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Spin probes in micelles

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Abstract. The results of studies of the molecular dynamics and structure of direct, polymeric and reverse micelles by the spin probe method using stationary ESR spectroscopy and electron spin echo spectroscopy are considered. The spin probes permit the determination of the characteristic rotation times, shapes and sizes of micelles and the local molecular mobility and polarity of different micelle regions. They also make it possible to record the processes involving the formation of micelles and premicellar aggregates and to determine the state of water in the cores of reverse micelles. Electron spin echo spectroscopy provides information about the detergent conformation and the permeability of the hydrocarbon regions of micelles. The bibliography includes 78 references.

I. Introduction

Spin probes are fine instruments for the study of complex heterogeneous systems.[1–4] Ordered micellar systems (direct and reverse micelles, microemulsions, vesicles, etc.) are important in solving many fundamental and applied problems (see, for example, Refs 6 and 7) and are convenient objects for investigations using the spin probe method. For these reasons, micellar systems have been of great interest for many years.[5] The continuing development of the ESR spectroscopic methods and the synthesis of new spin labels make it possible to solve many problems at a new level.

The present work discusses the recent results of studies on direct, reverse, and polymeric micelles by the spin probe technique.

II. Determination of the shape and size of micelles by ESR spectroscopy

The shape of a direct micelle formed by an ionic detergent in water near the critical micelle concentration (CMC) differs only slightly from spherical symmetry. The micelle consists of a hydrocarbon core, a water–hydrocarbon layer whose thickness is determined by the depth of penetration of water molecules into the hydrocarbon part of the micelle, hydrated polar groups, and a layer of aqueous solution adjacent to the micelle.[7] The charged polar groups form a compact zone several ångstroms thick on the surface of the micelle (the Stern layer), where the majority of the counterions compensating the total micelle charge are localised. The remaining counterions are located in the Gouy–Chapman layer (with a thickness up to several hundred ångstroms). They are totally dissociated and can be exchanged with other ions present in the solution.[8]

The micelle is a dynamic formation: the lifetime of a detergent molecule in the micelle is normally $10^{-7}-10^{-6}$ s, whereas the half-life of the micelle is $10^{-3}-1$ s.[7,9]

Different physicochemical experiments reveal different effective sizes of the micelle. For example, the rotational and translational dynamics of the micelle as a whole are determined by its outward size (R), evidently including the Stern layer, whereas the kinetics and recombination mechanism of hydrophobic active radicals[10] are governed by the size of the hydrocarbon core, where these radicals are dissolved.

Table 1 presents some parameters of alkyl sulfate micelles in water: the critical micelle concentration, the aggregation number, i.e. the average number of detergent molecules localised in the micelle, the micelle radius (R), and the rotational correlation time of the micelle as a whole calculated by the Stokes–Einstein equation using the values of R reported in Ref. 13.

$$\tau = \frac{4\pi\eta R^3}{3kT} \qquad (1)$$

Here η is the viscosity of water.

The rotational correlation time can be easily determined from the ESR spectrum of the spin probe,[1–4] and the radius of the rotating particle can be calculated by Eqn (1). Furthermore, the anisotropy of the rotation of the probe, i.e. the ratio of the rotation frequencies around different molecular axes,[2,14] can be determined from the ESR spectrum of the spin probe. If the rotating species is represented by an ellipsoid of rotation whose rotational anisotropy is determined by the shape of the particle, then the degree of nonsphericity of the particle, i.e. the ratio of the main axes of the ellipsoid, can be determined from the rotational diffusion data.

In order to find the rotational correlation time of the micelle and its nonsphericity from the ESR spectra of the spin probe, one important condition must be fulfilled: the spin probe should rotate only together with the micelle. In other words, rotation of the probe relative to the micelle is inadmissible.

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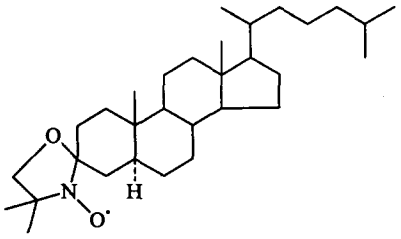
Table 1. Critical micelle concentrations, aggregation numbers, and rotational correlation times of micelles of sodium alkyl sulfates in water at 25 °C.

Detergent	CMC/M	n	R/Å		τ/ns
			I	II	
C-6	4.2×10^{-1}	17			
C-7	2.2×10^{-1}	22		16.0	0.40
C-8	1.3×10^{-1}	27	15.5	17.1	0.45
C-9	6.0×10^{-2}	33	18.0[a]	19.2	0.65
C-10	3.3×10^{-2}	41	19.8	21.3	0.90
C-11	1.6×10^{-2}	52	22.2	23.5	1.20
C-12	8.2×10^{-2}	64	25.2	25.6	1.50
C-14	2.05×10^{-3}	80			
C-16	4.5×10^{-4}	100			

Note. The first column indicates the number of carbon atoms in the detergent alkyl chain; the values of n are based on data reported in Ref. 12; (I) determined by the light scattering method[11] at [NaCl] = 0.1 M; (II) estimated from the sizes of detergent molecules.[13]
[a] [NaCl] = 0.2 M.

An attempt to determine the shape of a sodium dodecyl sulfate micelle (concentration 0.1 M) in water by the spin probe method has been undertaken.[15] This attempt is undoubtedly interesting since the spherical micelles adopt a cylindrical shape as the detergent and electrolyte concentrations are increased;[16] this process can be monitored by the spin probe method.

3-Doxylcholestane, with a molecular size comparable to the size of the micelle, was chosen[15] as the probe:



It was assumed that the probe rotates only together with the micelle and the nonsphericity of the micelle, i.e. the ratio of the main axes of the ellipsoid of rotation (d), was determined from the data on the anisotropy of the rotation. It turned out that the shape of the micelle at 22 °C is not spherically symmetrical but can be approximated by an ellipsoid of rotation whose long axis is 7.4 times longer than the short axis. The value of d increases as the temperature is increased, but even at 59 °C $d = 5.7$, i.e. the micelle is not spherical.

Unfortunately, in this case, the rotation of the probe itself relative to the micelle cannot be excluded. Also, one cannot rule out the fact that the rotational anisotropy is due not only to the nonsphericity of the micelle but also to the nonsphericity of the spin probe molecule. Therefore, it is difficult to agree with the authors above[15] that the sodium dodecyl sulfate micelles are nonspherical. However, further investigations with probes of various sizes differing in the shape and structure of the molecule might allow the separation of the two factors — rotation of the micelle and rotation of the spin probe itself — and provide a technique for the determination of the shapes and sizes of micelles using spin probes.

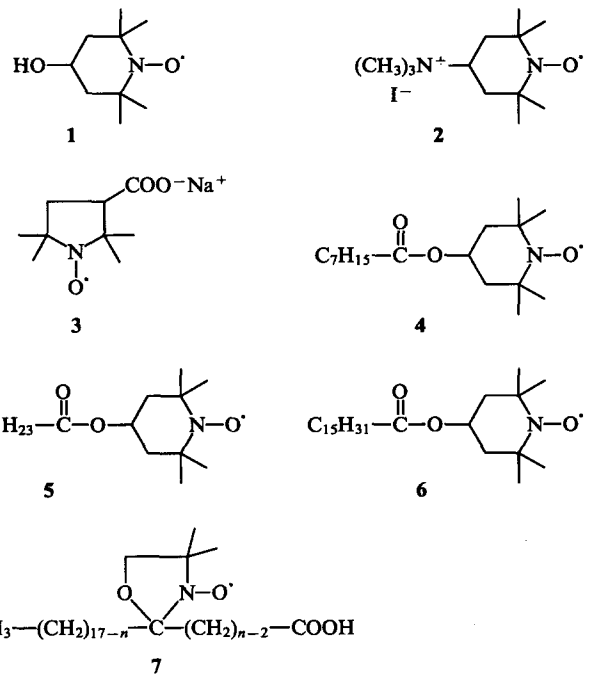
III. Direct micelles

Direct micelles are constructed in such a way that the molecules of a surface-active compound (surfactant) are combined via their hydrophobic hydrocarbon (or fluorocarbon) chains, whereas the polar groups are directed towards water.[7] Let us consider the results of studies on the local molecular dynamics and structure of such micelles by the traditional ESR spectroscopic and spin echo methods.

1. ESR spectroscopy of spin probes

A micelle is a complex heterogeneous system. Therefore, the question of the location of the probe in micelles is of fundamental importance. In essence, it concerns the region (hydrocarbon core, interface, the Stern layer, etc.) about which the spin probe provides information.

The formulae of several nitroxyl radicals used as spin probes in the study of the molecular dynamics and structure of direct micelles[17–21] are given below.



The solubility of radical **1** in water is 100 times higher than in heptane.[2] It is believed[17] that this radical is located in the aqueous solvate layer surrounding the micelles of anionic detergents such as sodium octyl sulfate $C_8H_{17}SO_4Na$ (SOS), sodium dodecyl sulfate $C_{12}H_{25}SO_4Na$ (SDS), and sodium hexadecyl sulfate $C_{16}H_{33}SO_4Na$ (SHS). This radical is located mainly outside the micelle; it has not found wide use as a spin probe for studying micellar systems.

The positively charged radical **2** and the negatively charged radical **3** interact electrostatically with the negatively charged surfaces of anionic detergents (radical **2**) and the positively charged surfaces of anionic detergents (radical **3**). Radical **2** is located closer to the surface of the sodium dodecyl sulfate micelle than radical **3** is to that of the dodecyltrimethylammonium bromide micelle. This explains the fact that the ESR spectra of radical **2** are more sensitive to the structure and dynamics of the micelle than those of radical **3**.[20]

The hydrocarbon regions of radicals **4**, **5**, and **6** are located in the hydrocarbon core of the direct micelle, but the nitroxy-group is located near the micelle surface.[18,20] When using probes **5** and **6**, one should keep in mind that these probes can themselves form micellar solutions.[18]

Doxylstearic acids **7** (n-DSA, n = 5, 7, 10, 12, 16) are located in direct micelles in such a way that the carboxy-group is in the polar layer of the interface, whereas the nitroxy-group resides in the hydrocarbon core of the micelle.[21]

Spin probes make it possible to find the critical micelle concentration, determine the polarity and local molecular mobility of micelle regions where the probe is located, and detect the formation of premicellar aggregates.

At the critical micelle concentration redistribution of the probe in solution occurs which results in an abrupt change in its ESR spectrum. At concentrations below the CMC, the probe is dissolved in water. If the concentration is above the CMC, the probe is located in the micelle or on its surface. At a detergent concentration equal to CMC, a sharp change in the polarity of the probe environment and in its rotational mobility occurs. As a rule, the values of CMC determined by the spin probe method differ insignificantly from the corresponding values determined by other methods. For example, CMC values of 0.14, 8.3×10^{-3}, and 5.5×10^{-4} M were found for sodium octyl, dodecyl, and hexadecyl sulfates, respectively using probe **2**.[17] These values differ only slightly from the CMC values presented in Table 1.

The determination of the polarity of the probe environment and of its location in the molecule is based on the fact that the isotropic hyperfine coupling constant of the unpaired electron of the radical with the nitrogen nucleus (a_N) and its g-factor depend on the polarity of the medium where the spin probe is sited.[1] For example, a_N = 17.16 G for the di(*tert*-butyl)nitroxyl radical in water, whereas in heptane[3] a_N = 15.10 G. For many nitroxyl radicals, the difference between the a_N values in water and heptane is ~2 G. The value of a_N changes monotonically as the polarity of the environment changes. Hence, measurement of a_N makes it possible to determine the polarity of the probe environment and to draw a conclusion as to where the probe is located in the micelle. For example, the formation of micelles by sodium hexadecyl, dodecyl, or octyl sulfates results in a 1.0, 0.62, or 0.32 G decrease in a_N for probe **2** (in water, a_N = 16.85 G for this radical) respectively. In the opinion of the authors[17,20] such changes may be due to two reasons. First, the longer the hydrocarbon chain of the radical, the closer is the spin probe to the micelle core. Second, the arrangement and polarity of the aqueous layer in the vicinity of the micelle surface can depend on the length of the hydrocarbon group of the detergent. In our opinion, the first reason is more probable.

The determination of the local molecular mobility is based on the measurement of the rotational correlation time[1-4] of the radical. This value is linked to the viscosity of the system by the Einstein–Stokes relation [see Eqn (1)] and characterises the microviscosity and the local molecular mobility of the micelle at the location of the probe. However, it is important to be sure that the rotation of the probe is governed by the local mobility rather than the rotation of the whole micelle. This condition is fulfilled if the rotational mobility of the probe is much greater than that of the micelle.

The rotational correlation times of probe **2** on the surfaces of micelles of sodium octyl, dodecyl, and hexadecyl sulfates (which amount to 5.8×10^{-11}, 2.2×10^{-10} and 1.6×10^{-10} s) are much lower than the rotational correlation times of the micelle as a whole (see Table 1) and 5–20 times greater than the rotational correlation time of the probe in water.[17] This is explained by the fact that the local microviscosity of the surface layer of the micelle, where the spin probe is located, is markedly greater than the microviscosity of water. However, it is important to emphasise that the mobility of the surface layer is rather high.

The conclusion about the high local mobility of the surface layer of the micelle is also confirmed by results obtained using spin probes with long hydrocarbon radicals. The rotational correlation times of radical **4** in a micelle of sodium octyl sulfate, radical **5** in a micelle of sodium dodecyl sulfate, and radical **6** in a micelle of sodium hexadecyl sulfate are 1.2×10^{-10}, 2.4×10^{-10}, and 1.6×10^{-10} s, respectively; they differ insignificantly from the rotational correlation times of radical **2**. The hydrocarbon regions of these radicals are dissolved in the micelle hydrocarbon core, whereas the nitroxy-group is located in the surface layer, and its mobility is determined predominantly by the local molecular mobility of the micelle in the vicinity of the surface layer.[18,19]

Of particular interest are the results in Ref. 21 obtained using doxylstearic acids (*n*-DSA), in which the nitroxy-group is bound to different atoms of the alkyl chain, as spin probes. These probes are located in the micelle in such a way that the carboxy-group is in the polar layer of the micelle, whereas the nitroxy-group is in the hydrocarbon core. The correlation times of these probes in micelles are fairly high (Table 2) and are comparable with the rotational correlation times of the micelle as a whole (cf. the data in Table 1).

Table 2. Rotational correlation times of doxylstearic acids in sodium dodecyl sulfate and dodecyltrimethylammonium bromide micelles at 25 °C (concentration 0.1 M) (cf. Ref. 21).

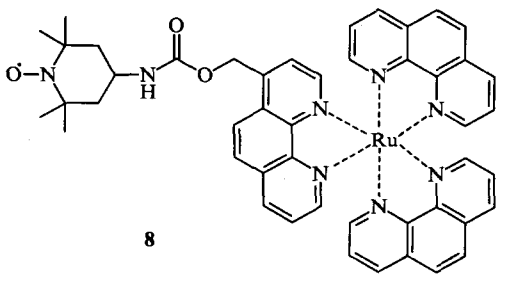
Detergent	τ/ns		
	5-DSA	12-DSA	16-DSA
Sodium dodecyl sulfate	1.1	0.82	0.43
Dodecyltrimethylammonium bromide	1.0	0.82	0.43

Apparently, the times observed are mainly determined by the intramolecular mobility rather than the rotation of the micelle as a whole. In the latter case, the values of τ for the three doxylstearic acids should not differ.

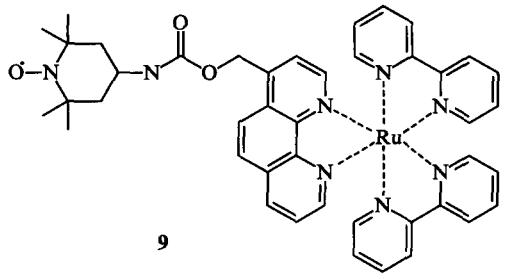
The local motions in the hydrocarbon core of the micelle occur at frequencies of $\sim 10^{-9}$ s^{-1}; the mobilities in the core of anionic (sodium dodecyl sulfate) and cationic (dodecyltrimethylammonium bromide) micelles are practically equal. The mobility of the hydrocarbon chains near the polar shell is lower than in the micelle centre. This explains the fact that the rotational correlation times of spin probes decrease as the nitroxy-groups move further away from the micelle surface.

Let us consider the results obtained using spin-labelled ruthenium complexes, whose formulae are shown below, as spin probes.[22] These complexes without spin probes are often used in the studies of photophysical processes in micelles.[23]

The sizes of the complexes are fairly large and comparable to the sizes of micelles (e.g. the diameter of complex **8** is ~18 Å). The rotational correlation times increase monotonically for micelles of sodium alkyl sulfates with hydrocarbon chains of different sizes (the number of carbon atoms varied from 7 to 14), while a_N decreases as the alkyl chain length increases. This is explained by the fact that the ruthenium complex is submerged deeper into the micelle the longer the hydrocarbon chain of the detergent. However, the difference between the a_N values for the complex in water and in the micelle is not high; for example, it does not exceed 0.4 G for $C_{14}H_{27}SO_4Na$. This implies that even for the largest micelles, the spin-labelled complex is located near the micelle surface and its mobility is determined by the molecular dynamics of the surface layers of the micelle. The rotational mobility of the complex is well correlated with the translational mobility determined from photophysical experiments.[24] The rotational and translational dynamics of large species, such as ruthenium complexes, on the micelle surface are probably correlated and the local molecular mobility of the micelle affects these motions similarly.



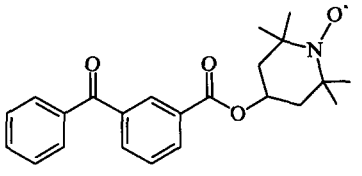
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9

The rotational mobility of the complex depends not only on the length of the hydrocarbon group of the detergent but also on the nature of the polar group: the rotational correlation times of the ruthenium complex in the sodium dodecyl sulfate micelle are greater than in the sodium laurate micelle. This difference arises from the fact that a micelle containing sulfate groups interacts with the complex more strongly than a micelle containing carboxy-groups (in both cases, the hydrocarbon group of the detergent contains 12 carbon atoms).

The rotational correlation time of the spin probe



in the micelle increases by a factor of ~2.5 [10] when the number of carbon atoms in a sodium alkyl sulfate molecule increases from 7 to 14. Unfortunately, the value of a_N has not been reported in Ref. 10. Therefore, it is difficult to reach a conclusion as to why its rotational mobility changes, i.e. due to a change in the microviscosity of the micelle or due to a change in the site of the latter in the micelle. In our opinion, the second reason is more important.

It is interesting to note that an attempt has been made to determine the lifetime of radical **2** on the micelle surface by analysing the widths of the ESR spectral lines. [17,24] This value characterises the rate of transfer of the spin probe from the micelle into the aqueous solution. The values of $> 5.7 \times 10^{-7}$, $\sim 0.93 \times 10^{-7}$, and $\ll 1.8 \times 10^{-7}$ s were obtained for micelles of sodium hexadecyl, dodecyl, and octyl sulfates respectively. These values differ only slightly from those characterising the lifetime of molecules of the respective detergents in micelles determined by other methods. [25]

Recently, [26] the results of measuring the rotational mobility of a spin probe (doxylstearic acid) were used to establish the compatibility of hydrocarbon and fluorocarbon ionic detergents in a micelle; [26] earlier, the spin probe method was used extensively to diagnose the compatibility of polymers in mixtures. [4]

The formation of premicellar aggregates has been detected in solutions of alkyl sulfate detergents by using spin-labelled ruthenium complexes as spin probes.[22] The ESR spectrum of a spin probe at concentrations of the detergent far below the CMC (for example 1.5×10^{-3} M for sodium dodecyl sulfate at CMC $\simeq 8.3 \times 10^{-3}$ M) represents a superposition of a narrow triplet (the spectrum of the probe in water) and a broad triplet arising from the molecules of the probe located on premicellar aggregates. These aggregates are small and their sizes are much smaller than those of a micelle. Several spin probe molecules are adsorbed on one premicellar aggregate. The spin probes are spaced so closely that their dipole interaction results in a noticeable broadening of the ESR spectrum. The formation of premicellar aggregates has been observed for sodium alkyl sulfates with 7 – 14 carbon atoms in the hydrocarbon chain.

Naturally, one cannot rule out the possibility that the formation of the premicellar aggregates can be initiated in this case by the spin probe molecules. However, it is important to emphasise that the conclusion that premicellar aggregates exist in detergent solutions [22] is in good agreement with the results of thermodynamic calculations,[7] photophysical measurements,[27] and data obtained by other methods.[28,29]

2. Electron spin echo modulation spectroscopy

The idea of applying the electron spin echo modulation method to determine the structure of the micelle consists in the following. The electron spin echo signal of the probes can be modulated by the weak dipole hyperfine interaction of the unpaired electron of the probe with the magnetic moments of the surrounding nuclei. The modulation depth depends on the number of surrounding atoms and their distance from the unpaired electron, provided that this distance does not exceed ~6 Å.[30] Usually, the depth of modulation by deuterium atoms is determined. Once the modulation depth has been determined, one can conclude which magnetic nuclei surround the spin label and how far away they are located.

Experiments on the determination of the micelle structure by the electron spin echo modulation method are normally performed in quickly frozen solid solutions at 4.2 K (the dipole interaction in the liquid is averaged to zero due to molecular motion). [31–41]

Much effort has been devoted to ensuring that the structure of the micelles does not change upon rapid freezing. For example, the radical-cation of *N,N,N′,N′*-tetramethylbenzidine (TMB) is readily formed when TMB is illuminated. This radical-cation is stable in micellar systems, but is quickly destroyed in homogeneous media.[42] It turned out that if this radical-cation is obtained in a micellar system which is then quickly frozen and allowed to thaw, then the ESR spectrum of the radical-cation is observed for a long time at room temperature.[34] A similar result is observed when the radical-cation is generated in a frozen micellar system, and the ESR spectrum is observed at room temperature.[33] According to the authors[31–41], these results imply that the micellar structure of the system is retained upon freezing.

There is also other evidence that the micellar structure is retained upon rapid freezing. In particular, the aggregation numbers of sodium dodecyl sulfate micelles in water at room temperature and in a frozen system differ only slightly. [43] The conclusion that the micellar structure is retained upon rapid freezing is also confirmed by electron microscopy. [44]

The most interesting data were obtained by the electron spin echo modulation method; doxylstearic acids, in which the nitroxy-group is linked to different carbon atoms of the alkyl chain, were used as spin probes.[31–41]

Let us now consider the results obtained for ionic and nonionic detergents.

a. Ionic micelles

Studies of the micelles formed by sodium, lithium, and tetramethylammonium dodecyl sulfates showed [31–34,41] that the structures of these micelles differ strongly, although the lengths of the alkyl parts of the detergent molecules are the same (12 carbon atoms). The differences in the structure and permeability of these micelles are governed by the nature of the counterion. Detergent molecules deuteriated at the terminal methyl groups, deuteriated water, and the deuteriated tetramethylammonium cation were used in these studies.

The modulation depth of the spin echo of sodium dodecyl sulfate micelles, which characterises the dipole interaction of the lone pair belonging to the spin label with the deuteriated terminal methyl groups of the detergent, increases monotonically as the nitroxy-group moves further away from the carboxy-group of the doxylstearic acid (i.e., as *n* in the formula of compound **7**, *n*-DSA, increases). This implies that the distance between the spin label and the terminal methyl groups increases.

The depth of modulation due to dipole interaction with the magnetic moments of the deuterium in D_2O decreases as the spin label moves further away from the carboxy-group, since this results in an increase in the distance between the spin label and the micelle surface. According to the authors,[32,33] the doxylstearic acids in a sodium dodecyl sulfate micelle have an extended conformation and the detergent molecules are ordered in such a way that the terminal methyl groups are located near the micelle centre. Water hardly penetrates into the hydrocarbon micelle core.

Quite different behaviour is observed in the case of micelles of tetramethylammonium and lithium dodecyl sulfates. They are characterised by a nonmonotonic variation of the spin echo modulation depth due to interactions with the terminal methyl groups of the detergent and with D_2O as the spin label in *n*-DSA moves away from the carboxy-group. Furthermore, the depth of modulation due to the interaction with D_2O is much greater for these micelles than the corresponding value for the sodium dodecyl sulfate micelles.

The features observed can be explained by the fact that the doxylstearic acid in micelles of tetramethylammonium and lithium dodecyl sulfates, in contrast to that in micelles of sodium dodecyl sulfate, has the bent conformation[32] drawn schematically in Fig. 1. Moreover, the structures of the micelles of lithium and tetramethylammonium dodecyl sulfates differ significantly from that of sodium dodecyl sulfate (Fig. 2). In the former case, the detergent molecules in the micelle are bent and the micelle has an open structure, where the counterion can be located between the anionic 'heads' of the micelle. As a result, water penetrates much deeper into the hydrocarbon core of these micelles than into the core of the sodium dodecyl sulfate micelle.

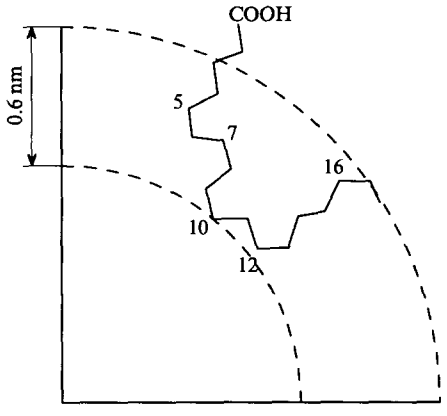


Figure 1. Conformation of *n*-DSA in a tetramethylammonium dodecyl sulfate micelle.[32] The numbers specify the carbon atoms to which the nitroxy-group is attached.

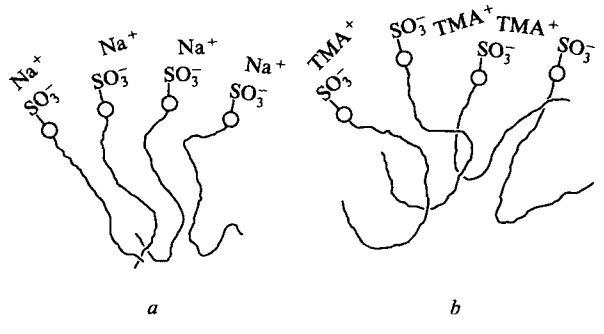


Figure 2. Fragments of a sodium dodecyl sulfate micelle (*a*) and a tetramethylammonium dodecyl sulfate micelle (*b*).[32] TMA^+ is the tetramethylammonium cation.

The results obtained[31–34,41] demonstrated that minor changes in the detergent structure, i.e. replacement of the Na^+ cation by Li^+ or the tetramethylammonium cation, result in significant changes in the micelle structure and in the permeability of the hydrocarbon core.

A study of the effect of urea on the structure of micelles of anionic (sodium dodecyl sulfate) and cationic (dodecyltrimethylammonium bromide) detergents has shown[35] that in both cases urea interacts with the polar groups of the micelle surface. Since this interaction is stronger for dodecyltrimethylammonium bromide, more urea molecules are solubilised on the micelle surface. This explains the fact that urea changes the CMC of dodecyltrimethylammonium bromide more strongly than that of sodium dodecyl sulfate.

The results obtained by the spin echo method are in good agreement with the results of studies on the effect of urea on the structure of the micelles of sodium dodecyl sulfate and dodecyltrimethylammonium bromide by ESR spin probe spectroscopy.[21] The latter show that urea is solubilised on the micelle surface and partially penetrates into the hydrocarbon core near the surface. Urea partially substitutes water in the micelle hydrate shell; this has a weak effect on the polarity but increases markedly the microviscosity of the micelle surface layer.

Crown ethers are also localised on the surfaces of sodium and lithium dodecyl sulfate micelles, giving rise to complexes of the crown ether with the counterion.[36,37] The complex is localised on the micelle surface; as a result, the hydration of the surface decreases.

The addition of an alcohol results in an increase in the penetration of water into the sodium dodecyl sulfate micelle core; at high concentrations of alcohol, destruction of the micelle can occur. The effect of the alcohol depends on the length and degree of branching of the alkyl chain of the aliphatic alcohol in the series 1-propanol < 2-propanol < 1-pentanol < 1-octanol.[38,39]

The spherical micelles of ammonium perfluoroctanoate $[CF_3(CF_2)_6COONH_4]$ were studied by the electron spin echo method[45] using doxylstearic acids **7** whose nitroxy-groups were linked to the hydrocarbon chain at the 5-, 12-, or 16-positions (5-DSA, 12-DSA or 16-DSA). The study of the structures of the micelles of perfluorinated detergents is undoubtedly of interest, since the properties of these micelles differ significantly from those of similar hydrogen-containing detergents. For example, the aggregation number (*n*) for the $CF_3(CF_2)_6COONH_4$ micelles is about twice that for the $CH_3(CH_2)_6COONH_4$ micelles.

It has been found that doxylstearic acids in ammonium perfluoroctanoate micelles are arranged in such a way that the carboxy-group is located in the polar layer of the interface and is surrounded by the polar groups of the detergent. The hydrocarbon chain of the spin probe is not directed to the micelle centre (along the fluorocarbon chains) but is located in the micelle core close to the interface. It turned out that the distances from different carbon atoms of the alkyl chain in *n*-DSA to the interface differ insignificantly. The nitroxy-groups of all *n*-DSA are accessible to water molecules, but the nitroxy-group of 12-DSA is slightly closer to the interface (it is surrounded by four water molecules) than the nitroxy-groups of 5-DSA or 16-DSA (each of them is surrounded by two water molecules). It is noteworthy that the local environment of the nitroxy-groups of 5-DSA in an ammonium perfluoroctanoate micelle is apparently not the same as that of 16-DSA. This follows from the fact[46] that the rotational correlation time of the probe determined by ESR is much lower for 5-DSA (2.3×10^{-10} s) than for 16-DSA (1.1×10^{-9} s).

b. Nonionic micelles

The micelles formed by nonionic detergents in water can solubilise organic compounds. These detergents have a low toxicity and are extensively used in the food and pharmaceutical industries.[47]

Typical representatives of nonionic detergents are polyoxyethylene compounds with the general formula[48] $n\text{-}C_nH_{2n+1}.(OCH_2CH_2)_mOH$. They consist of an alkyl chain comprising 8–12 carbon atoms and the more polar oxyethylene groups. The structure of the micelles formed by these detergents has been studied in detail by the spin echo method.[40,41]

Detergents containing a different number of carbon atoms in the alkyl chains (C_n) and a different number of oxyethylene groups (E_m) were used: $C_{12}E_6$, $C_{12}E_8$, C_6E_8, and C_8E_8. The detergent molecules were selectively deuteriated, either at the alkyl chain or at the oxyethylene groups. The same doxylstearic acids (7, *n*-DSA) with the spin labels at different carbon atoms of the alkyl chain were used as spin probes. D_2O was used to elucidate whether water can penetrate deeply into the micelle.

The following results were obtained.

1. The doxylstearic acid introduced as the spin probe into a micelle is predominantly localised in the polyoxyethylene part of the micelle and has a bent conformation (Fig. 3). The spin label does not penetrate deeply into the hydrocarbon core (for example, not more than by ~1 Å for the $C_{12}E_6$ micelle). The hydrocarbon and polyoxyethylene parts do not mix with each other and are separated by a distinct boundary.

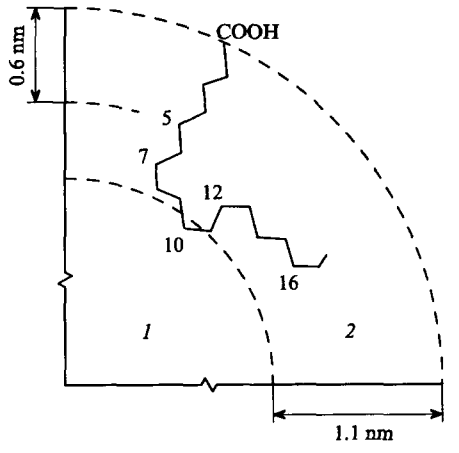


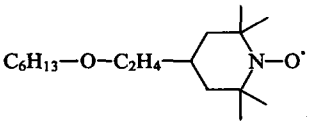
Figure 3. Conformation of *n*-DSA in a polyoxyethylene $C_{12}E_6$ micelle. The numbers specify the carbon atoms to which the nitroxy-group is attached:[40] (*1*) hydrocarbon core; (*2*), polyoxyethylene shell.

2. Water virtually does not penetrate into the micelle hydrocarbon core and penetrates only slightly into the outer polyoxyethylene shell. The polyoxyethylene layer is a reliable protection against the penetration of water into the hydrocarbon core. Only 1–2 oxyethylene moieties, located in the immediate vicinity of the micelle boundary are in contact with water. The longer the hydrocarbon and polyoxyethylene groups, the greater the difficulty with which water penetrates into the micelle. The surfaces of nonionic micelles are hydrated much more weakly than those of ionic micelles.

IV. Polymeric micellar systems

Polymer chains can be involved in the formation of ordered micellar structures in water. Polyelectrolyte complexes, i.e. the products formed by polyelectrolytes and surfactants,[49] are an example of these structures. The electrostatic interaction of the oppositely charged groups of the polyelectrolyte and the detergent and the hydrophobic interaction of the hydrocarbon regions of the detergent molecules play the major role in the formation of polyelectrolyte complexes. When a polyelectrolyte complex is formed, the detergent molecules form an internal macromolecular hydrophobic region (the micellar phase) reinforced by a polymer chain. Either water-soluble or insoluble polyelectrolyte complexes can be formed, depending on the polymer/detergent ratio in the aqueous solution. For example, the polyacrylic acid—dodecyltrimethylammonium bromide system at pH 6 with the concentration ratio of the surfactant and the polyacrylic acid monomer units $\varphi \leqslant 0.3$ yields a water-soluble complex whose composition (φ) is the same as that of the reaction mixture. The solubility of this complex is determined by the length of the polymer regions not bonded with detergent molecules. If the molar fraction of the detergent is increased, a complex is formed whose composition corresponds to $\varphi = 1$. Not all polyelectrolyte molecules dissolved in water participate in the formation of these complexes. However, all the units of the polymer chain participating in the complex formation interact with the detergent molecules. These complexes are insoluble in water and form precipitates.

A spin probe, whose structure is shown below, has been used to study the structure and molecular dynamics of both water-soluble and insoluble polyacrylic acid — dodecyltrimethylammonium bromide complexes.



The structure of this complex and the assumed location of the probe are presented in Fig. 4.

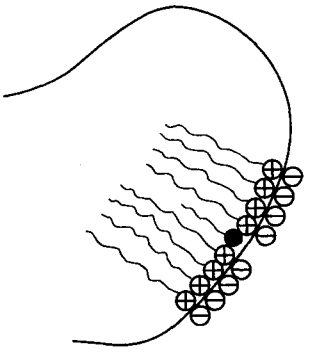


Figure 4. Structure of a polyelectrolyte–detergent complex.[50] The filled circle represents a spin probe.

The following results were obtained:[50]

1. The a_N constant for a polymeric micellar system (16.2 G) is lower than that for an aqueous solution of the polymer (16.9 G). Evidently, the nitroxy-group of the probe is located near the polymer chain of the complex and not in water (see Fig. 4).

2. The rotational correlation time of the probe in the polymer complex (7.2×10^{-10} s) is almost twice as long as that in a dodecyltrimethylammonium bromide micelle. This implies that the local mobility in polymeric micelles is much smaller than in spherical micelles of the same detergent. It cannot be ruled out that detergent molecules are more densely packed in a polymeric micelle than in a spherical micelle.

The rotational correlation time of a spin probe at $\varphi \leqslant 0.3$ does not depend on the composition of the complex. Moreover, the rotational correlation time of the probe in a water-soluble complex is almost equal to that in an insoluble complex. These results are consistent with the hypothesis of the block structure of polyelectrolyte–detergent complexes[49] and permit the conclusion that the phase separation accompanied by the formation of insoluble complexes does not result in an appreciable change in the molecular mobility and hence in the packing density of the detergent molecules in ordered polymeric micellar systems.

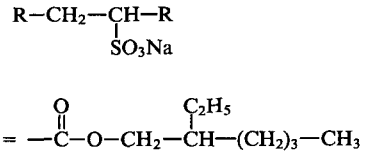
V. Reverse micelles

Many ionic and nonionic detergents form reverse micelles in nonpolar solvents.[51] These micelles consist of a polar core and a nonpolar shell. The main feature of these micelles is their ability to solubilise the polar molecules localised in the micelle core; for example, water molecules. When the water content is high, thermodynamically stable microemulsions are formed. Their use as microreactors opens up new prospects for conducting photochemical, catalytic, polymerisation, oxidation, and other processes. Reverse micelles are also of interest as models of biological membranes.[52–55]

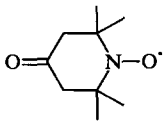
The conditions for the appearance of reverse micelles, their structure and properties, and the characteristics of the kinetics and mechanisms of the reactions occurring in them have been thoroughly studied by various physicochemical methods.[51–55] We shall discuss certain results obtained by the spin probe method.[56–65]

1. Ionic reverse micelles

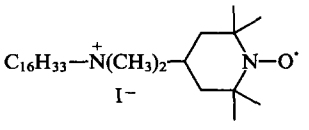
In the studies by the spin probe method particular attention has been devoted to reverse micelles of sodium bis(2-ethylhexyl)-sulfosuccinate or Aerosol OT (AOT).[56–59, 61, 62, 64]



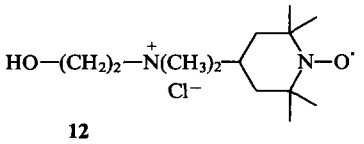
Various probes, soluble either in the aqueous core or in the hydrocarbon shell of the micelle, were used.



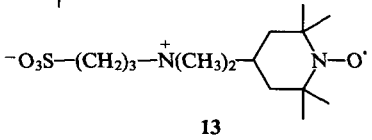
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12



13

n-DSA (where n = 5, 6, 7, 9, 10, or 16) were also used as probes.

It was shown by use of the light scattering technique [66] that the aggregation number of micelles formed by AOT molecules in nonaqueous media is ~23 in the absence of water. The micelle is almost spherical with a diameter of ~24 Å. The addition of water results in an increase in the micelle size and an improvement in its sphericity. Moreover, a cavity consisting of water molecules and surrounded by a monolayer of AOT molecules is formed inside the micelle. The monolayer thickness is ~11 Å and the radius of the aqueous cavity can be calculated (in ångstroms) according to the formula [58, 62, 67]

$$r \sim 1.5\, W_0,$$

where W_0 is the ratio of the concentrations of water and AOT in the system.

It is interesting to note that the length of the hydrocarbon part of the AOT molecule calculated on the basis of the standard interatomic distances in organic molecules [68] is 12.57 Å, whereas the length of the hydrophilic head ($Na^+O_3S^-$) is 5 Å.

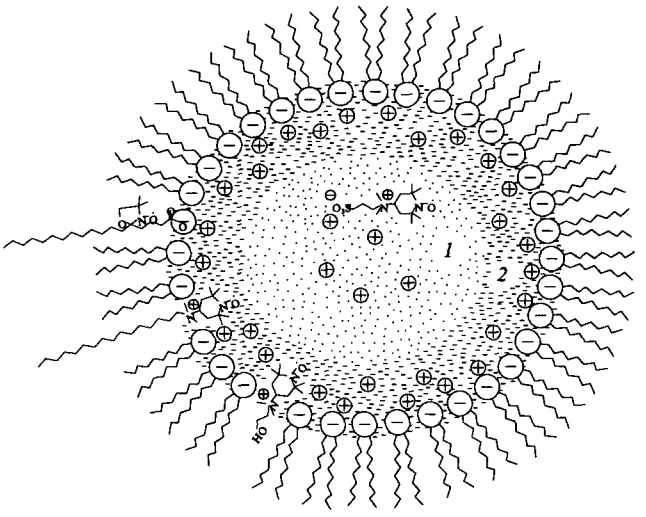


Figure 5. Schematic illustration of an AOT reverse micelle with spin probes:[62] (*1*) 'free' water; (*2*) hydrate layer.

Fig. 5 illustrates schematically an AOT reverse micelle in isooctane and shows the assumed locations of the probes.

The following questions are of interest when the results of studies on the molecular dynamics and structure of reverse micelles by the spin probe method are discussed.

1. What is the state of the water in the centre of a reverse micelle? Is the water 'free', i.e. with the properties of bulk-phase water, or does it participate in the formation of the hydrate layer?

2. Does water penetrate into the micelle hydrocarbon shell and is this penetration sufficiently deep?

3. What is the mobility of the micelle hydrocarbon shell, and how does this depend on the distance from the polar group and on the water content in the micelle?

The conclusion was reached on the basis of analyses of the isotropic hyperfine coupling constants and the rotational mobility of spin probes located in different micelle regions [52–59, 62, 64] that, for a high water content ($W_0 > 20$), the central region of the micelle contains 'free' water whose properties do not differ from those of the usual water. Not all the water solubilised in the micelle is free, a proportion of its molecules participating in the formation of the hydrate layer. For a low water content ($W_0 < 10$), all the water participates in the formation of the hydrate layer. For $10 < W_0 < 20$, the formation of free water begins.

Specimens with $W_0 = 30$ studied at low temperatures display a superposition of the ESR spectra for radicals **10** localised in water and in the micelle hydrocarbon shell. [58] The activation energy for probe transfer from the hydrocarbon shell to water was determined (~30 kJ mol^{-1}) from the temperature dependence of the line widths. The conclusion was reached [59] on the basis of detailed modelling of the spectra that fast probe exchange between the hydrocarbon shell and the hydrate layer and slow exchange between the hydrate layer and free water occur. However, the question why the frequency of probe exchange between the two aqueous phases is lower than between the aqueous phase and the hydrocarbon shell remains open.

Fig. 6 presents the dependence of the hyperfine coupling constant for doxylstearic acid in an AOT reverse micelle on the number of the carbon atom linked to the nitroxy-group. The value of a_N is a maximum for 5-DSA and decreases as n increases, i.e. as the nitroxy-group moves away from the micelle core. An analysis of the a_N constants for doxylstearic acids incorporated into the shells of micelles with different water contents led to the conclusion [62] that water penetrates into the hydrocarbon shell and that the accessibility of the shell to water is greater the closer the given shell region to the micelle centre and the higher the water content in the micelle core.

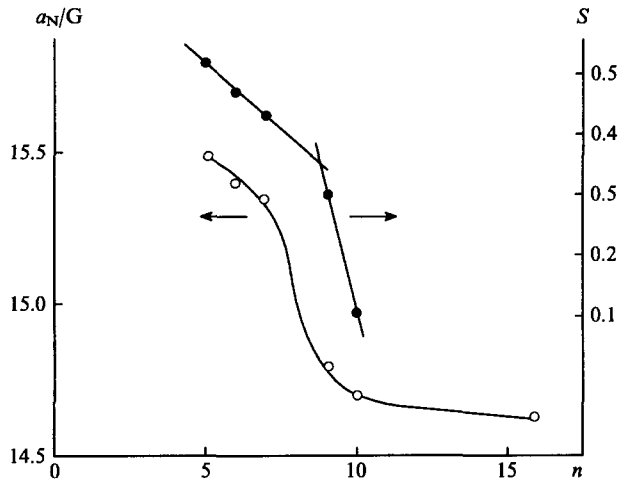


Figure 6. Dependence of the isotropic hyperfine coupling constant (a_N) and the order parameter (S) of the spin probe on the number of the carbon atom (n) to which the nitroxy-group in the n-DSA incorporated in the micelle is attached.[62]

The molecular mobility of doxylstearic acids in the shell of the AOT micelles was characterised[62] by the order parameter S calculated by the equation[69,70]

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})} \frac{a_0}{a_N}. \qquad (2)$$

Here A_{xx} = 6.3, A_{yy} = 5.8, and A_{zz} = 33.6 G are the main values of the hyperfine coupling tensor for doxylstearic acids, $A_{\parallel}$ and $A_{\perp}$ are the corresponding parameters determined from the experimental ESR spectra,[69,70] and a_0/a_N is a correction for the polarity of the probe environment: $a_0 = (1/3)(A_{xx} + A_{yy} + A_{zz})$, $a_N = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$. The S parameter is frequently used to characterise the strongly anisotropic rotation of spin labels, for example, the rotation of lipid spin labels in biomembranes.[69]

The S parameter depends on the frequency and amplitude of the motion of the spin label. In particular, the model of the rapid oscillation of the long axis of a lipid spin label (at frequencies above 10^8 s^{-1}) assumes that $S = 0$ if the oscillation half-amplitude is 90° and $S = 1$ if the oscillation half-amplitude is zero.[70] The S parameter is normally used to characterise the relative variation of the molecular mobility, for example, for constructing the flexibility profiles of biomembranes.[70]

The S parameter determined for doxylstearic acid in AOT reverse micelles decreases almost linearly as the spin label moves further away from the carboxy-group (Fig. 6).[62] Simultaneously, the rotation of the label becomes increasingly more isotropic. This implies that the amplitude of the movement of the hydrocarbon chain segment of the AOT molecule in the micelle increases as it moves further away from the micelle centre. In other words, the mobility of the micelle hydrocarbon shell increases as it approaches the terminal methyl groups. The conclusion that the molecular mobility of the micelle shell depends on the distance from its centre is consistent with the results[71] obtained by the ^{13}C NMR method.

The S parameter depends not only on the distance of the spin label from the micelle centre but also on the water content in the micelle: it increases with the diameter of the aqueous core of the micelle. An increase in the water content in the micelle is accompanied by a decrease in the intensity of the molecular motion in the hydrocarbon shell.

It is important to emphasise that the S value could be determined reliably only for micelles with $W_0 > 10$ whose radii were above 25 Å.[62] The rotation of small micelles (for $W_0 < 10$) as a whole and the lateral diffusion of the spin probe along the micelle surface to a large extent average out the hyperfine coupling anisotropy, thus preventing the correct determination of the S parameter.

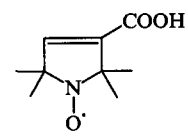
The structure and permeability of the AOT reverse micelle in isooctane were determined by the electron spin echo modulation method,[64] using the same doxylstearic acids as in the ESR studies of the structure of this micelle.

Analysis of the dipole interaction of the spin label with the magnetic moments of deuterium in D_2O and deuteriated isooctane led to the conclusion that the doxylstearic acid is incorporated into the micelle in such a way that the carboxy-group is located near the hydrophilic SO_3^- group of the detergent. The doxylstearic acid in the AOT micelle has an extended conformation similar to that in direct micelles of sodium alkyl sulfates. Isooctane virtually does not penetrate into the bulk of the micelle but readily enters the outer regions of the hydrocarbon shell. An increase in the volume of the aqueous cavity results in a decrease in the hydrocarbon shell permeability to isooctane. For a low water content ($W_0 < 10$) the area of the hydrocarbon shell–water interface is too small to accommodate all the polar 'heads' of the molecules at this boundary. An increase in the water content leads to a structural rearrangement. As a result, all the polar 'heads' are located at the interface. The results obtained[64] confirm the existing idea that the shell almost completely prevents the penetration of the hydrocarbon into the micelle core.

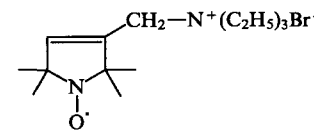
2. Nonionic reverse micelles

The compound $CH_3(CH_2)_8C_6H_4(OCH_2CH_2)_4OH$ readily forms reverse micelles in cyclohexane in the presence of a small amount of water.[72]

The following nitroxyl radicals were used in the study of the molecular dynamics and structure of these micelles by spin probe ESR spectroscopy.[65]



14

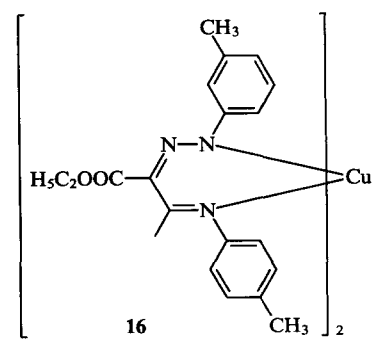


15

5-DSA was also used as the probe.

Radical **14** is soluble in water and cyclohexane, but its solubility in water is 10^3 times greater than in cyclohexane.[2] Radical **15** is only soluble in water and practically insoluble in cyclohexane and other nonpolar solvents. The 5-DSA radical is readily soluble in the micelle hydrocarbon shell and also in cyclohexane.

Apart from nitroxyl radicals, paramagnetic copper compounds were also used: $CuCl_2$ (water-soluble) and complex **16** (soluble in cyclohexane and other nonpolar solvents).



16

Specimens with $W_0 = [H_2O]/[\text{surfactant}] = 0.1-6.9$ were used (nonionic reverse micelles solubilise less water than ionic micelles).

For probe **14** in all the specimens with $W_0 > 0.3$, a superposition of the ESR spectra of the radicals in the aqueous core (a_N = 16.1 G in water) and in cyclohexane (a_N = 14.1 G) was

observed. The solubility of the radical in water is much higher than in cyclohexane, but the amount of cyclohexane in the specimen is much greater than that of water. As a result, the number of radicals dissolved in water is comparable to that in cyclohexane and a superposition of the spectra is therefore observed.

If $CuCl_2$ is added to the water involved in the formation of the micelle core, then the spectrum of radical **14** is observed only in cyclohexane. If paramagnetic complex **16** is added to cyclohexane, the ESR spectrum of the radical is observed only in the aqueous core of the micelle. In both cases, the disappearance of one of the spectra is caused by its broadening due to the exchange interaction with the paramagnetic copper ion. This method for the separation of complex spectra [2,73] is extensively used in the study of complex microheterogeneous systems. Not only paramagnetic copper compounds, but also iron compounds such as $K_3Fe(CN)_6$, are used as broadening agents that penetrate differently into different regions of a complex system.

Radical **15** is insoluble in cyclohexane or in the micelle hydrocarbon shell and is localised in the aqueous core. The results obtained using radicals **14** (with the addition of complex **16** to cyclohexane) and **15** are in good agreement.

The aqueous core of the micelle has a minimal local mobility for $W_0 = 0.6$ (for radical **15** $\tau = 5.4 \times 10^{-10}$ s and $a_N = 15.1$ G). An increase in the water content in the micelle results in a decrease in the rotational correlation time of the radical, while τ and a_N approach the corresponding values for this radical in water ($\tau = 0.5 \times 10^{-10}$ s, $a_N = 15.9$ G).

Comparison of the values of τ and a_N and of the temperature dependences of the rotational correlation times for radical **15** in the aqueous core of the micelle and in a model system — polyoxyethylene swollen in water — shows [65] that an aqueous cavity, whose formation involves free water molecules, appears in the micelle centre. The micelle core is inhomogeneous and water is not distributed uniformly along the oxyethylene chains, at least a fraction of the water being segregated as a separate phase in the centre of the micelle.

When complex **16** is added to cyclohexane, the intensity of the ESR spectrum of radical **15** localised in the aqueous core of the micelle decreases. This is explained by the dipole interaction of the complex with the radical depending on their distance of closest approach. [74–76] The distance of closest approach is the minimum distance that can be reached between the complex and the radical as they approach each other. When the water content in the micelle increases (W_0 increases from 0.6 to 6.9), the distance of closest approach of the complex (in cyclohexane) and the radical (in the micelle core) increases approximately by a factor of two. This is explained by the fact that an increase in the water content results in a decrease in the permeability of the micelle hydrocarbon shell to the molecules of cyclohexane and the organic compounds dissolved in it. The decrease in the shell permeability can be due to a decrease in the intensity of the molecular motion of the hydrocarbon chains.

The conclusion that the intensity of the molecular motions of the hydrocarbon chains of the micelle shell decreases with increase in the water content has been confirmed by studying the ESR spectra of the 5-DSA radical. This radical is almost totally solubilised in the micelle hydrocarbon shell. The ESR spectrum of the radicals dissolved in cyclohexane is fully broadened [is broadened until its complete disappearance? (Translator)] when complex **16** is added to cyclohexane. The radical is localised in the micelle shell so that the nitroxy-group is located in the region consisting of the polyoxyethylene groups. In the $1.8 < W_0 < 6.9$ range, ESR spectra indicate a highly anisotropic rotation of the probe. An increase in the water content in the micelle leads to a monotonic growth of the S parameter calculated according to Eqn (2) ($S = 0.35$ and 0.44, respectively for $W_0 = 1.8$ and 6.9). The reason is that an increase in the volume of the micelle aqueous phase results in a decrease in the intensity of the molecular motion of the micelle shell.

Thus the molecular structure, dynamics, and permeability of the hydrocarbon shells of nonionic reverse micelles depend markedly on the amount of water solubilised by the micelle core. [65]

It is interesting to note that the ESR spectra of spin probes **14** and 5-DSA for low water contents ($W_0 < 0.3$) indicate that a fast exchange (at frequencies above 10^8 s^{-1}) of the radicals localised in the micelle shell and in cyclohexane occurs. Evidently, a fast exchange between detergent molecules localised in the micelle shell and dissolved in cyclohexane also takes place under these conditions. If the content of water increases, the rate of exchange decreases, and the process becomes slow (on the ESR time scale).

VI. Conclusion

Spin probes are a unique instrument for studying the molecular dynamics and structure of ordered micellar systems. They make it possible to determine the characteristic rotational times and the shape of the micelles, to record the micelle formation process and the formation of premicellar aggregates, and to determine the local molecular mobility and polarity of different micelle regions. The use of electron spin echo spectroscopy provides interesting information about the conformational state and permeability of the micelle hydrocarbon regions. It has been found unexpectedly that small changes in the structure of the detergent molecule, for example, the replacement of the Na^+ cation by Li^+ or the tetramethylammonium cation, result in substantial changes in the packing, conformation, and permeability of the hydrocarbon core of an alkyl sulfate micelle. Water hardly penetrates into the hydrocarbon cores of nonionic direct micelles of polyoxyethylene detergents and penetrates into the outer polyoxyethylene shell only to a very slight extent.

Polymeric membrane systems, whose detailed investigation has recently begun, are of particular interest. It has been shown by the spin probe method that the local mobility of detergent molecules in a polymeric micelle is much lower than in micelles of the same detergent containing no polymer.

The studies on reverse micelles have revealed the state of water in the micelle core (bound water participating in the formation of the hydrate layer or free water possessing the properties of the usual water). It was found how the local mobility and permeability of the hydrocarbon shell of the micelle depend on its water content and on the distance from the shell to the micelle centre.

It is important to stress that the above principles and approaches, developed during the study of the molecular dynamics and structure of direct, reverse, and polymer micelles, are used successfully to study more complex ordered molecular systems, such as multicomponent emulsions and vesicles (see, for example, Refs 77, 78).

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