percentage of carboxyl groups in the polymer (the difference between 100% and the figure shown is the percentage of amide groups).

The description of the effect of polymer characteristics indicates the possibility of a large number of combinations that can be carried out in order to obtain the desired properties of drilling muds. Often, however, improvement of one property of mud is associated with deterioration of others.

Thus, the interaction of polymers with clays leads to a change in the technological characteristics of drilling muds. However, as it was already noted, at present there is no theory explaining the complexity of these processes. Although the first stage of formation of polymer-containing systems, is the adsorption of polymer macromolecules on the solid surface of the clay. Therefore, studies of polymer adsorption and the structure of adsorption layers still retain their paramount importance for the problem under consideration.

It should be noted that very important for explaining the features of polymers adsorption from concentrated and moderately concentrated solutions are the ideas developed by Lipatov Yu.S. and his school on the aggregative mechanism of adsorption, which

establishes the connection between the structure formation in polymer solutions and their adsorption.

Let us consider these ideas.

Polymer adsorption processes at the polymer-solid interface have a great influence on the results of chemical treatment of drilling muds. Polymer adsorption leads to the formation of an adsorption layer at the interface, the properties of which, like any surface layer, differ from the properties of the polymer in the volume. Adsorption phenomena at the interfacial boundaries lead to the fact that the polymeric material acquires additional heterogeneity associated with the formation of a surface layer.

Adsorption of polymers differs significantly from adsorption of low molecular weight substances. These differences are related not only to the macromolecular nature of molecules adsorbed from the solution but also to the fact that, in principle, each concentration of the solution from which adsorption is performed corresponds (except for extremely dilute solutions) to different conformations of a macromolecular ball, the degree of mutual penetration of balls and the degree of their aggregation, i.e. different shapes and sizes of adsorbed particles. At the same time, it is exactly the deviations from the usual regularities in polymer adsorption that particularly clearly characterize the colloid-chemical factors influencing adsorption and allow one to qualitatively explain the experimental data.

The main difference between the adsorption of macromolecules and the adsorption of low molecular weight substances is that due to the large molecular weight and flexibility of the polymer chain, all macromolecule groups or segments active for adsorption are never completely bound to the adsorbent surface [16-18]. As a result of conformational constraints imposed by the surface and statistical conformations of macromolecular balls in solution, the polymer chain is bound to the surface only by a relatively small fraction of p segments. It can be determined experimentally and calculated by equation (3):

$$p = \frac{P_b}{P_b + P_s} \quad (3),$$

where P_b , P_s - number of segments bound and not bound with a surface. The p -value serves as a fundamental characteristic of adsorption.

Thus, a part of polymer chain segments "lays out" on the surface and the other part extends into the solution volume in the form of loops of different configuration

or free ends. In the latter case, the chain adsorbed by the surface can be regarded as "anchored" bonded to it. As a result of incomplete bonding of macromolecule segments near the interface a near-surface layer of polymer solution appears where local concentration exceeds the average concentration of the polymer in the volume.

When the equilibrium concentration of solution is low, after initial binding of statistical ball in one point due to chain flexibility and thermal movement of the molecule the number of chain contacts to the surface may increase and, as it were, spread out. However, the increase in concentration and the effect of the excluded volume effects lead to the change in the conditions of interaction with the surface. There is a transition from adsorption of molecules with expanded conformation on the surface to adsorption in the form of a sequence of linked segments and segments forming loops extending into the solution. It is obvious that the adsorption layer thickness (the lengths of alternating sequences of linked segments and loops) and molecule conformations are determined by the number of contact points with the surface, which is greater with small degrees of surface coverage.

As the concentration of the solution increases, the structure of the adsorption layer rearranges and the conformation of the adsorbed molecules changes. At surface saturation the adsorption layer is formed by statistically coiled balls and is "monomolecular" in relation to them. Accordingly, as the surface is saturated, the value of p decreases.

This qualitative description of the adsorption mechanism did not take into account the intrinsic flexibility of the polymer chain, the molecular weight, the interaction energy of the polymer and the surface, and the nature of the solvent. Obviously, the p value, the lengths of the sequences of bound and free segments and the thickness of the adsorption layer depend on the above factors.

On the Figure 3 shows the theoretically calculated for the models dependences of the p value and the loop length P_b on the adsorption energy [7].

Such calculations have led to the following conclusions about the influence of the interaction energy and the surface on adsorption. If the polymer molecule is large enough, contact with the surface is realized by dividing the molecule into sequences of bound and unbound segments whose size and conformation of the chain sites extending into the solution are determined only by the nature and morphology of the surface and do not depend on the molecular mass. If all locations on the surface are capable of adsorption and the segments are able to adsorb and the molecule is flexible enough, the

loops will be short and the molecule will spread out near the surface, even if the adsorption energy is low. For a flexible molecule, an energy of the order of kT is enough for more than 70% of the segments to be in contact with the surface.

As a rough scheme, one can imagine the existence of two layers in the adsorption layer: a denser layer near or on the surface, but with a density lower than that of the monolayer, and a remote less dense layer consisting of loops and tails of "anchored" meshed chains, i.e. segments do not directly interacting with the surface.

At the initial sections of adsorption isotherms, the layer has a small thickness and high concentration of polymer in it [19].

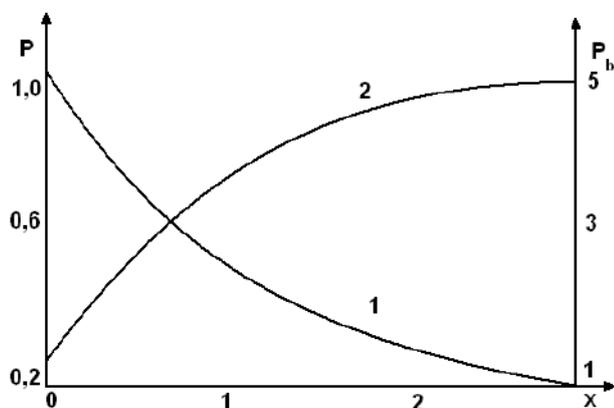


Fig. 3 - Dependence of the loop length P_l (1) and the fraction of bound segments (2) P_b as a function of adsorption energy.

At higher concentrations of the solution, the layer structure is rearranged; the newly sorbed molecules break the existing bonds. As a result, the total number of bonding points decreases, the layer thickness increases, and the concentration in the layer decreases.

Adsorption of macromolecules depends on the temperature, and thermal motion and molecular mobility increase, resulting in a decrease in the strength of bonding of segments to the surface. The influence of temperature on the size of molecular aggregates formed in solutions and capable of transferring to the adsorbent surface is very important.

Adsorption and the structure of the adsorption layer are highly dependent on the molecular weight of the polymer and the molecular-weight distribution [16]. The influence of molecular weight and molecular-weight distribution on adsorption is due to the nature and porosity of the adsorbent. In most cases for surfaces with high surface energy and on smooth adsorbents or adsorbents with small specific surface

area, an increase in adsorption with molecular weight is observed.

The difficulty in studying the adsorption interaction in highly dispersed systems lies in the fact that a number of interrelated phenomena occurs in them. At present, it has been established that the magnitude and character of adsorption depend significantly on the formation of macromolecule aggregates [16, 18] and the development of adsorbent coagulation [20-22]. On the other side, polymer adsorption causes the establishment of a new equilibrium: associations of macromolecules - individual macromolecules [23] and changes in the rate of coagulation of dispersions [24-26].

The general theoretical basis of the influence of adsorption layers on the properties of disperse systems was developed by P. A. Reh binder [27].

Stability of colloidal systems due to repulsive forces is usually achieved when the latter far exceed the forces of attraction of electromagnetic nature, which occurs when the particles approach each other. Quantitative theory of stabilization of charged colloidal particles is based on the analysis of repulsion and attraction forces depending on the distance between the particles.

The bases of the theory of stability of charged disperse systems were laid by B. V. Deryagin and L. D. Landau, as well as by Fervey and Overbeck (DLFO theory) independently of each other. It quantitatively takes into account the value of DEL interaction, i.e. electrostatic repulsion between particles.

The theory of dispersion stabilization by adsorbed polymer chains was proposed by Hesselink and coworkers [24, 28]. It also takes into account the repulsion effects as a result of overlapping adsorption layers and volume limitation. They obtained the basic equations for the interaction free energy between two planar surfaces on which the adsorbed sequences of segments, loops and tails are located. This theory takes into account the influence of tail size distribution on interaction of particles. Results of theoretical calculations show that the wider the distribution of tail sizes, the less flat the curve of dependence of free energy on the distance between the particles.

Electric-surface characteristics of polymer-containing disperse systems were not taken into account when considering the problem. Meanwhile, polymer macromolecules adsorbed on the heteropolar surface significantly influence on the DEL structure [29]. In turn, the potentials and charges of DEL influence on the conformational state of adsorbed macromolecules.

According to [30,31], modification of the dense part of DEL is connected with adsorption of only those links that are directly contacting with the surface, whereas changes in the diffuzzy part of DEL are caused by the influence of areas of adsorbed macromolecules extending into the solution volume in the form of loops and tails (Figure 4) [29].

The division of the DEL carried out by Lyklem [30, 31] is conditional, since the changes in the structure of both parts of the DEL are interrelated. Establishing the influence of polymer adsorption on the DEL structure makes it possible to study the structure of adsorption layers using the electrosurface characteristics of dispersed particles [29].

The influence of adsorption of nonionic polymers on the surface charge density of disperse particles depends on a number of factors. Under the action of the adsorption layer changes ξ - potential. The magnitude of the interfacial jump potential $\Delta\varphi$ arising from the contact between the particles of the dispersed phase and the liquid solution is composed of the ionic component due to the presence of ionic DEL on the interfacial surface and the dipole component related to the orientation of dipole water molecules near the adsorbent surface.

The polymer adsorption can also influence the distribution of ions in the diffuse part of the DEL.

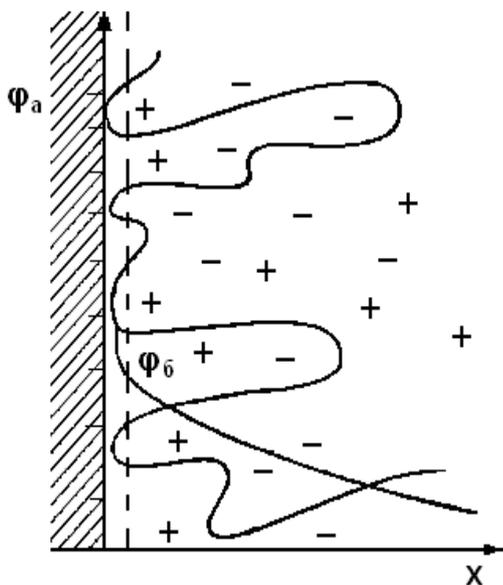


Fig. 4 - Schematic representation of a macromolecule adsorbed on a heteropolar interface and the change in potentials φ_a and φ_δ with the distance from the surface

As the degree of surface filling with adsorbed molecules in the surface layer increases, so does the dielectric permittivity and, consequently, the capacity of DEL.

Development of new chemically compatible polymers and materials for controlling properties of the solutions have been widely spread in the technology of wells drilling.

It should be noted that during the stabilization of drilling muds the synergetic improvement of technological characteristics in the process of interaction of polymer reagents takes place. Among such interpolymer systems there are widely known polyanionic water-reducing agents (CMC, Gypan, Methas), forming hydrophobic associations with nonionic high-molecular flocculants (POE, GPAA etc.).

In this regard, the problem of adsorption from polymer mixtures is of independent interest. Early works in this area [16] showed the presence of adsorption selectivity and differences in the adsorption kinetics of individual components of a polymer mixture. As a rule, one of the polymers, depending on the affinity to the surface, is adsorbed preferably. Preferred adsorption of one of the components can increase under the influence of another component incompatible with the first one. The greatest change in adsorption occurs when the solution separates into two phases. Because of the incompatibility of the components, the increase in adsorption of one of the components is accompanied by a decrease in the proportion of its segments bound to the surface.

Analysis of modern data on polymer compatibility theory in solutions and its application to the problem of adsorption from mixtures makes it possible to draw the following conclusions. In case of thermodynamic incompatibility of components in solution (but far from the phase separation point) the system can be described as a solution of polymer A in a solution of polymer B in a common solvent. Incompatibility with polymer B makes the solvent thermo-dynamically worse for each of the polymers, i.e. the influence on adsorption in this case can be described considering the role of thermodynamic quality of solvents in adsorption from concentrated and dilute solutions. Adsorption from a mixture here will proceed more easily than adsorption of one component from solution in a pure solvent, and the overall adsorption pattern will be determined by the ratio of components in solution and their affinity for the adsorbent surface.

In mixtures of polymers, not only the adsorbability of individual components changes but their mutual influence on the adsorption isotherms also occurs due to a complex change in the solution structure (the size of aggregates, the degree of their interaction with the adsorbent and with each other, etc.) and concentration growth [32-34]. When adsorbing from a mixture of polymers, depending on the adsorbent ratio, a certain inversion of adsorption may occur: at a lower

adsorbent content one of the components is sorbed to a lesser extent than the other, and as the adsorbent content increases the picture becomes the opposite.

Considered and some other features of adsorption from mixtures at different adsorbent contents suggest that the adsorbent influence on the nature of structure formation in the system by changing the ratio of aggregated and non-aggregated molecules as well as the aggregate size due to their possible collapse, which is especially noticeable at a different adsorbent – solution ratios. One can also assume the possibility of formation in the adsorption system of aggregates with different degrees of aggregation and activity against the adsorbent and changes in their proportion to the total amount at different adsorbent concentrations in the system.

The thermodynamic incompatibility of the components allows considering a solution of a mixture of two polymers as a solution of one polymer in a solvent which is a solution of the second component. Such a solvent due to thermodynamic incompatibility of components will be thermodynamically bad as compared to a pure solvent, which promotes aggregation of molecules of the first component and their preferential adsorption from the mixture. This is reflected in the absolute values of adsorption and in the form of isotherms.

Thus, another principal specific feature of equilibrium adsorption of polymer mixtures from solutions is clearly observed: the adsorption values, the degree of bonding of macromolecule segments by the surface and the form of isotherms depend on the adsorbent – solution relation. These regularities are inherent to the range of solution concentrations where aggregation processes of macromolecules are observed and concentration-dependent equilibrium between aggregated and non-aggregated macromolecules is set. The latter makes it possible for isolated macromolecules and their aggregates to move to the surface simultaneously. Changes in free energy during the adsorption of both lead, in the final analysis, to the effect of the adsorbent – solution ratio on the adsorption of polymers under equilibrium conditions.

3. Conclusions

1. The properties of polymers, above all their water solubility, depend on the type and number of functional groups, as well as the structure of the polymer crystal lattice. Not only polymer functional groups influence solubility of chemical reagents of organic origin, but also determine their reactivity, adsorption ability and structure formation in the reagent itself.

2. Polymer adsorption processes at the polymer-solid interface have a great influence on the results of chemical treatment of drilling muds. Polymer adsorption leads to the formation of an adsorption layer at the interface, the properties of which, like any surface layer, differ from the properties of the polymer in the volume. Or one can imagine the existence of two layers in the adsorption layer: a denser layer near or on the surface, but with a density lower than that of the monolayer, and a remote less dense layer consisting of loops and tails of "anchored" meshed chains, i.e. segments not directly interacting with the surface.

3. According to theory of stability of charged disperse systems DLFO quantitatively takes into account the value of DEL interaction and electrostatic repulsion between particles. As well as according to theory Hesselink takes into account the repulsion effects as a result of overlapping adsorption layers and volume limitation. This theory takes into account interaction between two planar surfaces on which the adsorbed sequences of segments, loops and tails are located. It is important to note electric-surface characteristics of polymer-containing disperse systems which significantly influence on the DEL structure. In turn, the potentials and charges of DEL influence on the conformational state of adsorbed macromolecules.

4. According to Lyklema the establishing the influence of polymer adsorption on the DEL structure makes it possible to study the structure of adsorption layers using the electro-surface characteristics of dispersed particles. Under the action of the adsorption layer changes ξ - potential. The magnitude of the interfacial jump potential $\Delta\phi$ arising from the contact between the particles of the dispersed phase and the liquid solution is composed of the ionic component due to the presence of ionic DEL on the interfacial surface and the dipole component related to the orientation of dipole water molecules near the adsorbent surface.

5. The question of the intercompatibility of polymers in the composition of drilling muds is very important. In mixtures of polymers, not only the adsorbability of individual components changes but their mutual influence on the adsorption isotherms also occurs due to a complex change in the solution structure (the size of aggregates, the degree of their interaction with the adsorbent and with each other, etc.) and concentration growth. As a result of macromolecules (ions) and their aggregates adsorption and intensity of interaction between surface and intermicrocellular liquid the technological properties of drilling muds change radically.

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