Hydrophobic interactions in adsorption layers of nonionic and anionic SAS and their influence on technological indicators of drilling fluids

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Abstract. During drilling, an important role is played by the ability of the used inhibiting, lubricating and other additives to drilling fluids to form dense, saturated adsorption layers (adlayers) on the contact surfaces. Of significant importance in the formation of saturated adlayers is the ability of hydrocarbon radicals of adsorbed SAS molecules to hydrophobic interactions, which lead to deeper lyophobization of the surface, providing high technological parameters of the drilling fluid.

At present, the nature of hydrophobic interactions of nonpolar molecules in aqueous solutions is unambiguously associated with the structural rearrangement of water near the active centers of the adsorbent surface. It is believed [1] that a rather dense structure of water is formed near the hydrophilic areas of the surface, the dipoles of which are normally oriented to the surface. At the same time, the formation of multilayers is unlikely near the hydrophobic surface, since in this case the spatial orientation of water molecules is formed due to thermal motion, and there is no equilibrium in the system. The surface of the adsorbent is energetically inhomogeneous, which is the reason for the formation of a distorted structure of bound water. As calculations show [2], water molecules adsorbed on active sites of bentonite are unable to form hydrogen bonds with each other and create a monomolecular layer on the surface of a clay particle. Therefore, the bound water molecules form chain or linked conformations.

From the point of view of analyzing the nature of hydrophobic interactions, it is most important to consider the behavior of water near lyophobic centers, which can be hydrophobic and hydrophobized (coated with SAS adlayers) surfaces, as well as hydrocarbon radicals of SAS macromolecules. Near hydrophobic surfaces, the formation of such a structure of water occurs, which inevitably leads to a decrease in the total area of phase separation due to the development of aggregation processes.

There are at least two approaches to interpreting the nature of hydrophobic interactions. The first approach, which can be conditionally called 'entropic', consists in the assertion of a forced decrease in the number of degrees of freedom of water molecules near the lyophobic surface due to the formation of new hydrogen bonds. Thus, according to the author [3], distortion and closure of hydrogen bonds in
the boundary layer of water occurs on a non-polar surface. This creates a higher degree of local ordering and leads to a significant increase in the free energy of the system due to a decrease in the entropy component. An increase in the free energy of the system determines the repulsive effect of water molecules on hydrophobic particles, forcing them to gather into aggregates and reduce the phase separation area.

On the other hand, according to [4], the structure of water adlayers adjacent to hydrophobized surfaces is less ordered compared to liquid water, and the mobility of bound molecules is higher than in the liquid phase. In this case, the density of the adsorbed phase on the hydrophobic surface is noticeably lower than the density of liquid water. All this leads to the appearance of voids in the adsorption layers that are not filled with water molecules. This state of the adsorbed phase is associated with the appearance of negative forces of wedging pressure, which cause the mutual attraction of hydrophobic surfaces.

It must be said that the ‘entropic’ approach in explaining the nature of hydrophobic interactions is more widespread, since it has a clear thermodynamic justification and many experimental confirmations.

From a practical point of view, the most interesting is the manifestation of hydrophobic interactions in the system: a surface hydrophobized with a SAS adlayer - an aqueous phase (surface/SAS//H₂O). Systems of this kind are encountered in the study of lubricating (metal surface/SAS//H₂O), inhibiting and anti-filtration (clay/surfactant//H₂O) properties of drilling fluids. An important characteristic of adlayers is the energy of hydrophobic interactions between hydrocarbon radicals of adsorbed SAS macromolecules.

In [3], a technique was proposed for assessing the energy of hydrophobic interactions between two particles coated with SAS adlayers. The energy of hydrophobic interactions U arising from the interpenetration of hydrocarbon chains of the adsorption layer can be found as follows:

\[ Y = \Delta \xi \zeta \]  

(1)

where:
- \( \xi \) - free energy released upon entering the state of association of each \(-\text{CH}_2-\) group;
- \( \Delta \) - average bulk density of \(\text{CH}_2\) - groups in adlayer;
- \( \zeta \) - overlap volume of adjacent adsorbed SAS layers.

Using equation (1), it is possible to calculate the energy of hydrophobic interactions for a wide variety of SAS classes used in drilling and to establish a correlation between the energy U values and other technological parameters of drilling fluids.

Let us consider nonionic SAS - polyalkylene glycols (PAG), the use of which as chemical reagents for drilling fluids can significantly improve the lubricating, inhibiting and anti-filtration properties of drilling fluids. The investigated PAGs are statistical copolymers of ethylene oxide (EO) and propylene oxide (PO) with a branched structure of the polyester skeleton [5-7]. The characteristics of the studied PAGs are presented in Table 1. The hydrophobic properties of these PAGs were characterized by the values of the hydrophilic-lipophilic balance (HLB), which were calculated using the equation proposed in [8]:

\[ \text{HLB} = 3,01 - 0,0023 \cdot \alpha + 0,371 \cdot E \]  

(2)

where:
- \( \alpha \) - molecular weight of the hydrophobic part;
- \( E \) - EO content in the molecule, %

The data of [5] indicate that a decrease in the mass fraction of OE is accompanied by a decrease in the HLB index and an increase in the hydrophobicity of macromolecules.

The critical micelle concentration (CMC) values were determined. Taking into account the results of [9], the method of iodine solubilization was chosen with the subsequent determination of the optical density D at the maximum point on the dependence D = f (logC), where C is the concentration of PAG in an aqueous solution. This technique is described in detail in [10]. It was found that with a
decrease in HLB, an increase in the CCM of PAG occurs. In addition, an increase in CMC is accompanied by a decrease in cloud point \( (T_p) \). The found experimental dependence of CMC on HLB for statistical copolymers of EO and PO differs radically from the analogous dependence for linear block copolymers of OE and OP (proxanols). Thus, it was shown in \([11]\) that a decrease in the HLB index of proxanol molecules is accompanied, respectively, by a decrease in the CMC values. Apparently, the increase in CMC with an increase in the total hydrophobicity of the molecules of the statistical copolymer is caused by the relatively weak fragmental screening of the polyoxypolypropylene core of the micelle by hydrophilic (oxyethylene) structural units. Therefore, a decrease in the HLB of molecules of such copolymers inevitably leads to an increase in the aggregation numbers of thermodynamically stable micellar structures characterized by an effective oxyethylene 'screen'. Let us calculate, using Eq. (1), the energy of hydrophobic interactions in an adsorption monolayer with an area of 1 \( \mu \text{m}^2 \) formed by the molecules of the studied PAGs. Overlap volume \( V \) is calculated using the following equation:

\[
V = \frac{2}{3} \pi \left( \frac{\delta}{2} \right)^2 \left( 3 \cdot R + \frac{5}{2} \cdot \delta \right)
\]

where: \( \delta \) – effective thickness of the adsorption monolayer;

\( R \) - radius of curvature of the adsorbent surface.

According to \([12]\), PAG molecules exist in aqueous solutions in meander conformations. The adsorption of PAG molecules on solid surfaces is apparently carried out in zigzag conformations. The thickness of the adsorbed polyoxypolyethylene chain is \( \sim 0.44 \) nm \([13]\), and the thickness of the zigzag conformation of polyoxypolypropylene is \( 1.97 \) nm \([12, 13]\). Taking into account the percentage of the structural units of the EO and PO, the parameter \( \delta \) is determined. The radius of curvature \( R \) was calculated in the approximation of flat surfaces with an area of 1 \( \mu \text{m}^2 \) at a given relative deviation from sphericity of 0.08%.

The average bulk density is calculated by the formula:

\[
\Delta = 16 \cdot R^2 \cdot \sigma \cdot n_c / 3 \cdot [ (R+\delta)^3 - R^3 ]
\]

where: \( \sigma \) - the number of adsorbed PAG molecules per unit surface area of the particles (calculated in the Langmuir adsorption approximation on an ideally hydrophilic (metal) surface);

\( n_c \) - the number of methyl and methylene groups of one molecule.

Free energy \( \xi \) is calculated using the following equation:

\[
\xi = r \cdot S \cdot \phi
\]

where: \( r \) - pre-association coefficient ( \( 1 > r > 0 \));

\( S \) - the degree of association (\( 0 < S < 1 \)), calculated for 1\% PAG solutions;

\( \phi \) - the change in the free energy of association of each CH2 group during micelle formation is equal to -1.08 k T.

It was shown in \([14]\) that in aqueous solutions of EO and PO copolymers, characterized by HLB values>30, the phenomenon of micelle formation is absent, and macromolecules of such copolymers exist as separate kinetically independent particles. However, the conducted studies of dilute aqueous solutions of PAGs with HLB = 32.23 reveal the ability of such PAGs to solubilize non-polar substances (for example, iodine). Thus, in true aqueous solutions, PAG molecules exist in micelle-like conformations characterized by effective screening of associated oxypropylene units by hydrophilic oxyethylene chains. Therefore, for the molecules of the studied PAG, the pre-association coefficient \( r \) is taken to be 1.

The degree of association \( S \) is calculated by the formula:

\[
S = \frac{(C - CMC)}{C}
\]

where: \( C \) - concentration of PAG in aqueous solution;

\( CMC \) - critical micelle concentration of the corresponding PAG.
According to the calculations, an increase in the energy $U$ is observed with a decrease in the HLB index of PAG molecules. Thus, the energy of hydrophobic interactions in the adlayer formed by PAG molecules with HLB $= 22.97$ is less than the energy of hydrophobic interactions in the adlayer of PAG molecules with HLB $= 5.83$ 2.5 times.

When comparing the technological parameters of drilling fluids with the calculated value of the energy of hydrophobic interactions in saturated adlayers of the studied PAGs, it is possible to state an improvement in technological properties, such as the wetting capacity ($P_o$), the filtration index ($F$) and the friction coefficient, with an increase in the energy of hydrophobic interactions. Thus, a twofold increase in the energy of hydrophobic interactions reduces the filtration rate of a clay suspension by a factor of two and decreases the initial rate of moistening by a factor of 1.4.

Let us now consider hydrophobic interactions in adlayers formed on the metal surface by molecules of anionic surfactants - light tall oil acids (LTOs), which are used as emulsion lubricating additives for drilling fluids [15]. Fatty acids LTO are 80% represented by unsaturated acids of the composition C16 -C20 and 15-17% - by the limiting composition C14 - C24. When acid is introduced into the drilling fluid, LTO is partially neutralized using various alkaline reagents (NaOH; hydrophobizing organosilicon fluid (HOF)) for this purpose. It is known [16] that during the neutralization of LTO acids with sodium alkylsiliconate, which is the basis of HOF, as a result of the polycondensation reaction, the formation of water-insoluble polyalkylsiloxanes characterized by high hydrophobicity occurs. Polyalkylsiloxanes, by binding to the oleophilic non-polar parts of the lubricant molecules, significantly improve the hydrophobization of the metal surface and increase the lubricating properties. This can explain the experimentally found increase in the efficiency of the lubricating action of the composition [LTO + HOF] in comparison with the composition [LTO + NaOH] at the same degrees of neutralization of the LTO. Let us calculate the energy of hydrophobic interactions in saturated adlayers formed on a metal surface using each of the considered lubricants. The data required to find the parameters of equation (1) are presented in Table 1.

| Lubricant additive composition | $\delta$, нм | $n_c$ | $\sigma$, м$^{-2}$ | $r$ | CMC, % |
|-------------------------------|-------------|-------|-----------------|---|-----|
| LTO: NaOH=5:1                | 11,43       | 20    | 8,21x10$^{14}$  | 1 | 0,108|
| LTO: HOF = 5:1               | 159,6       | 20    | 8,21x10$^{14}$  | 1 | 0,064|

The CMC values, when converted to neutralized fatty acids, were determined on a stalagmometer by the change in surface tension at the interface with hexane. The thickness of the chemisorption layer for the [LTO + HOF] composition was determined in the approximation of the normal orientation of fatty acid hydrocarbon radicals relative to the friction surface. Normal orientation, in this case, will be most likely as a result of hydrophobic stabilization of perpendicularly oriented non-polar chains by polyalkylsiloxanes. In the case of the [LTO + NaOH] composition, there is no stabilizing factor, and the hydrocarbon radicals of fatty acids in the friction zone are oriented almost parallel to the surface under the action of pressing forces.

Table 2 shows the values of the increments of Eq. (1) for both types of lubricant compositions, as well as the values of the energy of hydrophobic interactions in the surfactant adlayers.

| Lubricant additive composition | $\xi$, J  | $\Delta$, м$^{-3}$ | $\zeta$, м$^{-3}$ | $U$, J |
|-------------------------------|----------|-----------------|-----------------|-----|
| LTO: NaOH =5:1               | 3,96x10$^{-21}$ | 25,45x10$^{-23}$ | 6,99x10$^{-23}$ | 6,75x10$^{-18}$ |
| LTO: HOF 5:1                 | 4,16x10$^{-21}$ | 1,73x10$^{-23}$ | 13600x10$^{-23}$ | 97,88x10$^{-18}$ |
The data in Table 3 make it possible to quantitatively characterize the enhancement of hydrophobic interactions in the adlayer of fatty acid molecules upon the introduction of polyalkylsiloxane. It is shown that when using HOF as a neutralizing agent, the energy of hydrophobic interactions increases by a factor of 14, compared to the energy of hydrophobic interactions in adlayers formed by the action of NaOH on fatty acids. At the same time, as follows from Table 3, the enhancement of hydrophobic interactions provides the best values of the main technological parameters of the drilling mud treated with the [LTO + HOF] composition. In addition, it can be concluded that the energy of hydrophobic interactions in adlayers of nonionic surfactants is 1–2 orders of magnitude lower than the energy of hydrophobic interactions in adlayers of anionic SAS.

Table 3. The enhancement of hydrophobic interactions in the adlayer of fatty acid molecules upon the introduction of polyalkylsiloxane.

| Lubricant additive composition | Lubricant additive | U, J          | Pс, cm/h | F, ml | Friction coefficient |
|--------------------------------|--------------------|--------------|----------|-------|---------------------|
| ---                            | ---                | 10,7         | 36       | 0,60  |                     |
| LTO: NaOH =5:1                 | 2                  | 6,8 x 10^-18 | 6,5      | 17,6  | 0,19                |
| LTO: HOF 5:1                   | 2                  | 97,9 x 10^-18| 5,7      | 15,2  | 0,11                |

Thus, the higher the energy of hydrophobic interactions between hydrocarbon radicals in the adsorption monolayer of this SAS, the higher the energy of hydrophobic interactions between hydrocarbon radicals in the adsorption monolayer of this surfactant, the greater the efficiency of using this SAS to improve the technological performance of drilling fluids. Adlayers characterized by high values of the energy of hydrophobic interactions provide the best screening of the hydrophilic surface of the adsorbent, imparting high technological characteristics to drilling fluids.

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