Eur. Polym. J. Vol. 29, No. 8, pp. 1137–1142, 1993
Printed in Great Britain

0014-3057/93 $6.00 + 0.00
Pergamon Press Ltd

COMPLEXATION OF POLY(METHACRYLIC ACID) WITH POLY(ETHYLENE GLYCOL) NONIONIC SURFACTANTS IN AQUEOUS SOLUTIONS

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(Received 28 August 1992)

Abstract—The interaction between poly(methacrylic acid) (PMAA) and surfactants based on poly(ethylene glycol) in aqueous solutions has been studied by viscometry and potentiometric titration. The interaction proceeds in two stages with increasing concentration of the surfactants. At first, the polycomplex (PMAA · surfactant) is formed. The structural state of the surfactant in the polycomplex depends on the hydrophilic–hydrophobic balance of the surfactant. In the second stage at higher concentration of the surfactant, the polycomplex binds the micelles, forming an associate with two possible structures.

INTRODUCTION

The interaction between polymeric acids and micelle-forming derivatives of poly(ethylene glycol) (PEG) in aqueous solution has been thoroughly studied. Most detailed are the studies carried out by Saito *et al.* [1–4]. It has been shown that polyacrylic (PAA) and polymethacrylic acids (PMAA) form complexes with micelles of alkyl and alkylphenyl monosubstituted PEGs. Complexes form because of two factors:

(a) existence of H-bonds between the non-dissociated carboxylic groups of the polyacids and the oxygen atoms of PEG;
(b) the hydrophobic interactions in the system.

The latter factor needs further elucidation. A typical characteristic of the interaction of polyacids with micelle-forming PEG derivatives is the forming of complexes at surfactant concentrations lower than its own critical micelle concentration (CMC).

Complex formation of PMAA and PAA with micelles of PEG–monolaurate (PEGML) in dilute aqueous solutions has been studied [5–7]. The association of PMAA with the micelles of PEGML is accompanied by an exothermal effect. The formed polycomplex is capable of binding some additional surfactant. In the case of PMAA excess, PEGML micelles are distributed among the PMAA macromolecules according to "all or none" principle, i.e. some of the macromolecules are bound to the maximum possible amount of PEGML, while the remaining PMAA is free [7].

PMAA and PAA are known to form polycomplexes with PEG in aqueous solutions [8–11]. Introducing hydrophobic groups into the PEG chain significantly stabilizes the polycomplexes even when PEG derivatives do not form micelles [12, 13]. Varying the hydrophilic–hydrophobic balance in the substituted PEG makes it possible to alter CMC in the aqueous solution. Thus complexation of polyacids with PEG derivatives can be studied with respect to the organization condition of the latter i.e. individual macromolecules or micelles.

This paper refers to the complexation of PMAA with PEG alkylethers, viz. decyl and dodecylethers of PEG, with various molecular weights.

EXPERIMENTAL PROCEDURES

PMAA was prepared by radical polymerization of methacrylic acid in benzene at 60° under N_2 with AIBN as initiator. The molecular weight of PMAA was $1.8 \cdot 10^5$ as determined viscometrically at 30° in 0.002 N HCl using the relation $[\eta] = 6.6 \cdot 10^{-4} M^{0.5}$ [14]. n-Decanol and n-dodecanol were purchased from Fluka. Monosubstituted PEGs—decylether $C_{10}H_{21}O—(—CH_2—CH_2—O)_n—H$ (D-PEG) and dodecylether $C_{12}H_{25}O—(—CH_2—CH_2—O)_n—H$ (DD-PEG) with various lengths of the PEG chain were prepared by addition of ethylene oxide to the appropriate alcohol under argon. NaOH was used as catalyst (from 0.02 to 0.5 wt% with respect to the alcohol) at temperatures 150–200°. Molecular weights of the PEG derivatives were determined by GPC and are listed in Table 1. The aqueous solutions of D-PEG and DD-PEG showed pH values between 7 and 10 depending on the amount of NaOH used as catalyst. The solutions were neutralized to pH 6–7 prior to the experiments by addition of 0.1 N HCl.

The products of the addition of ethylene oxide to the alcohols were analysed by GPC. A Waters 244 instrument equipped with combinations of Ultrastyragel columns of 100, 100, 500 and 1000 A in THF solution, maintained at a flow rate 1 ml/min at 45°, was used. RI was used for detection and the PEGs were used as calibration standards. The analysis showed no detectable content of unreacted alcohols or non-substituted PEGs.

CMCs of the PEG derivatives were determined by iodophotometry [15]. The data are listed in a table. Potentiometric measurements were taken on a Radelkis OP 208/1 (Hungary) apparatus equipped with a combined glass electrode OP 0808 P. Viscometric data were obtained with an Ubbelohde viscometer.

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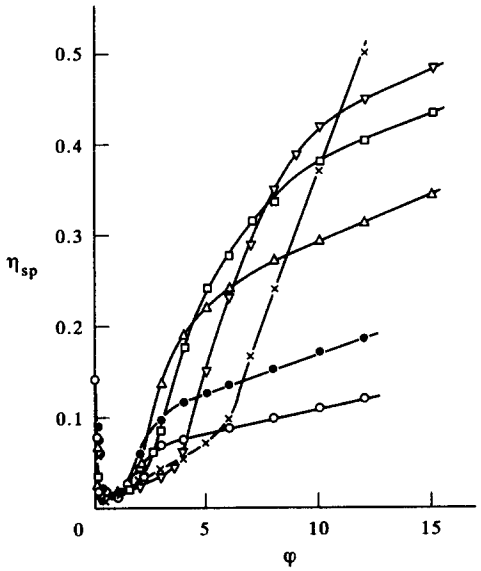

Fig. 1. Dependence of η_{sp} of the aqueous solutions of PMAA + D-PEG mixtures on the weight ratio [D-PEG]/[PMAA]. PEG chain length, n: ○,9; ●,13; △,24; □,35; ▽,46; X,85; $C_{PMAA} = 0.1$ g/dl, 25°.

RESULTS AND DISCUSSION

Figure 1 shows the dependencies of the specific viscosity (η_{sp}) of the aqueous solutions of (PMAA + D-PEG) mixtures with various PEG chain lengths on the weight ratio of the components, ϕ = [D-PEG]/[PMAA], at a fixed PMAA concentration of 0.1 g/dl.

For D-PEG$_1$ with $n = 9$, CMC = 0.03 g/dl corresponding to $\phi = 0.3$ on Fig. 1. At $\phi = 0.1$ $\eta_{sp} = 0.075$, i.e. considerably below $\eta_{sp} = 0.144$ for the solution of pure PMAA; thus D-PEG$_1$ associates with PMAA at concentrations appreciably below CMC. That result means that, at this D-PEG$_1$ concentration, a polycomplex forms between PMAA and the individual macromolecules of D-PEG. It should be noted that the critical (minimum) molecular weight of the non-substituted PEG when complexing with PMAA under the same conditions is about 2000 [8]. Meanwhile D-PEG$_1$ has PEG chain of $\bar{M}_n \approx 370$, i.e. five times shorter, meaning that the decylic group introduced into PEG significantly stabilizes its polycomplex with PMAA. The same effect was observed with other hydrophobically substituted PEGs in their complexing with PAA and PMAA [12, 13, 16]. The reason lies in the additional free energy gain in the system when the hydrophobic groups of the substituted PEG are transferred from the aqueous media into the hydrophobic domains of the polycomplex.

On increasing the D-PEG$_1$ concentration, complex formation progresses and η_{sp} reaches a minimum at $\phi = 1$. The data in Fig. 2 show that the pH of the solution increases when H-bonds are formed between the non-dissociated carboxylic groups of PMAA and the oxygen atoms of PEG. As seen from the figure, pH increases up to $\phi = 1$, corresponding to the saturation of PMAA with H-bonds with D-PEG. Comparing the dependencies of η_{sp} and pH on ϕ leads to the conclusion that, at $\phi = 1$, there exists a polycomplex (PMAA · D-PEG$_1$) with the maximum amount of bound D-PEG$_1$ for these conditions. The free molecules of D-PEG$_1$ appear in the solution above $\phi = 1$. At a certain concentration, they are able to associate with the already formed particles of the polycomplex (PMAA · D-PEG$_1$). The particles of the polycomplex lyophylizate and their molecular weight increases. These two factors cause an increase of η_{sp}. On further increasing of the surfactant concentration, saturation of polycomplex with D-PEG$_1$ is reached and then η_{sp} increases less due only to the increased D-PEG$_1$ concentration.

Lyophylization of the particles of the polycomplex when bound to additional amounts of D-PEG$_1$ and the accompanying conformational changes in the associate might lead to an increase of the degree of dissociation of COOH-groups. Therefore the pH of the solution in this range of D-PEG$_1$ concentration slightly decreases (see Fig. 2). Further increase of surfactant concentration results in some increase of pH, which might be due to binding of free COOH-groups of PMAA in the polycomplex on the association with a greater amount of D-PEG$_1$.

The dependence of η_{sp} on ϕ for D-PEG$_1$ with $n = 13$ is analogous to the discussed dependence for D-PEG$_1$. The only difference is the more drastic increase of η_{sp} at the lyophylization of the polycomplex (PMAA · D-PEG$_2$) when associated with D-PEG$_2$. The greater value of η_{sp} for the system

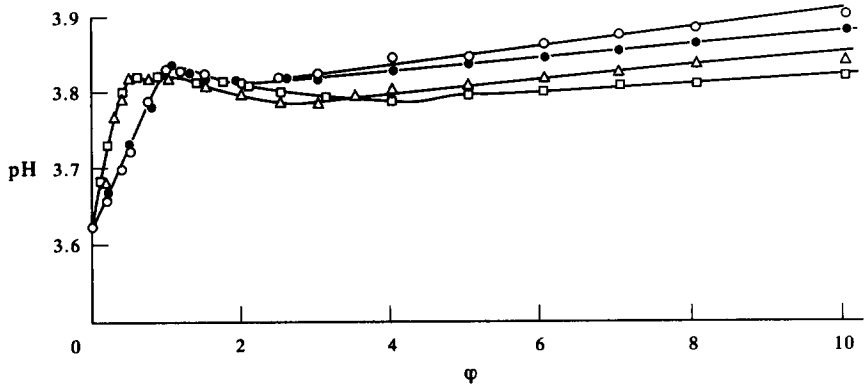

Fig. 2. Dependence of pH of the aqueous solutions of PMAA + D-PEG mixtures on the weight ratio [D-PEG]/[PMAA]. PEG chain length, n: ○,9; ●,13; △,24; □,35; $C_{PMAA} = 0.1$ g/dl, 25°.

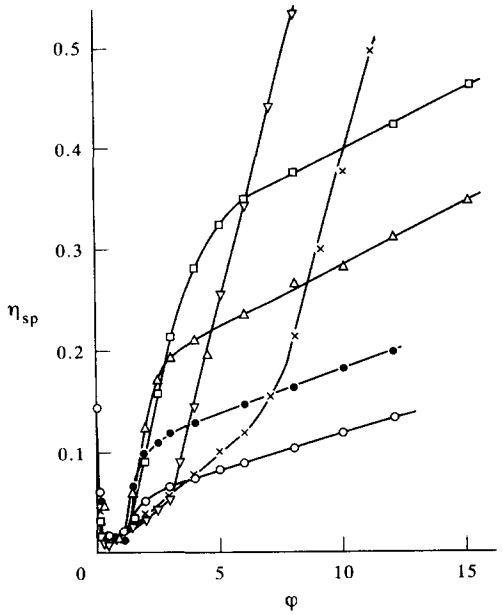

Fig. 3. Dependence of η_{sp} of the aqueous solutions of PMAA + DD-PEG mixtures on the weight ratio [DD-PEG]/[PMAA]. PEG chain length, n: ○,9; ●,16; △,26; □,38; ▽,94; X,114; $C_{PMAA} = 0.1$ g/dl, 25°.

PMAA–D-PEG$_2$ compared to the system PMAA–D-PEG$_1$ could be explained by the enhanced lyophilic ability of D-PEG when the PEG chain is increased. Figure 2 shows that, for both D-PEG$_2$ and D-PEG$_1$, PMAA is saturated by H-bonds at $\phi = 1$. This fact should be emphasized for the following reason.

Of great interest is the answer to the question in what structural organization the macromolecules of the surfactant in the polycomplex with PMAA are, whether micelles or as individual PEG chains forming linear sequences of H-bond with the macromolecules of PMAA. It is known that non-substituted PEGs form with PMAA polycomplexes of equimolar content, i.e. one PMAA base-unit per PEG base-unit, so that the weight ratio [PEG]/[PMAA] = 0.5 [8–10]. That means if the PEG chains in D-PEG$_2$ and D-PEG$_1$ in the polycomplex form linear arrangements of H-bonds with PMAA, pH maximum should correspond to the ratios $\phi = 0.63$ for D-PEG$_1$ and $\phi = 0.58$ for D-PEG$_2$. The estimation is done with respect to the alkyl group in D-PEG which does not participate in the formation of the H-bonds. The maximum at $\phi \approx 1$ suggests that not all the PEG units can form H-bonds with the COOH-groups of PMAA. It is possible if the macromolecules of D-PEG in the complex are present as micelles and not all PEG units can bind to PMAA because of structural hindrance. The same phenomenon has been found in the complexation of PMAA with the micelles of PEGML [5, 7]. Hence, when PMAA complexes with D-PEG$_1$ and D-PEG$_2$, the surfactants in the polycomplex exist as micelles.

The case of D-PEG with longer PEG chain is different. D-PEG$_3$ with $n = 24$ forms a stable polycomplex of equimolar stoichiometry, as seen from the minimum η_{sp} and the maximum pH corresponding to $\phi \approx 0.5$ (Figs 1 and 2). Consequently, the organization state of surfactant macromolecules in the polycomplex (PMAA · D-PEG$_3$) is close to the state in the polycomplex between PMAA and the linear non-substituted PEGs.

Having reached the minimum of η_{sp}, further increase of D-PEG$_3$ concentration leads to insignificant increase of η_{sp} due to the free D-PEG$_3$ molecules in the solution. On reaching $\phi \approx 1.5$, η_{sp} sharply rises for the same reason—the association of D-PEG$_3$ macromolecules with the polycomplex (PMAA · D-PEG$_3$)-at $\phi \approx 1.5$. It should be noted that the ratio $\phi = 1.5$, at which η_{sp} sharply rises, corresponds to a total D-PEG$_3$ concentration of 0.15 g/dl and is below the CMC.

The systems consisting of PMAA with D-PEG$_4$, D-PEG$_5$ and D-PEG$_6$ behave like the system PMAA–D-PEG$_3$. On increasing PEG molecular weight, an increase of ϕ values at which there is rise of η_{sp} is observed and also the absolute value of the rise is increased. But at the beginning of the η_{sp} rise in all cases, D-PEG concentration is lower than the corresponding CMC. The excluded volume of the compact particles of the polycomplex (PMAA · D-PEG) is negligibly small compared to the free volume of the solution. Therefore that could not be a reason for the decrease of CMC of D-PEG in the presence of the polycomplex. Hence, the polycomplex is able to bind the free macromolecules of D-PEG. The

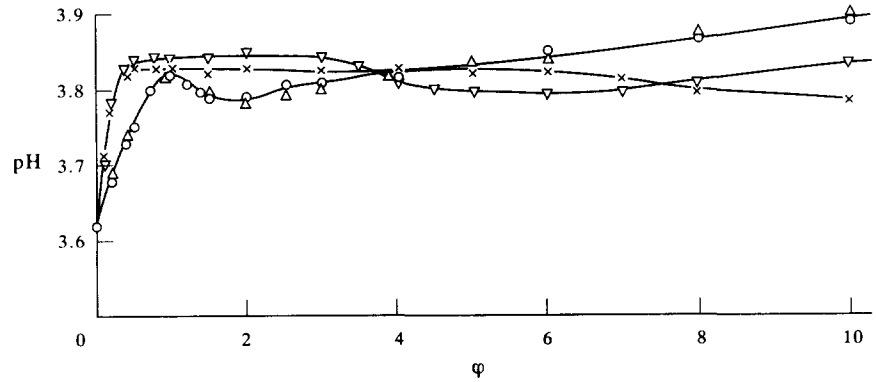

Fig. 4. Dependence of pH of the aqueous solutions of PMAA + DD-PEG mixtures on the weight ratio [DD-PEG]/[PMAA]. PEG chain length, n: ○,9. △,26; ▽,94; X,114; $C_{PMAA} = 0.1$ g/dl, 25°.

formation of the associate of the polycomplex with D-PEG does not proceed monotonously on increasing the amount of the free surfactant macromolecules but is due to the critical concentration.

It might be explained by the association of individual surfactant macromolecules into micelles when interacting with the particle of the polycomplex. The structural state of all surfactant macromolecules in the associate cannot differ. That means the associate is a hydrophilic compound of PMAA with the micelles of the surfactant. The stoichiometry of the associate, in contrast to the polycomplex, will be determined by the hydrophilic–hydrophobic balance of the surfactant. The increasing of ϕ with increasing PEG chain length with rise of η_{sp} is explained by the enhanced hydrophility of the surfactants which leads to hindrance to micelle formation. That is why the concentration of D-PEG macromolecules should be higher so that they could associate with the polycomplex via formation of micelles. The absolute value of the η_{sp} rise increasing with lengthening of the PEG chain might be due to two reasons. The first lies in the conformation changes in the polycomplex when associating with surfactant micelles. The longer the PEG tails of the micelles, the higher is the surfactant's lyophylization ability. Thus the conformation of the formed associate is more extended and its hydrodynamic volume is larger. The second reason lies in the molecular weight of the associate. If the number of surfactant molecules in a micelle does not decrease with increasing PEG chain length, the molecular weight of a micelle will increase. It will lead to the possibility of binding a greater amount of surfactant by an equal number of H-bonds between PMAA and the D-PEG micelle tails. In fact, that means increased molecular weight of the associate and η_{sp} rise increases.

The rise of η_{sp} is linearly dependent on ϕ, i.e. on surfactant concentration. This dependence might be explained by pronounced cooperative character of the association between the surfactant and PMAA.

The high positive cooperativity of the interaction might lead to the existence of only two types of particles, viz. particles of the pure polycomplex (PMAA · D-PEG) and associates of PMAA with the surfactant with the maximum number of bound micelles. The case will be discussed in detail.

According to the Huggins' equation, η_{sp} of the polymer solution is:

$$\eta_{sp} = [\eta] \cdot C + K'[\eta] \cdot C^2$$

where $[\eta]$ is the characteristic viscosity of the polymer solution, k' is the Huggins' constant, C is the concentration of the polymer. For dilute solutions, C^2 may be neglected.

Then η_{sp} of the solution containing only the particles of the polycomplex and of the associate will be:

$$\eta_{sp} = [\eta]_{PC} \cdot C_{PC} + [\eta]_A \cdot C_A \qquad (1)$$

where $[\eta]_{PC}$ and $[\eta]_A$ are the characteristic viscosities of the solutions of the polycomplex and the associate, and C_{PC} and C_A are their concentrations. The formation of the associate starts at a certain critical concentration of the surfactant designated as C^*. If the surfactant concentration in the solution reaches higher C values, it means that C–C^* surfactant macromolecules associate to the polycomplex. Moreover, some of the polycomplex is included in the associate. With regard to the latter fact, C_A is given by:

$$C_A = C - C^* + a(C - C^*) \qquad (2)$$

where the coefficient a represents the weight ratio of surfactant to polycomplex in the associate. The polycomplex concentration can be represented as:

$$C_{PC} = C^0_{PC} - a(C - C^*)$$

where C^0_{PC} is the initial concentration of the polycomplex at the point $C = C^*$. Substituting the expressions for C_A and C_{PC} in equation (1) after some rearranging, the dependence of η_{sp} on C is obtained:

$$\eta_{sp} = A + B \cdot C \qquad (3)$$

where $A = (C^0_{PC} + a \cdot C^*)[\eta]_{PC} - (1 + a) \cdot C^*[\eta]_A$ and $B = a \cdot ([\eta]_A - [\eta]_{PC}) + [\eta]_A$ are constants because a and C^* are characteristic constant parameters of the surfactant. Hence, from equation (3) it follows that η_{sp} is a linear function of C for cooperative association of the surfactant to the polycomplex according to the principle "all or none".

If in the solution there is coexistence of associates with different amounts of the surfactant, η_{sp} will be determined by the ratio $\eta_{sp} = [\eta]_A \cdot C_A$ where according to the ratio (2) $C_A = (1 + \bar{a})(C - C^*)$ where $\bar{a}$ is already the average value of the associate assembly which is dependent on surfactant concentration. Then

$$\eta_{sp} = (1 + \bar{a})[\eta]_A \cdot C - (1 + \bar{a})C^* \cdot [\eta]_A$$

where the coefficient at C is no longer a constant: $\bar{a}$ and $[\eta_A]$ should increase with increase of C.

Figures 3 and 4 show the dependencies of η_{sp} and pH of the solutions of PMAA and DD-PEG of various molecular weights on the weight ratio [DD-PEG]/[PMAA] = ϕ. The dependencies are qualitatively analogous to the earlier dependencies discussed for the system PMAA–D-PEG, but it is worth noting some of the quantitative differences.

First, the drastic increase of η_{sp} is observed at lower surfactant concentrations at the same n values compared to that for the system PMAA–D-PEG (compare $DD\text{-}PEG_3$ and $DD\text{-}PEG_4$ with $D\text{-}PEG_3$ and $D\text{-}PEG_4$). It is reasonable because the longer alkyl group in DD-PEG favours the micelle formation. The comparison of CMC for D-PEG and DD-PEG supports this statement (see Table 1). If the absolute values for the η_{sp} rise of D-PEG and DD-PEG having the same n are compared, they are found to be almost equal for the first four samples. This finding supports the assumption that lyophilic effectiveness is connected with the PEG chain length only.

Secondly, the pH dependence for the system $PMAA\text{–}DD\text{-}PEG_3$ shows that the components of the polycomplex are in a ratio $\phi \approx 1$. Noting the above discussion, it means that $DD\text{-}PEG_3$ macromolecules occur as micelles in the polycomplex because of the existing linear sequences of the H-bonds between the components meaning that the ratio $[DD\text{-}PEG_3]$/[PMAA] should be 0.57. At the same time, as seen above, $D\text{-}PEG_3$ with the same n forms with PMAA a complex of structure analogous to the polycomplex

Table 1. Molecular weight characteristics and CMC of D-PEG and DD-PEG samples

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	n*	CMC (g/dl)
D-PEG$_1$	550	670	1.22	9	0.03
D-PEG$_2$	730	810	1.11	13	0.07
D-PEG$_3$	1200	1300	1.09	24	0.18
D-PEG$_4$	1700	1900	1.12	35	0.33
D-PEG$_5$	2200	2400	1.10	46	0.45
D-PEG$_6$	3900	4500	1.15	85	0.64
DD-PEG$_1$	600	670	1.12	9	0.0045
DD-PEG$_2$	900	950	1.06	16	0.0075
DD-PEG$_3$	1350	1450	1.08	26	0.016
DD-PEG$_4$	1850	1950	1.05	38	0.055
DD-PEG$_5$	4300	4800	1.12	94	0.27
DD-PEG$_6$	5200	7200	1.38	114	0.48

*n, average polymerization degree of PEG chains.
$n = (\bar{M}_n - M)/44$, where M is the molecular weight of the alkoxy group in the substituted PEG, M = 157 for D-PEG and 185 for DD-PEG.

of PMAA with linear PEG. This is due to the longer alkyl group in DD-PEG stabilizing the surfactant micelle structure in the polycomplex. With the greater PEG chain length in DD-PEG (DD-PEG$_4$, etc.), surfactant micelles become less stable resulting in the formation of linear sequences of the H-bonds with equimolar stoichiometry of the polycomplex.

Summarizing the experimental data and the discussion, it may be stated that the interaction between PMAA and PEG-based surfactants proceeds in two stages with respect to the surfactant concentration. In the first stage, the polycomplex is formed. According to the hydrophilic–hydrophobic balance of the surfactant, its structural state in the particle of the polycomplex might be different. The surfactant forms micelles in the polycomplex below a certain ratio of PEG chain length to the chain length of the alkyl group. On increasing PEG chain length, linear sequences of H-bonds are formed between the components. In the second stage, the formed polycomplex binds additional surfactant which is included in the associate as micelles. The complexation is accompanied by significant conformational changes in the polycomplex due to the lyophilizating surfactant. The formation of the associate is of pronounced cooperative character. The structure of the associate could be of two kinds with respect to the structural state of the surfactant in the polycomplex and its lyophilizing abilities. If the polycomplex contains the surfactant as individual macromolecules when associating with the micelles, a homogeneous structure should be formed.

All surfactant macromolecules should form the same micelle structures when associated with PMAA macromolecule, structure A, Fig. 5(a). It is real as no conservation of the linear sequences of the component bonds could be expected in the extended conformation of the associate. Such structural changes when the associate is formed are probably typical of the systems PMAA–D-PEG$_3$, D-PEG$_4$, D-PEG$_5$, D-PEG$_6$, DD-PEG$_4$, DD-PEG$_5$ and DD-PEG$_6$.

When the polycomplex contains the surfactant macromolecules as micelles, in principle, two versions are possible. If the lyophilizing capacity of the surfactant micelles is high enough, the interaction between the polycomplex and the micelles will lead to formation of an associate with structure A. At low lyophilizing capacity of the surfactant micelles (short PEG chains), it is possible for an associate with structure B to be formed. Such an associate is a particle of the polycomplex, interacting with the surfactant micelles only in the surface layer. The interaction may occur via formation of H-bonds between the surface free segments of PMAA and the PEG chains. Hydrophobic interactions play a significant role in the complexation between polyacids and surfactant micelles and this role must increase with shortening of the PEG chain. Then the formation of the hydrophilic associate with structure A becomes less probable. The interaction between the polycomplex surface and the surfactant micelles is the compromise variant when the hydrophobic particles of the polycomplex raise to a certain extent their thermodynamic affinity for the solvent.

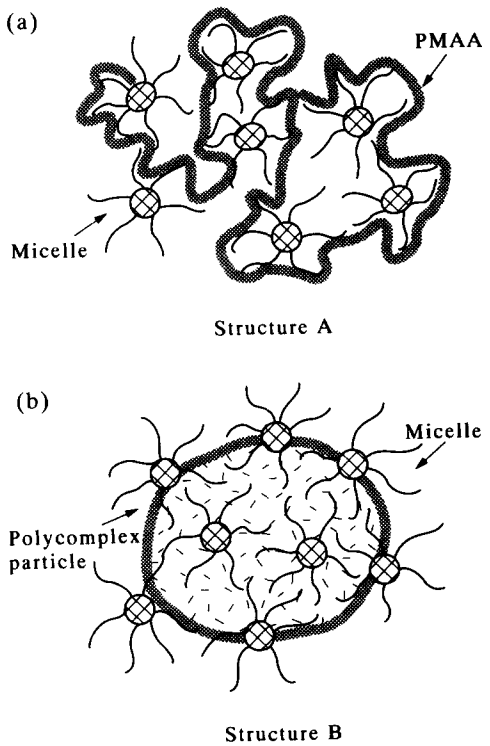

Fig. 5. Scheme of the probable structures A and B of the associate between the polycomplex (PMAA · surfactant) and surfactant micelles in aqueous solution.

Acknowledgement—The authors thank the Bulgarian National Foundation "Scientific Researches" for financial support.

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