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Abstract

Complexation between anionic, cationic ionomers as oil-soluble amphiphilic copolymers and various oil-soluble surfactants proceeds in dilute ionomer solution in THF, *m*-xylene and chloroform with surfactant molecules of various degree of aggregation as well as with surfactant reversed micelles containing water. Sulfonated polystyrene or styrene-*N*-ethyl-4-vinylpyridinium bromide copolymers were used as ionomers, while sodium bis(2-ethylhexyl) sulfosuccinate, octadecyltrimethylammonium bromide, and primary aliphatic amines were used as surfactants. The formation of ionomer–surfactant complexes with well-defined limiting compositions (φ) is established. The value of φ depends on the nature of the ionomer salt/acid group, the aggregation state of the surfactant, the type of low-polarity solvent, and the chemical nature of the surfactant. The character of the ionomer–surfactant complexation reaction and the structure of the new polymer–colloidal complexes are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Interactions of polymers and low-molecular mass compounds have been attracting the interest of researchers for quite some time. A good example of this is the present symposium.

Up to now, complexes of polyelectrolytes and oppositely charged surfactants have been studied in more detail [1]. Such complexes appear due to

coulombic attraction of polyelectrolyte chain units and surfactant ions, and are additionally stabilized via hydrophobic interactions of hydrocarbon surfactant fragments in water (Scheme 1). Electrostatic interactions play a decisive role in the formation of such complexes.

In principle, one could anticipate formation of complexes based on polymers and surfactants when there are no strong electrostatic or donor–acceptor interactions of partners. When a polymer has amphiphilic structure, the possibility of poly-

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mer–surfactant complexation should be determined by the hydrophilic-lipophilic balance (HLB) of the components.

A hypothetical scheme of complexation reactions and the structure of the formed complexes are shown below (Scheme 2). If one has an amphiphilic copolymer containing both polar and nonpolar hydrophobic chain units in the most simple case, then one will anticipate different complexation routes with surfactant depending on the nature of solvent. In low-polarity solvent, copolymer polar chain units will interact with polar groups of surfactant with the formation of joint associates or multiplets. In aqueous solutions, hydrophobic interactions between nonpolar copolymer chain units and hydrocarbon fragments of surfactant may lead to the formation of mixed aggregates or micelles.

The possibility of occurrence of such complexation reactions, structure and properties of the resultant complexes should depend decisively on the HLB of the partners and polarity of solvent.

The hydrophobic interactions between components in aqueous solutions and the structure of polymer–surfactant associates are well studied [1], and have been discussed in several presentations at this symposium as well. We also have carried out a study of complexation and structure of such complexes [2]. However, the complexation of the components in low-polarity solvents remains practically unexplored.

Therefore in this paper we will review the results of our studies of copolymer–surfactant complexation in low-polarity solvents.

2. Experimental

Anionic and cationic ionomers with nonpolar backbone based on polystyrene, containing small amounts of either sulfonated groups with various counterions or quaternized vinylpyridine chain units have been used in our studies, Fig. 1. Cationic octadecyltrimethylammonium bromide surfactant, anionic aerosol OT double tail surfactant and nonionic surfactants—primary aliphatic amines of homologous series were used in our work. Low-polarity solvents, i.e. *m*-xylene, chloro-

form and THF with various dielectric constants have been chosen for these studies.

Synthesis of anionic ionomers is described in [3], while cationic ionomer obtained via radical copolymerization of styrene and 4-vinylpyridine with the further quaternization of 4-vinylpyridine chain units using ethyl bromide, was kindly provided to us by Dr D. Peiffer. Molecular weight characteristics for the studied ionomers are indicated in Fig. 1. Distilled water and purified low-polarity solvents were used in all studies [4]. We used 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (PTSNa), obtained from Eastman Kodak, as water-soluble probe solubilized into AOT-H₂O reversed micelles to detect those micelles in velocity sedimentation experiments. AOT surfactant was purchased from Fluka and thoroughly dried before application. Cationic surfactant and aliphatic amines were purchased from Aldrich and dried under vacuum (cationic surfactant) before application.

Velocity sedimentation experiments were performed using a Beckman-E analytical ultracentrifuge at $\omega = 48\,000$ rpm and $T = 25^\circ\text{C}$. Vapor pressure osmometry experiments were carried out at various temperatures using mostly a Wescan-233 vapor pressure osmometer as is described in [5,6].

Solutions of AOT-H₂O reversed micelles were prepared via dissolution of surfactant in water at a constant $[\text{H}_2\text{O}]/[\text{AOT}] = 5.0$ molar ratio. Solutions of ionomers and ionomer–surfactant mixtures were prepared under constant stirring for 24 h prior to the measurements.

Scheme 1. Complex between a polyelectrolyte and an oppositely charged surfactant.

Scheme 2. Hypothetical complexation between amphiphilic copolymers and low molecular weight surfactants.

3. Results and discussion

Some general trends of polymer–surfactant association can be outlined on the example of anionic AOT surfactant and sulfonated polystyrene ionomers. The peculiarity of AOT surfactant is that it can be either in a slightly aggregated, nearly molecularly dispersed state or in the form of reversed micelles depending on the polarity of solvent and the presence of added water. This has allowed us to study the influence of the surfactant aggregation state on interaction with ionomers.

Table 1 shows the data on solubility of ionomers in *m*-xylene. Ionomers with > 2.6 mol% of zinc sulfonated groups are insoluble in *m*-xylene. Ionomers with sodium sulfonated groups lose solubility in *m*-xylene even at 1.4 mol% of such groups. In the presence of AOT, one can dissolve nearly all ionomers besides the one with the highest content of zinc sulfonated groups, (7.3 mol%), which is partially soluble.

What is the reason for the increased solubility of ionomers in the presence of AOT?

The fundamental property of ionomers is the aggregation of ionomer salt groups in low-polarity solvents and in the bulk. Aggregation accompanies the formation of intra and interchain associations, thus lowering substantially ionomer solubility. It has been shown earlier that addition of low-molecular mass aliphatic alcohols, acids and some amines, in other words, amphiphiles may cause an increase in ionomer solubility in low-polarity solvents [7–9]. It was suggested that added amphiphiles act as cosolvents for ionomer salt groups, initiating the breakdown of associations and thus increasing ionomer solubility in low-polarity solvents.

One can expect that AOT molecules interact with ionomer polar groups in a similar way. How does this interaction proceed and what is the final product of such interaction?

Velocity sedimentation (ultracentrifugation) and vapor pressure osmometry techniques were used to study complexation between ionomers and AOT surfactant. A detailed discussion of sedimentograms for ionomer–AOT mixtures is

given elsewhere [5,6]. The data on interaction of ionomers and AOT reversed micelles containing water will be discussed below. Velocity sedimentation technique in the traditional Schlieren mode as well as the scanner mode were used in the present work. Application of the scanner mode allows to independently register sedimentation of AOT micelles by monitoring the change in optical density of solution with hydrophilic probe (PT-SNa) solubilized in a water pool of AOT reversed micelles.

Fig. 2 shows Schlieren and scanner sedimentograms of mixtures of ionomer and AOT-H₂O reversed micelles, upper part of the figure, as well as polystyrene and AOT-H₂O reversed micelles, below in the same figure.

In the case of polystyrene and AOT micelles mixture, only one 'step' is observed in the scanner mode which corresponds to individual, i.e. not bound AOT micelles, (sedimentation coefficient of that component coincides with the one for indi-

Table 1

The influence of AOT surfactant on ionomer solubility in *m*-xylene^a

Ionomer		Solubility of ionomers in <i>m</i> -xylene	
Abbreviation	<i>m</i> (mol%)	Without AOT	With added AOT
SPZn	1.3	Soluble	Soluble
	2.6	Insoluble	Soluble
	4.3	Insoluble	Soluble
	7.3	Insoluble	Partially soluble
SPNa	1.4	Insoluble	Soluble
	2.7	Insoluble	Soluble

^a Ionomer concentration is 0.05 (base mol l⁻¹); AOT concentration is 0.02 (mol l⁻¹).

vidual AOT micelles). Two peaks are present in the Schlieren mode. An estimation of their sedimentation coefficients allows to attribute these peaks to the individual components—polystyrene and free AOT micelles, respectively. Since polystyrene and AOT micelles are sedimenting separately in their mixture one can conclude that there is no interaction between components in this case.

In the case of ionomer and AOT micelles, both Schlieren and scanner sedimentograms show relatively slow and fast components. Estimation of the sedimentation coefficient of the slow component allows to ascribe this component to the free AOT micelles. Ionomer and most of AOT micelles compose fast sedimenting component. Since ionomer and micelles undergo sedimentation altogether, one can conclude that ionomer interacts with AOT micelles with the formation of a complex. Similar results were obtained in the case of interaction between ionomers and AOT surfactant in slightly aggregated and molecular dispersed states [6].

Important information on the character of ionomer–AOT complexation has been obtained from the analysis of the dependence of the ionomer sedimentation coefficient upon surfactant concentration in the mixture. Fig. 3 shows dependencies of sedimentation coefficients of ionomer, polystyrene, their mixtures with AOT and re-

Polymers

Surfactants

$R-N(CH_3)_3^+Br^-$: $R = C_{18}H_{37}$ $R-NH_2$: $R = C_8H_{17}$ and $C_{18}H_{37}$

Solvents

m-Xylene ($\epsilon=2.2$), Chloroform ($\epsilon=4.8$), THF ($\epsilon=7.5$)

Fig. 1. Objects of investigation.

versed micelles of AOT containing water, upon surfactant concentration. The data for ionomers with various content of zinc sulfonated groups are shown in the same figure.

Some general trends can be observed in the example of ionomer with less content of salt groups, SPZn ($m = 1.3$ mol%). In the absence of AOT, the ionomer sedimentation coefficient is about three times higher than that of polystyrene with the same molecular weight. This difference can be mainly attributed to compaction of the ionomer coils due to predominant intrachain association of the ionomer salt groups in dilute solution. Successive addition of AOT to the ionomer solution is accompanied by a decrease in the sedimentation coefficient with the further approach of saturation. Similar dependence is char-

Fig. 2. Sedimentation profiles (Schlieren, dn/dx ; and scanner, absorbance) in SPZn—ionomer and polystyrene (PS) solutions with added (AOT- H_2O) reversed micelles in m -xylene. $[SPZn] = [PS] = 0.05$ (base mol l^{-1}); $[AOT] = 0.02$ (mol l^{-1}); λ (Abs) = 358 nm.

Fig. 3. Sedimentation coefficient versus AOT concentration in SPZn and PS solutions with added (AOT- H_2O) reversed micelles in m -xylene. $[SPZn] = [PS] = 0.05$ (base mol l^{-1}). Open symbols with a dot and the other symbols were obtained in the scanner and Schlieren modes, respectively.

acteristic of the ionomer with twice higher content of salt groups, SPZn ($m = 2.6$ mol%), while the plateau region appears at higher surfactant concentrations. In contrast to ionomers, the sedimentation coefficient of polystyrene remains unchanged upon surfactant addition, which indicates no interaction between polystyrene and AOT.

Two conclusions can be made based on the above data. Firstly, leveling off of the dependence of ionomer sedimentation coefficient on surfactant concentration indicates the formation of ionomer–AOT complexes of limiting composition, which remains unchanged after reaching a certain concentration of surfactant in the mixture. Secondly, in spite of an increase in the molecular mass of ionomer due to complexation, one still observes a decrease in sedimentation coefficient as the result of complexation. One can suggest that ionomer–surfactant interaction is accompanied by disruption of intrachain associates of ionomer salt groups in dilute solution, unfastening and expansion of the ionomer coils, which results in the observed decrease in the sedimentation coefficient.

We have estimated the limiting compositions of complexes using ultracentrifugation and vapor

Table 2

The quantity of bound AOT molecules or (AOT-H₂O) reversed micelles, F , per one ionomer salt/acid group for the ionomer–AOT complexes of the limiting compositions^a

Ionomer (m (%))	Surfactant	F^*		N^+
SPZn (1.3)	(AOT-H ₂ O) micelles	28.0	0.40 micelles	70.0
SPNa (1.4)	(AOT-H ₂ O) micelles	46.0	0.66 micelles	70.0
SPZn (2.6)	(AOT-H ₂ O) micelles	24.0	0.34 micelles	70.0
SPNa (2.7)	(AOT-H ₂ O) micelles	34.0	0.48 micelles	70.0
SPZn (4.3)	(AOT-H ₂ O) micelles	19.0	0.27 micelles	70.0
SPH (4.5)	(AOT-H ₂ O) micelles	15.0	0.21 micelles	70.0
SPNa (1.4)		23.0	–	12.0
SPZn (1.3)	(AOT-H ₂ O) micelles	14.0	–	12.0
SPZn (2.6)	(AOT-H ₂ O) micelles	15.0	–	12.0

^a Solvent, *m*-xylene; methods, vapor pressure osmometry and velocity sedimentation (scanner mode).

* Calculated; [H₂O]/[AOT] = 5.0 (mol mol^{−1}).

⁺ Either aggregation number of (AOT-H₂O) reversed micelles, or apparent aggregation number of AOT molecules without added ionomer.

pressure osmometry techniques. We will not discuss here the procedures of such estimations, since they are described in detail elsewhere [5,6]. Table 2 shows the data on the limiting compositions of complexes for ionomers and AOT surfactant in slightly aggregated state and reversed micelles containing water. The aggregation numbers of AOT without added ionomer in *m*-xylene are given in Table 2.

One has to first stress the way of expressing limiting compositions of the complexes. Since it has already been shown that AOT surfactant does not interact with polystyrene it is reasonable to express complex composition as the amount of surfactant molecules bound to one ionomer ionogenic group. This type of composition expression has been used for the data presented in Table 2.

The first point to stress is the limiting compositions of such complexes. Thus, there are ~15–30 AOT molecules bound to one ionomer ionogenic group on average. What is the structure of such a complex?

Based on sedimentation data indicating conformational transitions of ionomers upon complexation and the data on limiting compositions of complexes, the structure of formed complexes can be schematically presented as is shown, Scheme 3.

As one can see in this scheme, an interaction of ionomers and surfactant molecules leads to unfas-

tening and expansion of the ionomer coils. Ionomer ionogenic groups are playing the role of ‘molecular anchors’, which bind surfactant micelles or induce aggregation of surfactant molecules on the ionomer chain.

The driving force of complexation is the increase in the entropy due to the substitution of self contacts of ionomer salt groups for their contacts with surfactant molecules with the concurrent unfastening and expansion of ionomer coils. Besides, an introduction of ionomer salt groups into a polar region composed of aggregates of surfactant polar groups should also lead to a decrease in the electrostatic component of the free energy of the system. Eventually, one can also expect that the nonpolar hydrocarbon backbone of the ionomer will stabilize complex particles in low-polarity solvents.

One can expect that the structure and composition of such complexes will depend on the chemical nature of components, their HLB, the initial aggregation state, and solvent polarity. The discussion of some of these factors is given below.

The influence of counterion of ionomer ionogenic group on the limiting composition of complexes will be addressed first. As one can see in Table 2, ionomers with sulfonated groups and various counterions are characterized by increased composition while passing from less polar to more

polar ionogenic group in the row $-\text{SO}_3\text{H} \leq \text{SO}_3(\text{Zn})_{1/2} \leq \text{SO}_3\text{Na}$. For the same ionomers the tendency to form self aggregates increases while solubility in low-polarity solvents decreases in the same order [10,11].

The nature of the polar group of surfactant molecules also influences the character of complexation and limiting compositions of complexes. We have studied the influence of the polar group of surfactant using nonionogenic surfactant—primary aliphatic amines. Table 3 shows the limiting compositions of ionomer-surfactant complexes for octyl and octadecylamines in *m*-xylene.

In the absence of added ionomer, octylamine is slightly aggregated and forms trimers–tetramers. Octadecylamine is nearly in the molecular dispersed state. Complexation leads to aggregation of surfactant on the ionomer chain analogous to the case with AOT surfactant. Thus, formed joint associates include from seven to 13 molecules of

octylamine per ionomer ionogenic group. However, in contrast to complexes with AOT, the limiting composition of ionomer–octylamine complex is higher for the ionomer with zinc sulfonated groups compared to the ionomer with sodium sulfonated groups, even though sodium sulfonated groups are more polar. This effect may be attributed to additional donor–acceptor interactions between the zinc counterion and amino group of octylamine.

The influence of the length of hydrocarbon nonpolar fragment of surfactant molecules on limiting composition can be analyzed with the example of the same amines of a homologous series. The limiting compositions of ionomer complexes with octylamine and octadecylamine differ substantially, Table 3. In the case of octylamine, seven to 13 surfactant molecules are bound to one ionomer group, while in the case of octadecylamine this number drops down to three to four molecules. A decrease in the limiting composition for the high homologue correlates well with the decrease in the degree of aggregation of amines in *m*-xylene without added ionomer. As was already pointed out, octylamine forms trimers–tetramers, while octadecylamine does not aggregate at all.

In order to analyze the role of low-polarity solvent in the complexation we have studied ionomer–AOT complexation in THF which is more polar than *m*-xylene. However, ionomers form self aggregates in THF and also interact with AOT surfactant. The data on limiting compositions of the formed complexes are given in Table 3. Joint aggregates are formed as the result of complexation analogous to the case with *m*-xylene solvent. However, one has to stress an important result. In the absence of ionomer, AOT surfactant forms dimers and thus nearly does not aggregate. In the presence of added ionomer the complexes are formed with the compositions of nine to 14 AOT molecules per ionomer ionogenic group. This means that in the process of complexation, in THF ionomer chains induce aggregation of nearly molecularly dispersed AOT surfactant. Interestingly, a similar trend of induced association of surfactant molecules on the ionomer chain is observed in the case of complexation of cationic ionomers and cationic surfactants in chloroform, Table 3.

Scheme 3. Structures of ionomer–AOT and ionomer–(AOT– H_2O) reversed micelles complexes.

Table 3

The quantity of bound surfactant molecules, F , per one ionomer salt group for the ionomer–surfactant complexes of the limiting compositions^a

Ionomer (m (%))	Surfactant	Solvent	F^*	N^+
SPZn (1.3)	AOT	THF	9.0	2.0
SPZn (4.3)	AOT	THF	9.0	2.0
SPNa (2.7)	AOT	THF	14.0	2.0
SPZn (1.3)	Octylamine	<i>m</i> -Xylene	13.0	3.5
SPNa (1.4)	Octylamine	<i>m</i> -Xylene	7.0	3.5
SPZn (1.3)	Octadecylamine	<i>m</i> -Xylene	3.0–4.0**	No aggregation
QSPN (4.2)	Octadecyltrimethylammonium bromide	Chloroform	16.0	2.0
QSPN (4.2)	AOT	Chloroform	18.0	8.0

^a [Ionomer] = 0.05 (base mol l⁻¹). T = 27°C for THF, 31°C for chloroform and 40°C for *m*-xylene. Method, vapor pressure osmometry.

* Calculated value.

** Assumed value.

⁺ Apparent aggregation number of surfactant molecules without added ionomer.

4. Conclusions

The interaction between ionomers and surfactants in low-polarity solvents leads to the formation of peculiar polymer–colloidal complexes, in which ionomer ionogenic groups are playing the role of ‘molecular anchors’ binding surfactant micelles, aggregates and inducing aggregation of molecularly dispersed surfactant on the ionomer chains. The alteration in HLB, solvent polarity, chemical nature of both surfactant and ionomer components allows to design ionomer–surfactant complexes of certain structure and limiting compositions.

Our preliminary studies indicate that the obtained complexes possess interesting properties related to solubilization of various low-molecular mass compounds, formation of stable oil-in-water microemulsions characterized by a wide range of content of polar phase, and viscosity modification of low-polarity solvents which may open up new areas of practical applications for such complexes.

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