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SHORT COMMUNICATION

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Molecular structure and dynamics of poly(methacrylic acid) and poly(acrylic acid) complexes with dodecyl-substituted poly(ethylene glycol)

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Abstract The molecular dynamics and the structure of molecular complexes formed by micelles of dodecyl-substituted poly(ethylene glycol) with poly(methacrylic acid) and poly(acrylic acid) in aqueous solutions were studied by viscosimetry, pH measurement, and electron spin resonance spin-probe techniques. At low surfactant concentrations, the conformation of the complex is a compact globule. The local mobility of surfactant molecules in such a complex is much slower than that in the "free" micelle. At high surfactant concentration, the nonionic micelles and polyacids form hydrophilic associates. The associates have the conformation of extended coils. In an associate, a major part of the micellar poly(ethylene glycol) groups is free. The local mobility of the micellar phase depends on the number of micelles involved in an associate. The mobility of surfactant molecules is slower in the complexes of poly(methacrylic acid) than in the complexes of poly(acrylic acid).

Keywords Nonionic surfactant · Polyacid–surfactant complex · Spin probe · Molecular mobility

Introduction

Presently, polymer water-soluble associative micellar systems are of great interest because of their prospective industrial applications in enhanced oil recovery, the food industry, cosmetics, microencapsulation, for controlled drug release, and as rheology modifiers. Polymer associative systems can be formed either owing to self-association of polymers [1, 2, 3, 4, 5] or as a result of the interaction of polymers with surfactant molecules [6, 7, 8, 9].

Polyacids (PA) [poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA)] are known to form complexes in aqueous solutions with nonionic surfactants, for instance, with the poly(ethylene glycol) (PEG) [10, 11, 12]. Prerequisites for the formation of the complexes and their characteristics have been discussed in detail [10, 11, 12, 13, 14, 15].

At low concentrations of surfactant the complex has a compact globule. The size of the PA coil in such a globule is smaller than that for the free PA, with the carboxylic groups bound to the PEG groups of the detergent. The globular structure of the complexes transforms into a hydrophilic associate as the concentration of the micelles increases. The globular complex can be characterized by a certain composition, while the composition of the associate species depends on the micelle concentration in solution. For the major part, the surfactant PEG chains are free in the associate. The polymer coil is in an extended conformation. Further increase in the surfactant concentration results in "free" micelles in solution [13, 14, 15]. The hypothetical structures of the compact globular complex and the extended conformation of the associate are shown schematically in Fig. 1.

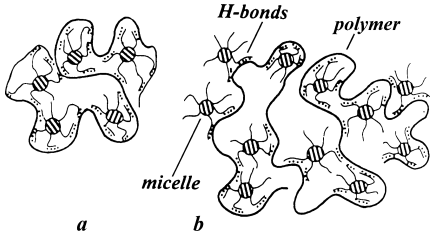


Fig. 1 The hypothetical structure of the polyacid (*PA*)–nonionic surfactant complex (**a** compact coil, low content of surfactant) and associate (**b** extended coil, high content of surfactant)

In this paper we discuss the molecular dynamics and the structure of the complexes of $CH_3(CH_2)_{11}$–O–$(CH_2CH_2O)_{38}H$ (DD-PEG) micelles formed with PMAA or PAA. We show that there is a correlation between the conformation of the polymer coil and the local molecular dynamics in these complexes. Both these characteristics specify important features of polymer–surfactant micellar systems [7, 16]. We also show that the formation of hydrogen bonds between surfactant and PA affects the acid–base equilibrium in the solutions investigated.

Experimental

PMAA and PAA were obtained by radical polymerization of methacrylic and acrylic acids, respectively, in benzene solution under argon at 60 °C. 2,2′-Asobis(isobutyronitrile) was used as the initiator. The polymers were fractionated according to method described in Ref. [17]. The molecular masses were determined by viscosimetry [18, 19]. Fractions of the molecular mass 5.7×10^5 for PMAA and 4.7×10^5 for PAA were separated and used in further experiments. DD-PEG (molecular mass 1,900, $M_w/M_n = 1.05$) was obtained by the technique described in Ref. [14].

The critical concentration of micelle formation (cmc = 0.055 g dl^{-1}) of DD-PEG in aqueous solution was determined by the iodometric method [20]. Potentiometric investigations were performed using a Radilkis OP 208/1 pH meter (Hungary) and an OP 0808P combined glass electrode. The viscosities of the solutions were measured using a Ubbelohde viscosimeter at 25 °C.

The molecular dynamics of the surfactant molecules in micellar systems was studied by the spin-probe technique [21]. The electron spin resonance (ESR) spectra of the 5DSA, 16DSA, RSH, and R15 nitroxide radicals were obtained using a RADIOPAN SE/X 2544 (Poland) X-band ESR spectrometer at 20 °C. In the case of fast motion the rotational correlation time, τ, of the spin probes was determined according to the well-known equation [22]:

$$\tau = 6.65\Delta H_{(+1)}\left(\sqrt{I_{(+1)}/I_{(-1)}} - 1\right)10^{-10}. \quad (1)$$

$I_{(+1)}$ and $I_{(-1)}$ are the intensities of the low-field and high-field components of the ESR signal, respectively. $\Delta H_{(+1)}$ is the width of the low field component. To determine the rotational correlation times for the slow-motion region the experimental spectra were compared with the theoretical spectra [23, 24]. The principal values of the hyperfine (A_{xx}, A_{yy}, A_{zz}) and **g** (g_{xx}, g_{yy}, g_{zz}) tensors of the spin probes used for simulation of the ESR spectra are given in Table 1.

Results and discussion

Conformation of PA–surfactant complexes

The dependencies of the specific viscosity, η_{sp}, and the pH of aqueous solutions of PA and DD-PEG on the mass ratio ϕ = [DD-PEG]/[PA] at constant concentration of polymer, [PA] = 0.1 g dl^{-1}, are shown in Fig. 2. It is seen that η_{sp} decreases as ϕ increases to 0.5–0.6 and to 1.0 for PMAA and PAA, respectively, while the pH value increases. The increase in pH is caused by the formation of hydrogen bonds between the PA and PEG chains. The interaction between PA and micelles of DD-PEG results in a compact globular complex (Fig. 1a), as a result of which the specific viscosity decreases.

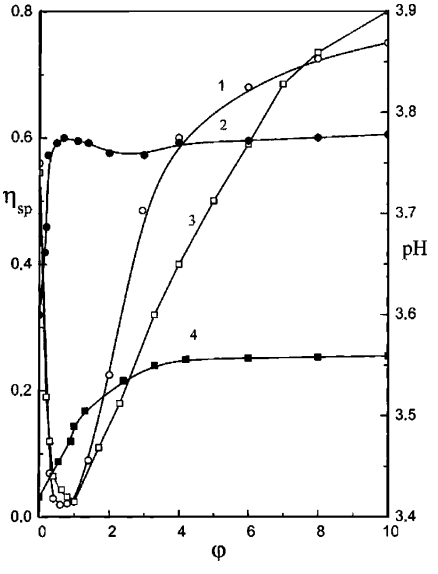
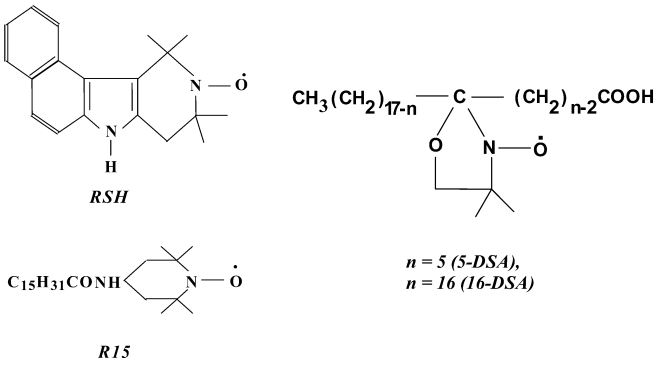


Fig. 2 The dependencies of the specific viscosity η_{sp} (*1*, *3*) and pH (*2*, *4*) of aqueous solutions of poly(methacrylic acid) (*PMAA*) (*1*, *2*) and poly(acrylic acid) (*3*, *4*) mixtures with $CH_3(CH_2)_{11}$–O–$(CH_2CH_2O)_{38}H$ (*DD-PEG*) on the mass ratio of the components, ϕ = [DD-PEG]/[PA], at constant concentration of PA (0.1 g dl^{-1})

Table 1 The principal values of the hyperfine (A_{xx}, A_{yy}, A_{zz}) and **g** (g_{xx}, g_{yy}, g_{zz}) tensors of the spin probes

Spin probe	A_{xx} (G)	A_{yy} (G)	A_{zz} (G)	g_{xx}	g_{yy}	g_{zz}	Reference
R15 and RSH	7.7	5.6	36.9	2.0093	2.0063	2.0022	16
5DSA and 16DSA	6.3	5.8	33.6	2.0088	2.0061	2.0027	25



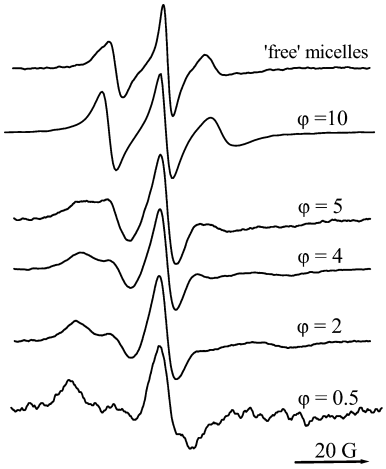


Fig. 3 Electron spin resonance (*ESR*) spectra of the 5DSA spin probe in free DD-PEG micelles and in the PMAA–DD-PEG system at various mass ratios of the components in aqueous solutions of PMMA (0.3 g dl^{-1})

At $\phi = 0.5$ the specific viscosity of PMAA and DD-PEG aqueous solutions is approximately the same as at $\phi = 1$, while the pH peaks at $\phi = 0.5$–0.6, i.e, the number of hydrogen bonds is as much as possible. At $\phi = 0.5$ the specific viscosity reaches its minimum and increases with ϕ at $\phi > 1$. This is due to the formation of a hydrophilic associate instead of a globular complex between DD-PEG micelles and PMAA. At $\phi > 1$ the PMAA macromolecule interacts with a greater number of DD-PEG micelles than it does in the compact complex at $\phi = 0.5$. As a consequence, DD-PEG chains do not all form the hydrogen bonds with the PMAA in the associate. The "unbound" DD-PEG chains provide the hydrophilicity of the associate (Fig. 1b). The unexpected slight reduction in pH at $\phi > 1$ seems to be due to lowering of the pK_a of the PA carboxylic groups when the compact globular complex transforms into the hydrophilic associate.

The PAA–DD-PEG system (Fig. 2) behaves in a like manner except that the maximum number of hydrogen bonds between PAA and DD-PEG micelles is formed at $\phi \approx 4$ and the maximum pH and minimum η_{sp} are observed at higher ϕ than those for the PMAA–DD-PEG system. It was established earlier that complexes of PEG molecules with PAA are less stable than complexes with PMAA [26]. This feature seems to be responsible for the observed quantitative differences between the PAA–DD-PEG and PMMA–DD-PEG systems. It should be mentioned that aqueous solutions of PMAA (or PAA) and other PEG nonionic surfactants [13, 14, 15] demonstrated similar characteristics.

Molecular dynamics of surfactant molecules in PA–surfactant complexes

The complexes of PMAA

To investigate the molecular dynamics of the micellar phase of the PMAA–DD-PEG complexes, 5DSA, 16DSA, RSH, and R15 spin probes were used. In all cases the concentrations of surfactant were significantly higher than the cmc. It is likely that the mobility of the RSH and 5DSA (R15 and 16DSA) probes is specified by the molecular mobility of similar parts of the micelles. Therefore, the RSH and 5DSA as well as the R15 and 16DSA probes demonstrate similar results. However, the results obtained for the former and latter couples are different; therefore, we restrict our attention to the 5DSA and R15 probes only.

The paramagnetic fragment of 5DSA is located near the hydrocarbon core of the DD-PEG micelle [27]. The ESR spectra of this probe in the PMAA–DD-PEG system at different ϕ and at constant concentration of PMAA (0.3 g dl^{-1}) are shown in Fig. 3. At $\phi = 0.5$ the ESR spectrum of the 5DSA probe in the PMAA–DD-PEG complex differs dramatically from that in the free micelle. The rotational correlation times of the probe are 1.8×10^{-8} s and 1.9×10^{-9} s in the complex and free micelles, respectively. Thus, the local mobility of the micellar phase in the complex is much slower than that in the free micelles.

As discussed earlier, the hydrophilic associates are formed at $\phi > 1$. However, the ESR spectra of the spin probe remain invariable as the surfactant concentration increases up to $\phi = 4$. This observation suggests the absence of free micelles and an insignificant variation of the local mobility of the micellar phase with transformation of the globular complex into an associate at $\phi \leq 4$. As the concentration of DD-PEG increases further, the ESR spectra transform gradually to those typical of free micelles. These changes can be caused by the reconstruction of the associate structure or by the free micelles in the solution.

It may be suggested that the paramagnetic fragment of the R15 probe is localized near the interface of the micelle [28]. This feature allows differentiation between bound and unbound surfactant molecules since hydrogen bonding with the PA takes place with those poly

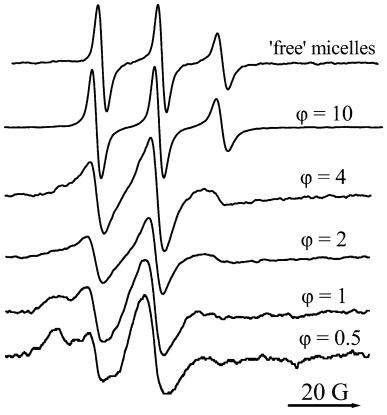


Fig. 4 ESR spectra of the R15 spin probe in the free DD-PEG micelles and in the PMAA–DD-PEG system at various mass ratios of the components in aqueous solutions of PMAA (0.3 g dl^{-1})

(oxyethelene) units which are localized at the micellar interface. This speculation is supported by the observation that at $\phi = 0.5$ the ESR spectrum of the R15 probe is the superposition of two spectra with rotational correlation times $\tau_1 = 9\times10^{-9}$ s and $\tau_2 = 1.4\times10^{-9}$ s and relative contributions $w_1 = 90\%$ and $w_2 = 10\%$, respectively (Fig. 4). Since $\tau = 7\times10^{-10}$ s for the free micelles, the local mobility of the micellar phase in the complex is significantly lower than that in the free micelles. The probes rotating "slowly" are likely to localize near the surfactant molecules bound by hydrogen bonds to the polymeric chain (Fig. 1b), whereas probes rotating "rapidly" localize near the unbound surfactant. The rotational correlation times of probes localized in different parts of the micelles remain unchanged with the surfactant concentration in limits of $\phi = 0.5$ and 1, while the number of rapidly rotating spin probes increases up to 25% at $\phi = 1$. Most likely the relative number of unbound PMAA surfactants in the complex increases with the surfactant concentration. As a consequence, the contribution from rapidly rotating probes increases as well.

At $\phi = 2$, 3, and 4 the ESR spectra of the R15 probe correspond to the rotational correlation times $\tau = 3.5\times10^{-9}$, 3×10^{-9}, and 2.6×10^{-9} s. There are no free micelles in the system until $\phi > 4$; therefore, all the observed features are caused exclusively by the variation in the local mobility of surfactant molecules in the associate. Free micelles seem to appear at $\phi = 5$. At $\phi = 10$, the ESR spectra of the R15 probe are identical to those inherent to free micelles.

The complexes of PAA

The PAA–DD-PEG system was studied as function of ϕ at a constant concentration of PAA (0.3 g dl^{-1}). In the PAA–DD-PEG complex the paramagnetic fragment of the 5DSA probe localizes near the hydrocarbon core of the micelles, similarly to the PMAA–DD-PEG system [27].

At $\phi = 0.5$, the ESR spectra of 5DSA in the PAA–DD-PEG complex differ markedly ($\tau = 5\times10^{-9}$ s) from those observed in the free micelles ($\tau = 1.9\times10^{-9}$ s) and in the PMAA–DD-PEG complex ($\tau = 1.8\times10^{-8}$ s). As the surfactant concentration increases to $\phi = 2$, the ESR spectra of the spin probe remain intact since at these concentrations of detergent all the micelles are involved in the complex, with the local mobility in the micellar core being unchanged. When the surfactant concentration increases further the rotational correlation time decreases. The reasons are likely twofold: the first is the rebuilding of the complex (Fig. 1); the appearance of free micelles is the second. At $\phi = 3$ and 5 the ESR spectra correspond to the correlation times $\tau = 3.5\times10^{-9}$ and 2.5×10^{-9} s, respectively. At $\phi = 10$, the ESR spectra in the free micelles and in the PAA–DD-PEG system are practically identical owing to the high concentration of free micelles in the latter system.

Similar observations were obtained for the other spin probes. For example, at $\phi = 1$ the rotational correlation time of the RSH spin probe is 5.2×10^{-9} s in the PAA–DD-PEG complex. This time is noticeably longer than that in the free micelles (1.3×10^{-9} s); however, it is shorter than the rotational correlation time for the RSH probe in the PMAA–DD-PEG complex, where $\tau = 1.3\times10^{-8}$ s. An increase of ϕ to 2 does not influence the correlation time. However, as the surfactant concentration increases further, the rotational correlation time in the PAA–DD-PEG system decreases and approaches the value of τ in the free micelles. $\tau = 3.3\times10^{-9}$ s for $\phi = 4$, 2.6×10^{-9} s for $\phi = 5$, and 1.4×10^{-9} s for $\phi = 10$.

At $\phi = 1$ the ESR spectrum of the R15 probe corresponds to $\tau = 2\times10^{-9}$ s. This spectrum differs appreciably from the spectrum of the same probe in the PMAA–DD-PEG system. The difference is caused by the faster surfactant mobility in the PAA–DD-PEG complex in comparison with the PMAA–DD-PEG complex. In the PAA–DD-PEG complex, there is no superposition of the ESR spectra characterized by the different rotational correlation times as was observed in the PMAA–DD-PEG complex. Most likely, the difference in the molecular mobility of the R15 probes located in different sites of the PAA–DD-PEG complex is not sufficient to be detected in our experiment. As the surfactant content increases, the rotational correlation time decreases. It approaches the value inherent to the probe in the free micelles. $\tau = 1.4\times10^{-9}$ s for $\phi = 2$, 1.3×10^{-9} s for $\phi = 3$, 1×10^{-9} s for $\phi = 4$, 9×10^{-10} s for $\phi = 5$, and 8×10^{-10} s for $\phi = 10$.

Conclusion

At low surfactant concentration, the complexes of DD-PEG nonionic micelles with PMAA and PAA in aque-

ous solutions have a compact globular structure. The local mobility of the surfactant molecules in these complexes is slower than that in the free micelles owing to hydrogen bonding between the PEG chains and nondissociated carboxylic groups of PA. The local mobility of the surfactant molecules in the PMAA–DD-PEG complex is slower than that in the PAA–DD-PEG complex. This is due to different segmental mobility of PAA and PMAA and to the lesser stability of the PAA–DD-PEG complex. At high surfactant concentration, the PA and DD-PEG micelles form hydrophilic associates instead of globular complexes. These associates have the conformation of an extended coil. In an associate, micellar PEG groups are essentially free and the local mobility of surfactant bound to a polymeric chain is less than the mobility of surfactant which is not attached to a polymer. As the number of micelles in solution increases, the number of unbound polymeric chain surfactant molecules in the associate also increases. As a result, the mobility of the surfactant molecules in the micellar phase increases with the surfactant concentration.

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