

Spin probes in micellar and polymer self-associating systems*

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The results of studies of micellar and self-associating polymer systems by spin probe ESR spectroscopy are summarized. The local dynamics and structures of low-molecular-weight micelles built of cationic surfactants bearing long alkyl chains (from C₁₆ to C₂₂), gels of hydrophobically modified polymers, polymer micelles, micellar complexes of nonionic surfactant (Brij58) with hydrogels based on polyacrylic acid, and associates formed in aqueous solutions of poly(diphenylenesulfophthalide) are discussed. Interest in these systems is caused by prospects of their practical use as carriers in drug delivery, in biotechnology, for the enhancement of oil production, and in other purposes.

Key words: ESR spectroscopy, stable nitroxide radicals, spin probe, self-associating systems, micelles, polymer complexes, associates.

A new area of research was created at the end of the 1960s at the Institute of Chemical Physics of the Academy of Sciences of the USSR: stable nitroxide radicals. In 1977 the founders of this prospect M. B. Neiman, A. L. Buchachenko, E. G. Rozantsev, and G. I. Likhtenshtein were awarded the State Prize of the USSR. Interest in stable nitroxide radicals remains until the present time. This is primarily explained by possibilities of their practical use for the inhibition of polymerization processes, manufacturing of new polymers with specified properties, in biology, medicine, *etc.* International conferences on nitroxide radicals are held every three years in different countries (Hungary, Finland, Germany, Italy, France, Russia, *etc.*). The last conference (SPIN-2014) took place in September, 2014 in Zelenogradsk (Kaliningrad Region).¹

A. L. Buchachenko and his followers have studied in detail the electronic structure of stable radicals, their reactivity, complex formation with organic ligands, and possibilities of their practical use. The results obtained at that time were summarized in the monograph.² This direction is actively developed nowadays. The results obtained in the recent years are presented in the monographs.^{3,4}

A promising application widely received a great popularity of stable radicals is using them as spin labels and probes for investigation of the molecular dynamics and

structures of micellar, polymer, and biological systems. One of the first works on the application of spin probes for studying polymers was published in 1968 (see Ref. 5).

In the present review, we summarized our recent results on self-associating micellar and polymer systems obtained using spin probe ESR spectroscopy. Interest in these systems is caused by prospects of their practical use in biotechnology, dye manufacturing, pharmaceutical and petroleum industries, *etc.*^{6–8} It should be especially emphasized that self-associating systems, for examples, micelles, can act as microreactors, in which radical processes occur in other manner than in homogeneous media.^{9–11}

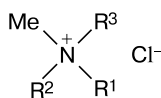
Local dynamics of long-chain surfactant micelles in aqueous media

Surfactants with long (C₁₆–C₂₂) hydrocarbon chains possess unusual viscoelastic properties in aqueous solutions. Micelles "built" of these surfactants can form a lattice of "engagements" similar to polymer solutions. Unlike polymers, this network is "dynamic," *i.e.*, capable of decomposing and reducing upon mechanical actions.^{6,12} In the presence of polymers, for example, hydrophobically modified polyacrylamide, the viscosity of aqueous solutions of surfactants increases substantially,^{13,14} which is especially important for the formation of systems applied for the enhancement of the productive performance of petroliferous strata and other practical purposes.¹⁵

[†] Deceased.

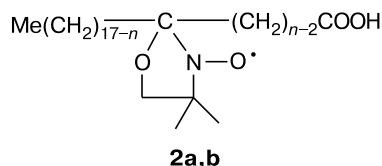
* Dedicated to Academician of the Russian Academy of Sciences A. L. Buchachenko on the occasion of his 80th birthday.

Cationic surfactants of general formula **1** with long saturated hydrocarbon chains containing one or two hydroxyl groups in the polar head have recently been synthesized.¹⁶ A very low critical micelle concentration (CMC) in a range of 10^{-4} – 10^{-5} M is a specific feature of these surfactants. They contain saturated alkyl hydrocarbon chains with the number of carbon atoms from 16 to 22. In addition, the polar head of the surfactant can include one or two hydroxyl groups.

**1a–e**

Compound 1	R ¹	R ²	R ³
a (C ₂₂ -2OH)	C ₂₂ H ₄₅	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
b (C ₁₈ -2OH)	C ₁₈ H ₃₇	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
c (C ₁₆ -2OH)	C ₁₆ H ₃₃	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH
d (C ₂₂ -OH)	C ₂₂ H ₄₅	Me	CH ₂ CH ₂ OH
e (C ₂₂ -C ₂ H ₅)	C ₂₂ H ₄₅	Me	Et

The following stable nitroxide radicals were used as spin probes: 5-doxylstearic acid (5-DSA, **2a**) and 16-doxylstearic acid (16-DSA, **2b**). These probes are slightly soluble in water and are usually localized in hydrophobic regions of the complicated systems.^{3,4,17}

**2a,b**

2: $n = 5$ (5-DSA) (**a**), 16 (16-DSA) (**b**)

Probe 5-DSA is incorporated into the micellar system in such a way that its paramagnetic fragment is located in the hydrocarbon core of the micelles at a distance of 5–7 Å from the interface.¹⁷ Its motion is correlated with the motion of surrounding surfactant molecules. In this case, the model "Microscopic Order and Macroscopic Disorder" (MOMD) was used, as a rule, for the calculation of spectra.¹⁸ The essence of the model is as follows: it is accepted that each particle in which a spin probe (for example, micelle) is solubilized is a microscopically ordered system, whereas the micellar solution as a whole is macroscopically disordered. This model is widely used for analysis of spin probe ESR spectra in micelles, emulsions, and polyelectrolyte–surfactant complexes.^{17,19,20}

The shape of the 5-DSA radical can be presented as a rotation spheroid and, therefore, anisotropy of Brownian motion of this probe was taken into account when analyzing the spectra.²¹ The parameters of the model are rotation diffusion coefficients relative to the perpendicular

(R_{\perp}) and parallel (R_{\parallel}) major symmetry axes of the rotation ellipsoid. The average correlation time τ is related to the rotation diffusion coefficients by the equation

$$\tau = 1/6R_{av},$$

where $R_{av} = (R_{\perp}^2 R_{\parallel})^{1/3}$. The angle β between the direction of the major axis of the rotation spheroid and axis Z (coincides in direction with P_z , viz., direction of the orbital of an unpaired electron of the N–O group) of the hyperfine (or Zeeman) coupling tensor of the paramagnetic fragment is also a parameter of the model.³ We accepted in the calculations that for the 5-DSA radical the angle is $\beta = 27^\circ$ and the ratio of rotation diffusion coefficients relative to different axes is $n = R_{\parallel}/R_{\perp} = 25$ (see Ref. 22).

An important parameter of the MOMD model is the ordering parameter (S) that characterizes the local organization of the studied system. This parameter depends on both the local organization of the studied system and the spin probe structure.¹⁸ Therefore, the same spin probe is usually used for comparison of the degrees of ordering of different organized molecular systems. Parameter S depends on the orientational potential and is determined by the equation¹⁸

$$S = 1/2 \langle 3\cos^2\theta - 1 \rangle,$$

where θ is the angle between the direction of anisotropy of the medium and the major axis of the spin probe rotational spheroid. The higher the S parameter, the higher the degree of local ordering of the considered system.

The ESR spectra of the 16-DSA probe were simulated in the framework of isotropic Brownian rotation ($n = R_{\parallel}/R_{\perp} = 1$) ignoring anisotropy of the medium. In this case, the paramagnetic fragment is localized near the terminal methyl group of the spin probe. Its rotation is most likely to be described by a model that does not differ strongly from the isotropic rotation model. Indeed, it has previously been shown that the rotation of the 16-DSA probe in polyelectrolyte–surfactant micellar complexes is well described by this model.²³

The question about the location site of the paramagnetic fragment of the spin probe in a micelle is also important. An answer to this question can be obtained by analysis of the isotropic hyperfine coupling constant (a_N), which depends on the polarity of the environment. For probe 5-DSA, a_N is equal to 15.9 G in water and 13.8 G in heptane,²³ 15.2 G in a sodium dodecyl sulfate (SDS) micelle¹⁷ and 15.0 G in the studied micelles. Therefore, we may conclude that in these micelles the paramagnetic fragment of the probe is localized in the micellar core some further from the interface than in an SDS micelle. Two variants are possible for the 16-DSA probe. In low-molecular-weight micelles, for example, SDS micelles ($a_N = 15.2$ G),¹⁷ the spin probe exists in the "bent" conformation and the paramagnetic fragment is localized at ap-

proximately the same distance from the interface as that for the 5-DSA probe. At the same time, in polyelectrolyte—surfactant complex the 16-DSA probe has an "extended" conformation and the paramagnetic fragment is localized near the "center" of the micelle, where the polarity of the environment is lower than that near the interface ($a_N = 14.6$ G).²³ In the studied micelles, a_N for 16-DSA is 14.9 G. These data show that the 16-DSA probe has a "bent" conformation in the studied micelles and in SDS micelles. The location of paramagnetic fragments of probes 5-DSA and 16-DSA in the studied systems differ insignificantly.

Let us consider the influence of some factors on the local characteristics of the spin probes in micellar solutions.

Temperature effect on the local dynamics of the spin probes in aqueous solutions of the surfactants. The following results were obtained by the study of the temperature dependence of the ESR spectra of spin probes 5-DSA and 16-DSA within the temperature interval 20–90 °C (surfactant concentrations in solution was, as a rule, 10 mmol L⁻¹).

1. The phase transition from the "solid" state of the surfactant to the state of a micellar solution was observed in C₂₂-2OH (**1a**) micelles in the temperature range 50–60 °C. A smooth change in the ESR spectra is observed with temperature (no phase transition) in aqueous solutions of C₁₈-2OH (**1b**), C₁₆-2OH (**1c**), and C₂₂-OH (**1d**). These systems exist in the micelle condition in the whole temperature range studied.

2. A change in the hydrocarbon chain length in a surfactant molecule from C₁₆ to C₂₂ insignificantly affects the local dynamics. Moreover, the introduction of two OH groups into the polar head of the C₁₆-2OH molecule also exerts a weak effect on the molecular mobility. However, the introduction of two OH groups into the polar head of the surfactant molecule with the long hydrocarbon chain (C₂₂) results in the appearance of the phase transition at 50–60 °C and also in a significant decrease in the local mobility.²⁴

Influence of the temperature and structure of the micelle on the ordering parameter of probe 5-DSA in micellar surfactants. The results of the study of the temperature dependences of parameter S of probe 5-DSA for all studied micellar systems²⁴ are of special interest (Fig. 1).

A shared characteristics is observed: the ordering parameter decreases with temperature. At the same time, a distinct correlation is observed for micelles C₂₂-OH (**1a**), C₁₈-2OH (**1b**), and C₁₆-2OH (**1c**): ordering parameter S increases with the elongation of the hydrocarbon chain of the surfactant molecule. This is also accompanied by an increase in the hydrophobic interaction and, as a consequence, the degree of ordering of the molecular system increases. However, the highest ordering (at 60 °C and higher) is observed for the micellar system C₂₂-2OH (**1a**). It is most likely that the formation of a micellar ordered

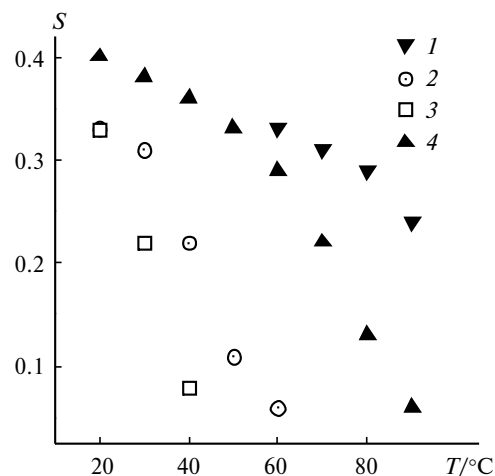


Fig. 1. Temperature plots of the ordering parameter (S) of probe 5-DSA (**2a**) in micellar solutions of C₂₂-2OH (**1**), C₁₈-2OH (**2**), C₁₆-2OH (**3**), and C₂₂-OH (**4**) (10 mmol L⁻¹).

system is favored by a combination of the hydrophobic interactions between long hydrocarbon "tails" and hydrogen bonds between the OH groups of the surfactant molecules.

Thus, the local mobility of surfactant molecules in micelles changes insignificantly with the elongation of the hydrocarbon chain, whereas the ordering parameter of the micelle increases noticeably. The increase in the ordering parameter is due to the enhancement of hydrophobic interactions with the elongation of the hydrocarbon "tail" of a surfactant molecule.²⁴

Local mobility of gels of hydrophobically modified polyacrylamides and their interaction with cationic long-chain surfactants

Hydrophobically modified polymers are polymers bearing the hydrophilic main chain and a small number of lateral or terminal hydrophobic groups. These groups are capable of self-associating in an aqueous medium to form domains (or micelles).^{25–28}

Hydrophobic groups are self-associated already at a rather low polymer concentration in solution both intra- and intermolecularly.^{29,30} Formation of intermolecular self-associates is accompanied by a sharp increase (by several orders of magnitude) in the viscosity of the solution, whereas physical gels are formed, as a rule, at concentrations of 1–2 wt.%. The concentration range of gel formation and stability of network nodes depend, first of all, on the length and number of hydrophobic groups in the macromolecule. The number of nodes is small, as a rule, but their properties determine the properties of the gels to a significant extent.

The gels of hydrophobically modified polyacrylamide were studied. The gel structure is schematically presented in Fig. 2.

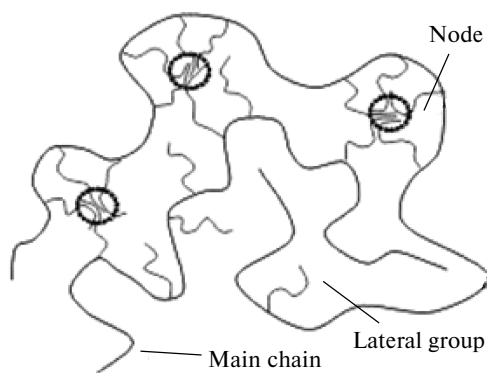
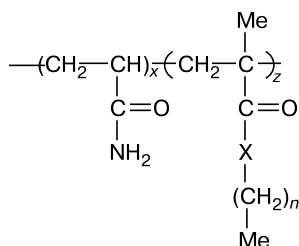
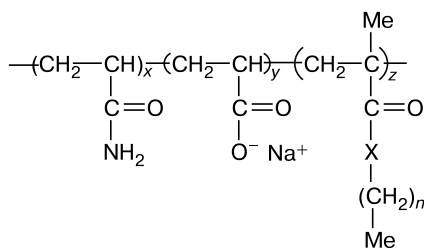


Fig. 2. Schematic structure of hydrophobically modified polyacrylamide.

Hydrophobically modified polyacrylamides can be "binary" (3) and "ternary" (4).³¹ The polymers contain a small number of lateral hydrophobic (alkyl) groups consisting of nine (C₉) or twelve (C₁₂) carbon atoms. Triple copolymers along with specified components contain in their main chains a different number of charged groups (sodium acrylate, SA).^{20,32,33}



3



4

X = NH ("amide copolymer"), O ("ester copolymer"),
n = 8 (C₉), 11 (C₁₂).

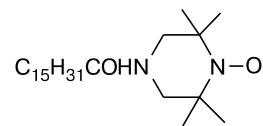
The studies were performed for 1% and 2% gels of binary polymers with different amounts of hydrophobic groups (C₉, 0.5 and 1.5 mol.%) and different lengths of the hydrophobic groups (C₁₂ and C₉).^{19,20,33}

Comparison of the local mobility of the gel network nodes and low-molecular-weight micelles. To understand specific features of the local dynamics of the gel network nodes of hydrophobically modified polymers, it is necessary to answer the question: does the local mobility of alkyl groups

forming nodes of the gel networks differ from the mobility of similar groups in low-molecular-weight micelles?

To solve this problem, we used probes 5-DSA (2a), 16-DSA (2b), and R15 (5) and the gels of the "amide" and "ester" copolymers, whose hydrophobic groups contain 12 carbon atoms (C₁₂). In this case, the model of isotropic rotation³³ was used in analysis of the spectra.

The rotation correlation times of all the probes in the gel network nodes are independent of the type of polymer (amide or ester) used for gel preparation and significantly exceed the rotation correlation times of the same probes in SDS micelle.



5

Micelles of SDS were chosen, because their hydrophobic core and the hydrophobic core of the gel network nodes of the considered polymers are formed by alkyl groups including 12 carbon atoms.

The sharp distinction between the local mobility of the gel network nodes and SDS micelles is evidently due to the fact that the hydrophobic groups forming polymer micelles (gel network nodes) are bound to the macromolecule. It should be mentioned that a similar regularity (decreasing local mobility of the micellar phase compared to "free" micelles) was repeatedly observed for the formation of polyelectrolyte—surfactant complexes.^{23,34}

Influence of the macromolecule structure on the local mobility of the gel network nodes. The following conclusions were made by the study of the influence of the structure of hydrophobically modified polyacrylamides on the local mobility of gel nodes.²⁰

1. The local mobility of the gel network nodes is almost independent of the content of alkyl groups on the polymer chain (when changing the content of alkyl groups from 0.5 to 1.5 mol.%). It is not surprising, since the local mobility of the nodes is determined by the mobility of the hydrophobic groups rather than the number of these groups.

2. The change in the alkyl group length (C₉—C₁₂) exerts almost no effect on the local mobility of the nodes. This conclusion is not unexpected: differences in the rotational mobility of the probe are small even in "free" micelles of sodium alkyl sulfates C₁₂ and C₉.³⁵ Interestingly, a change in the method of binding alkyl group with the macromolecule (through the ester or amide group) either nearly do not affect the local mobility of the nodes.

Local mobility and organization of the gel network nodes in the presence of surfactants. There is a basic question about changing local mobility of the gel network nodes in the presence of surfactants, *i.e.*, how the association of hydrophobically modified polymers with surfactants occurs.

The ESR spectra of the 5-DSA probe in micelles of surfactant C₁₈-2OH (10 mmol L⁻¹) in the gel network nodes of binary hydrophobically modified polyacrylamide

and in the gel network nodes in the presence of the surfactant are presented in Fig. 5. The analysis³³ shows that spectrum 3 (see Fig. 3) is the spectrum of the probe in mixed micelles formed by hydrocarbon fragments of the network nodes and surfactant molecules.

The dependences of the rotation correlation time of the spin probe 5-DSA and its ordering parameter on the surfactant concentration in the gel of the binary copolymer are shown in Fig. 4. Similar dependences are observed for the local characteristics of mobility and ordering of the gel network nodes of the "ternary" copolymer in the presence of C₁₈-2OH and the gel network nodes of the "binary" copolymer in the presence of the long-chain (C₂₂-C₂H₅) surfactant.

The rotation correlation times of the probe decrease with an increase in the surfactant content in the system, which is due to an increase in the local ordering of the nodes. The ordering parameter of the probe in the gel network nodes increases. This is a general regularity which

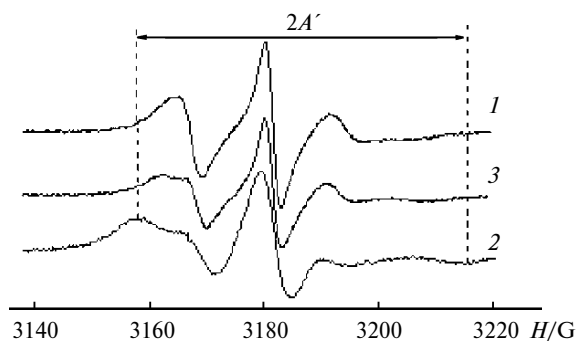


Fig. 3. ESR spectra of probe 5-DSA (**2a**) in micelles C₁₈-2OH (10 mmol L⁻¹) (1), in lattice nodes of the binary polymer gel (1 mol.% of groups C₁₂) (2), and in lattice nodes of the gel of the same polymer in the presence of surfactant C₁₈-2OH (10 mmol L⁻¹) (3) at 24 °C.

is observed for all studied systems. The observed regularity is explained by the fact that surfactant molecules penetrate into the nodes of the gel networks upon the formation of mixed micelles.

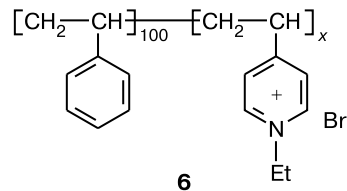
The formation of mixed micelles results in a simultaneous increase in the local mobility and degree of ordering of the nodes.

Polymer micelles

Macromolecules of ionic amphiphilic block copolymers combine the properties of polyelectrolytes, micelle-forming polymers, and surfactants. Interest in these copolymers is caused by their capability of self-organizing into segregated nanostructures and by prospects of their practical use in catalysis, target drug delivery to cells, modification of surfaces, etc.^{36,37} The study of the local structure and dynamics of such nanosystems is important for understanding their properties and extending the area of their practical use.³⁸

In dilute aqueous solutions, ionic amphiphilic diblock copolymers form micellar aggregates with the hydrophobic insoluble core and lyophilizing polyelectrolyte crown.

One of the amphiphilic diblock copolymers capable of forming polymer micelles is the diblock copolymer of polystyrene and poly-*N*-ethyl-4-vinylpyridinium bromide (PS-PEPB) (**6**).



$x = 100, 200$

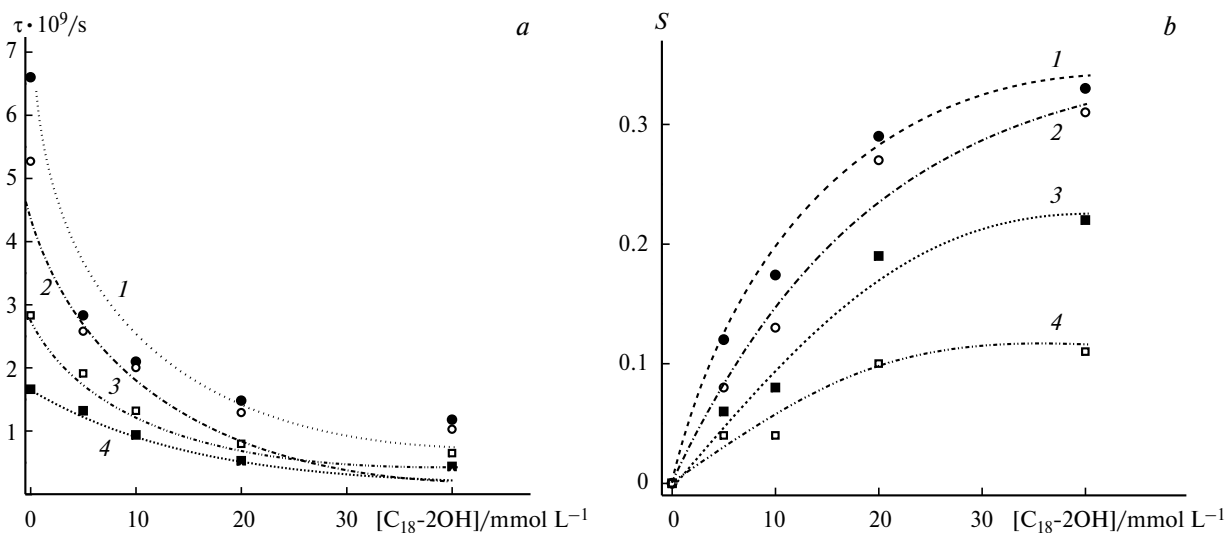
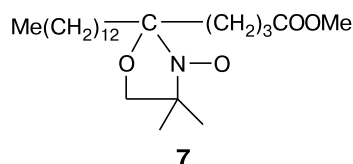


Fig. 4. Rotation correlation time (τ) of spin probe 5-DSA in lattice nodes of the binary copolymer gel (a) and the probe ordering parameter (S) (b) on the concentration of surfactant C₁₈-2OH at 24 (1), 30 (2), 50 (3), and 70 °C (4).

Spin probes 5-DSA (**2a**), 16-DSA (**2b**), and methyl ester of 5-doxylostearic acid (methyl 5-doxylostearate, (5-DSE, **7**) were used in order to determine the local mobility of the PS core of the micelles and to reveal differences in properties of the nanophase of the PS core and PS macrophase in the solid state.



The analysis of the principal values of the hyperfine coupling tensor A_{zz} , which are determined from the distance between the maxima of the utmost broad peaks in the ESR spectra of frozen solid solutions of radicals³⁹ 5-DSA, 16-DSA, and 5-DSE at 77 K in solid polystyrene and in the polystyrene core of the PS-PEPB micelle suggested that the spin probes in the micelle core exist in a more polar environment than in solid polystyrene. The near-boundary region core—crown into which water partially penetrates can be considered to be the most probable site of probe localization.³⁸ The localization sites of the spin probes in the micelle are schematically presented in Fig. 5.

It turned out that for all probes the rotation correlation times in the polystyrene core in the micelle is approximately two times lower than those in the polystyrene macrophase.

The obtained results indicate a substantial difference in the polarity and local dynamics of the layer adjacent to crown of the PS core of PS-PEPB micelles and polystyrene in the solid phase. First, the local mobility of the spin probe in the micelle core is higher than that in the polystyrene block.

These results suggest a more "friable" structure of the near-boundary layer of the PS core of the micelle com-

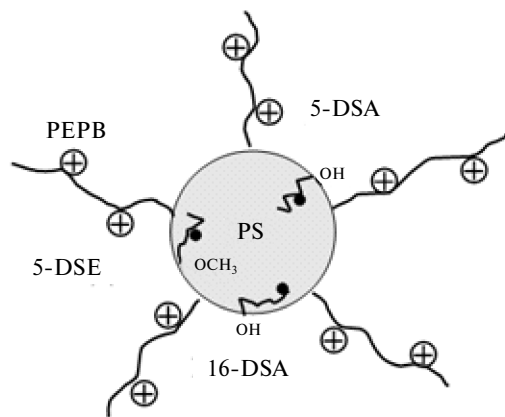


Fig. 5. Scheme of possible localization of spin probes in the polymer micelle core.

pared to the PS structure in the block. A higher "friability" of the near-boundary layer of the PS core can be due to both partial mixing of the PS and PEPB blocks at the crown—core interface and penetration of water molecules into this area. It is not excluded that the micellar core can be bilayered, *i.e.*, can consist of the external (less dense and more polar) layer and internal central layer close in properties to the corresponding homopolymer. The rotation correlation times of the probes in the micelle core are independent of the length of the polyelectrolyte block forming the crown core.³⁸ In other words, the local structure and mobility of the external part of the polystyrene core are independent of the thickness of the polyelectrolyte crown.

Micellar complexes of the nonionic surfactant with the hydrogen based on polyacrylic acid

Polymer systems based on acrylic and methacrylic polymers are widely used in medical practice, which is caused by their non-toxicity and biocompatibility. These polymers are not subjected to metabolism in the living organism. We determined the regularities of the local dynamics of micellar complexes of nonionic surfactant Brij58 ($C_{16}H_{33}(CH_2CH_2O)_{20}OH$, **8**) with the hydrogels based on polyacrylic acid.⁴⁰ Such complexes are of interest as possible carriers of drugs of prolonged action.

When studying the local dynamics of micelles, 16-DSA was used as the spin probe. The hydrogel based on cross-linked polyacrylic acid (PAA) with included surfactant **8** was obtained at room temperature by the polymerization of acrylic acid in the presence of surfactant **8** and *N,N'*-methylenebis(acrylamide) (MBAA) as a cross-linker. The degree of cross-linking of the gel was varied performing polymerization in the presence of various amounts of the cross-linking agent. When the probe mobility in the hydrogel was studied, a solution with the required pH and the swollen hydrogel (with or without micelles) were solubilized in a vessel and left to stay for 24 h at room temperature. Then the sample was taken from the solution, the liquid was removed from the surface with a filter paper, and the ESR spectra were recorded at room temperature (20 °C).

The following results were obtained.⁴⁰

1. Based on the comparison on the isotropic hyperfine coupling of the probe in micelles (free" and solubilized in the hydrogel, $a_N = 14.6\text{--}14.8$ G) and in water ($a_N = 15.9$ G), we concluded that the paramagnetic fragment of the probe is localized in the hydrophobic region of the micelle, not far, most likely, from the interface.

2. The ESR spectra of the spin probe in water at different pH (without hydrogel and without micelles) are independent of the pH and correspond to the rotation correlation time equal to $1 \cdot 10^{-10}$ s. The spin probe in acidic media (in water) decays rather rapidly (already at $pH < 7.0$) and,

hence, the ESR spectra were recorded only in neutral and alkaline media.

3. The ESR spectrum of the probe in "free" micelles (without hydrogel) in acidic and alkaline media is independent of the pH of the medium and corresponds to a rotation correlation time of $6.2 \cdot 10^{-10}$ s. It should be mentioned that water penetrates poorly into the hydrophobic core of the micelle in which the spin probe is localized. This explains why the spin probe localized in micelles does not decay in acidic media.

4. In the presence of surfactant **8** in the hydrogel, the spin probe is localized in the hydrophobic core of the micelle. It is important that a strong dependence of the rotation correlation time of the probe on the pH of the medium is observed (Fig. 6).

The rotation correlation time of the probe in micelles in the swollen gel is almost independent of the network thickness. In an alkaline medium, the rotation correlation times of the probe are nearly the same as in free micelles ($6.2 \cdot 10^{-10}$ s). In an acidic medium, the rotation correlation time is much longer ($15 \cdot 10^{-10}$ s). This is explained by two factors. First, the gel is in the "compressed" state in an acidic medium. Second, a higher number of hydrogen bonds between the non-dissociated carboxyl groups of PAA and surfactant micelles are formed in an acidic medium than in an alkaline medium. We believe that the second reason is the main. The number of hydrogen bonds is negligible in an alkaline medium. In this case, surfactant micelle binding with the hydrogel exerts almost no effect on the local mobility of the micelles. The scheme of the complex formation between the surfactant and hydrogel in acidic and alkaline media is shown in Fig. 7.

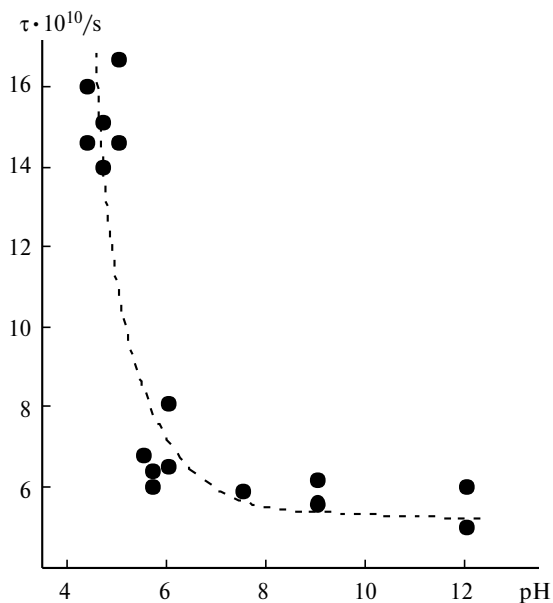


Fig. 6. Rotation correlation time (τ) of spin probe 16-DSA vs pH of the medium in micelles of Brij 58 localized in the PAA hydrogel.

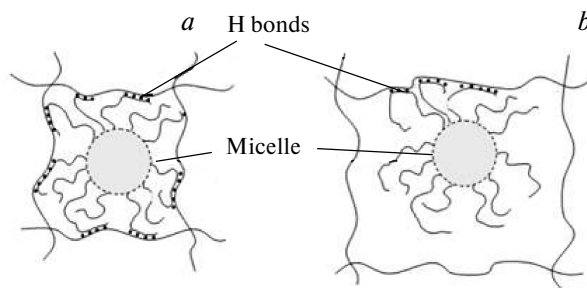
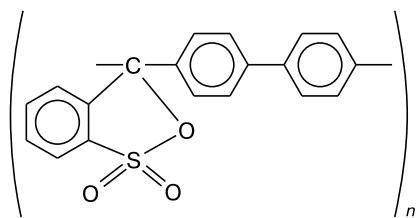


Fig. 7. Scheme of complex formation of the surfactant with the hydrogel in acidic (a) and alkaline (b) media.

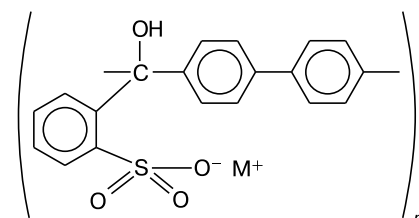
The ESR spectra of the spin probe in the solution above the hydrogel were recorded. The probe decays in the acidic medium and, hence, an attempt to record the ESR spectrum was unsuccessful. The ESR spectrum of the solution above the polymer in alkaline and neutral media is identical to the spectrum of the probe in water (correlation time $1 \cdot 10^{-10}$ s). This means that there are no micelles in the solution above the polymer even in alkaline media (otherwise the probe would be localized in the micelles and its rotation correlation time would be $6.2 \cdot 10^{-10}$ s). It is likely that micelles are absent because they do not escape from the polymer "captive" even in an alkaline medium, whereas the probe is located in the solution above the hydrogel in the equilibrium concentration (*i.e.*, freely leaves the micelles). Therefore, if a hydrophobic substance would be placed instead of the spin probe into micelles of surfactant **8** or other nonionic surfactant based on poly(ethylene glycol), in neutral or alkaline medium this substance would be equilibrated with the substance in the solution. The practical use of these systems can be assumed, since a drug can be hydrophobic. In other words, the system studied can potentially serve as a depot for hydrophobic drugs of prolonged action.

Structuring in aqueous solutions of poly(diphenylenesulfophthalide)

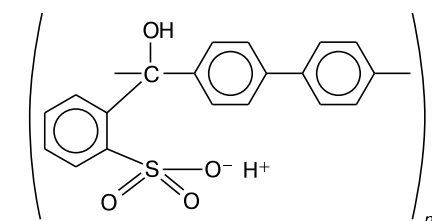
Poly(diphenylenesulfophthalide) (PDPSP) (**9**) is a polymer containing aromatic diphenylene fragments in the main chain of the macromolecule and side cyclic sulfophthalide groups.⁴¹ The interaction of PDPSP with alkaline metal hydroxides results in sulfophthalide ring opening without changing the structure of the main chain and in the formation of polymer salts with the most probable structure **10** (see Refs 42 and 43). In order to elucidate the possibility of using PDPSP derivatives in diverse areas, such as dye manufacturing, biotechnology, and others, water-soluble derivatives PDPSP-H(M) (**10**) and PDPSP-H(M) (**11**) were synthesized and their solutions were studied by the light scattering and spin probe methods.⁴⁴



9



10



11

The dynamic light scattering data showed a unimodal particle size distribution in an aqueous solution of PSPSP-H(P) with an average unimodal hydrodynamic diameter of 20 nm. This value corresponds to the dimension of the coil of an individual macromolecule with a molecular weight of $1.58 \cdot 10^5$ (this is the molecular weight of the initial polymer) containing ~95 vol.% of the solvent and to the size of associates of ~20 macromolecules of a dense globular structure.

The question about the structure of these particle (whether they are individual macromolecular coils or associates) was answered by spin probe ESR spectroscopy.⁴⁴ The spin probes used were 5-DSA, 16-DSA, and 5-DSE. Similar results were obtained when using different probes.

Coils of individual macromolecules in solution are "transparent" for the solvent. These are labile aggregates through which solvent molecules pass freely. The local mobility of probe molecules in the polymer coil practically does not differ from the mobility of the same probe in the initial solvent.⁴⁵

The detected rotation correlation times of the 16-DSA probe in a solution of macromolecules PDPSP-H(P) ($9.5 \cdot 10^{-9}$ s) is much longer than the rotation correlation time of this probe in water ($< 1 \cdot 10^{-10}$ s²³). It follows from this that the probe is localized in slowly moving hydrophobic regions of the associates and, which is especially important, the macromolecules exist as associates rather than individual polymer coils.

Association is caused by the interaction of hydrophobic fragments of the macromolecules with enhanced rigidity due to biphenylene groups. The local mobility of the associates differs insignificantly from that of polymers in the glassy state, for example, polystyrene. Similar results were obtained by the study of associates in solutions of polymer salts using spin probe ESR spectroscopy.¹⁰

The method of spin probe ESR spectroscopy is an efficient tool for studying micellar and polymer self-associating systems. As a rule, these systems are formed in aqueous media due to the hydrophobic interaction of nonpolar groups.

The local mobility in the hydrocarbon core of low-molecular-weight micelles changes insignificantly with the elongation of the hydrocarbon chain of the surfactant (C₁₆–C₂₂) molecule, whereas the ordering parameter increases noticeably. The ordering parameter increases due to the enhancement of hydrophobic interactions.

The hydrophobic interactions of the alkyl groups of the hydrophobically modified polymers (for example, hydrophobically modified polyacrylamide) result in the formation of "macromolecular micelles" in aqueous media that differ sharply from the properties of low-molecular-weight micelles. A polymer gel is also formed due to these interactions. The gel network nodes of hydrophobically modified polymers are associates of alkyl groups. The introduction of surfactants into the polymer gel results in an increase in the local mobility of the gel network nodes, and the network nodes become more labile. This is accompanied by the formation of mixed micelles consisting of hydrocarbon fragments forming nodes of the gel networks and surfactant molecules. The use of surfactants makes it possible to purposefully affect the local mobility of the nodes and, as a consequence, the macroscopic properties of the gels.

Polymer micelles built of amphiphilic ionic diblock copolymers, for instance, of diblock copolymer of polystyrene and poly(*N*-ethyl-4-vinylpyridinium bromide), are of special interest. The core of this micelle consists of polystyrene blocks, and the crown consists of poly(*N*-ethyl-4-vinylpyridinium bromide) blocks. The micellar core is not homogeneous and consists of the external (less dense and more polar) layer in which water has penetrated in part and of the internal central layer, whose properties are similar to those of the corresponding homopolymer.

It has been found by the study of the micellar complexes of the nonionic surfactant (Brij58) with the hydrogel based on polyacrylic acid that the local mobility of the hydrocarbon core of a micelle in acidic media is much lower than that in alkaline media. This is explained by the fact that much more surfactant molecules in a micelle

participate in complex formation in acidic media compared to alkaline media. However, even in alkaline media the surfactant micelles cannot leave the hydrogel, whereas the spin probes localized in the micelle are located in the external aqueous medium. This result provides wide possibilities for using such complexes as drug carriers in target drug delivery.

In aqueous solutions of poly(phenylenesulfophthalide) derivatives, the macromolecules exist as poorly mobile associates, whose local mobility insignificantly differs from the local mobility of glassy polystyrene, rather than as individual coils. This conclusion is important for practical use of the systems studied.

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