

Effect of Polymer Molecular Weight on the Polymer/Surfactant Interaction

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A thermodynamic analysis of the interaction between fourteen different molar mass poly(ethylene oxide)s (PEO) and sodium dodecyl sulfate (SDS) based on the measured surfactant-binding isotherms is given. The surfactant-binding isotherms were determined by the potentiometric method in the presence of 0.1 M inert electrolyte (NaBr). It was found that there is no PEO/SDS complex formation if $M_{\text{PEO}} < 1000$. In the molecular weight range $1000 < M_{\text{PEO}} < 8000$, the critical aggregation concentration (cac) and the surfactant aggregation number are decreasing as the polymer molecular weight increases. The saturated bound surfactant amount is proportional to the number concentration of the polymer in this molecular weight range. If M_{PEO} exceeds ~ 8000 , the cac does not depend on the polymer molar mass, and the saturated bound amount of the surfactant becomes proportional to the mass concentration of the polymer. It was also observed that independently of the polymer molecular weight the surfactant aggregation number increases as the equilibrium surfactant monomer concentration increases from the cac to the critical micellar concentration (cmc). Finally, it was demonstrated that only one polymer molecule is involved in the complex formation independently of the polymer molecular weight.

Introduction

The interaction of surfactants with macromolecules has been the subject of investigations since the early 1950s. First, the protein/surfactant systems were investigated because of their biological importance. Later, with the appearance of well-defined synthetic polymers, the research was extended to the polymer/surfactant interaction. Beyond their scientific interest, polymer/surfactant systems have received considerable attention because of their numerous industrial applications (e.g., pharmaceutical and biomedical applications, detergency, enhanced oil recovery, food and mineral processing).^{1–3}

Ionic surfactants interact with neutral, flexible polymers in the form of surfactant aggregates, that is, the surfactant interaction is cooperative similarly to the micelle formation.⁴ Because of the cooperative nature of the polymer/surfactant interaction, it can be characterized by a critical interaction concentration of the surfactant, which is usually called the critical aggregation concentration (cac) in the literature. Below this concentration, there is no interaction between the surfactant and the polymer. As the surfactant concentration exceeds the cac, the surfactant starts to bind to the polymer. As the total surfactant concentration increases, the bound amount rapidly increases, which is accompanied by a slow increase of the equilibrium (monomer) surfactant activity. Finally, the equilibrium surfactant activity reaches the critical micelle concentration (cmc), and free micelles form in the solution. At the cmc, the polymer may be saturated with the surfactant; however, the binding process is not necessarily completed at this surfactant activity.^{5–10}

The polymer/surfactant complex can be viewed as a “string of beads” in which the polymer chain connects micelle-like surfactant aggregates by wrapping around them.^{11,12} The size

of the polymer-bound surfactant aggregates is much smaller than that of the free micelles.^{13–17} However, as the equilibrium surfactant concentration increases, the surfactant aggregation number also increases. Despite this increase, at the cmc, the size of the surfactant aggregates is still smaller than that of the free micelles.

The above general picture of the interaction is supported by investigations performed by a wide variety of experimental techniques including surface tension,^{4,18–20} conductivity,^{4,14,18,21} and viscosity^{4,14,19,22} measurements; dialysis equilibrium;^{20,23,24} ion-selective electrodes,^{3,25–27} light-²⁸ and neutron-^{29,30} scattering, fluorescent,^{13–15} and trace electrolyte probes;^{16,17} NMR;^{31–33} and isothermal titration calorimetry^{34–39} (for further references, see ref 1–3). Furthermore, the polymer/surfactant interaction has been described at different levels of approximations by thermodynamic models^{40,41} as a chemical equilibrium, phase separation, or adsorption, as well as by small system thermodynamics,⁴² molecular interaction models,^{43–46} and the combination of these.⁴⁷ In the recent years, there has been still significant activity in the field of polymer/surfactant interaction. Several studies have been published addressing questions such as the structure of the polymer/surfactant complex,³³ the effect of polymer molecular weight,³⁸ the type of the surfactant counterion,^{36,48–51} and the effect of temperature³⁹ on the interaction.

Despite the extensive experimental and theoretical research, there are still some important aspects of the polymer/surfactant interaction that have been hardly investigated yet. Such an aspect is the role of the polymer molecular weight, a parameter that is generally neglected. This approach is supported by the investigation of Schwuger¹⁸ who found that the SDS does not interact with PEO if the PEO molecular weight is smaller than 1500. Above this molecular weight, the cac first decreased slightly up to about $M_{\text{PEO}} = 4000$, then it became independent from

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the polymer molecular weight. Tokiwa and Tsujii⁵² also demonstrated a minimum molecular weight requirement for the PEO/SDS interaction. Francois et al.¹⁴ found that the PEO/SDS interaction is independent of the PEO molecular weight from 6000 to 900 000. Recently, Dai et al.³⁸ investigated the effect of PEO molecular weight on the PEO/SDS interaction by isothermal titration calorimetry in the $M_{\text{PEO}} = 400\text{--}8000$ molecular weight range. They observed different enthalpy profiles in the function of the molecular weight and identified $M_{\text{PEO}} = 900$ as the minimum molar mass for the interaction.

Bernazanni et al. have very recently presented a combined isothermal titration calorimetry (ITC) and ^{13}C , ^1H , and ^{23}Na NMR study⁵³ of the PEO/SDS interaction in the low and moderate molecular weight ranges of the polymer. On the basis of their ITC measurements, the authors concluded that the minimum molar mass of the appearance of the PEO/SDS interaction is $M_{\text{PEO}} \approx 350$ and $M_{\text{PEO}} \approx 3800$ is the critical molecular weight above which the interaction is independent of M_{PEO} . They also suggested that the surfactant aggregates bind in a stepwise manner on the PEO. The detailed NMR investigations of this paper indicated the validity of the generally accepted necklace model for the PEO/SDS interaction and excluded the possibility that the polymer chains are solubilized deeply in the hydrophobic core of the PEO/surfactant aggregates.

The aim of the present work was to perform a systematic investigation of the effect of the polymer molecular weight on the neutral polymer/ionic surfactant interaction. The investigations were done using the classical PEO/SDS system, and the interaction was monitored over an extremely wide PEO molecular weight range (between 2×10^2 and 8×10^6 on 14 different samples). The binding isotherm of the SDS was measured potentiometrically by means of a newly developed membrane electrode.⁵⁴ On the basis of the experimental isotherms, a thermodynamic analysis of the PEO/SDS complex formation is given.

Experimental Section

Materials. The sodium dodecyl sulfate (SDS) was prepared from pure *n*-dodecanol (Jansen, 99+%) by sulfation with chlorosulfonic acid (Merk) at $0\text{--}5^\circ\text{C}$.⁵⁵ The recipe given in ref 55 was slightly modified. The synthesis was performed in CCl_4 medium, and the reaction mixture was neutralized by sodium carbonate. The prepared salt was twice recrystallized from hot 1:1 benzene/ethanol mixture. Because of the recrystallization procedure, the amount of contaminants in the purified samples is significantly lower than in the original alcohol used in the synthesis. Gas chromatographic analysis of the products showed 3×10^{-5} mole fraction of dodecanol in the samples; a combined liquid chromatographic/mass spectrometric analysis showed that the total amount of other homologue salts is less than 5×10^{-3} mole fraction. The solutions were prepared from dried (for 72 h at 40°C in a vacuum) surfactants and bidistilled water. The critical micelle formation concentration of the recrystallized SDS was 8.16 mM from conductometric measurements at $t = 25^\circ\text{C}$.

The investigated poly(ethylene oxide)s (PEO) were Aldrich products and were used without further purification. The PEO molecular weights were accepted as claimed by the manufacturer. According to the classical investigations, the reaction mechanism of PEO synthesis suggests a narrow (Poisson) distribution of the molecular weight, which is "much narrower that can be obtained by polymer fractionation".⁵⁶ Altogether, fourteen different polymer molecular weights were used for the investigations ($M_{\text{PEO}} = 200, 300, 400, 600, 900, 1500, 2000, 3400, 4600, 8000, 1 \times 10^5, 1 \times 10^6, 8 \times 10^6$).

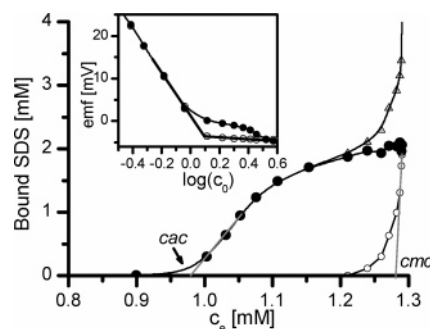


Figure 1. Determination of the amount of polymer-bound surfactant (solid circle) by means of the total (triangle) and micelle (open circle) bound amount measured in the presence and absence of PEO, respectively. The inset of the figure gives a typical plot of the emf measured between a DS^- and a Br^- ion-selective electrode as a function of total SDS concentration (c_0) in the absence (open circle) and presence (solid circle) of PEO.

Potentiometric Measurements. The electromotive force (emf) values of the

$\text{Ag}/\text{AgBr}/0.1\text{ M NaBr}/\text{membrane}/0.1\text{ M NaBr},$
 $c_{\text{PEO}}, c_{\text{SDS}}/\text{AgBr}/\text{Ag}$

galvanic cell were determined by means of a Radelkis research pH meter at $25.00 \pm 0.05^\circ\text{C}$.

The surfactant-selective membrane was prepared in our laboratory by a newly developed technique, which is based on the substitution of a fraction of the chlorine atoms bound to the poly(vinyl chloride) (PVC) backbone by trimethylamine.⁵⁴ By means of the prepared slightly charged polymer, high-quality surfactant-selective electrode membranes could be prepared, which had Nernstian response and short response time. The new method offers a simple alternative to the preparation of the chain-end functionalized PVC membranes described in the literature.⁵⁷ The details of functionalization of the PVC and the construction of the SDS-selective membrane electrodes have been described elsewhere.⁵⁴

The medium (10 cm^3 ; 0.1 M NaBr and c_p polymer) was placed into the measuring cell and titrated with an SDS stock solution (of the same NaBr and polymer concentration). The equilibrium emf values were read at each titration step.

The measured emf values were converted into surfactant monomer concentration by means of a self-calibration procedure. In the absence of the polymer, the emf versus $\log(c_{\text{SDS}})$ function was found to be linear up to the cmc (with a slope of 58.6 mV). In the presence of polymer, the emf versus $\log(c_{\text{SDS}})$ function is linear only below the cac. This linear part was used as a calibration curve to calculate the normal potential and the response of the electrode in the case of each individual potentiometric titration in order to determine the equilibrium surfactant monomer concentration c_e above the cac. By using this approach, any shift in the normal potential and in the response of the electrode could be eliminated, which gave rise to the high accuracy and reproducibility ($\pm 0.01\text{ mM}$) of the measurements. A typical set of measurements are shown in the inset of Figure 1.

Calculation of the Surfactant-Binding Isotherm. The exact binding isotherm of an ionic surfactant on a nonionic polymer ($B(c_e)$) can be calculated from the expression⁵⁸

$$c_0 = c_e \langle e^y \rangle + Bm_{\text{pol}} + c_{\text{mic}} \quad (1)$$

where B is the amount of surfactant bound to unit mass of the polymer (mmol/g), c_0 is the total surfactant concentration, and

c_e is the equilibrium monomer surfactant concentration in a polymer-free reference system^{16,17,58}. c_{mic} is the concentration of the micelles in monomer unit, m_{pol} is the polymer concentration (grams of polymer in unit volume), $y = e\Phi/kT$ is the dimensionless electric potential, and the brackets denote volume averaging. The factor $\langle \exp(y) \rangle$ takes into account that in the presence of macroions (ionic surfactant aggregates) the distribution of small ions (e.g., surfactant molecules) is not uniform in the solution. This factor can become important in low ionic strength solutions where it must be determined from independent measurements.^{16,17} In our case, the measurements were performed in the presence of a large amount of inert electrolyte (0.1 M NaBr); thus, because of the high ionic strength, the $\langle \exp(y) \rangle$ factor becomes practically equal to one.

In a high ionic strength solution, the difference between the total and the equilibrium surfactant concentrations gives the sum of the micelle- and polymer-bound surfactant concentrations ($c_0 - c_e = m_{pol}B(c_e) + c_{mic}(c_e)$). If the measurements are restricted below the cmc, then the binding isotherm can be determined directly ($B(c_e) = \{c_0 - c_e\}/m_{pol}$). However, in the close vicinity of the cmc (and above the cmc), where free micelles start to form, the amount of micelle-bound surfactant has to be determined independently (e.g., by performing the measurement in the absence of polymer). Then, the amount of the polymer-bound surfactant can be calculated ($B = \{c_0 - c_e - c_{mic}(c_e)\}/m_{pol}$) as illustrated in Figure 1.

Results and Discussion

Effect of Polymer Molecular Weight on the cac. It is well-established in the literature that because of the hydrophobic interaction of the surfactant molecules a pseudo-phase separation takes place in the surfactant solutions: With increasing surfactant concentration, the surfactant activity reaches a practically constant “monomer solubility” limit, the cmc. If the total surfactant concentration exceeds the cmc, then the free monomer activity remains almost constant ($a_e \approx \text{cmc}$) and the excess amount of surfactant separates into the “micellar phase”.

In the presence of polymer, the surfactant starts to separate into a polymer/surfactant complex at the critical aggregation concentration ($\text{cac} < \text{cmc}$). However, contrary to the cmc, the cac is not a monomer solubility limit, because with increasing total surfactant concentration the equilibrium monomer concentration (c_e) rises from the cac to the cmc (see Figure 1). The thermodynamic reason for the different character of the cmc and the cac is that the micellar phase is a one-component system, while the polymer/surfactant complex is a two-component (pseudo-phase) system. This means that with decreasing number of the available polymer-binding sites (component A) the concentration of the surfactant monomer (component B) must increase. This is a similar case to the formation of an AB_x precipitate, where the equilibrium concentrations of components A and B are determined by the solubility product ($L = [A] \cdot [B]^x$).

In Figure 2, the cac is plotted as a function of PEO molecular weight. As reflected by the figure, the aggregation behavior of the SDS can be divided into three regions in the presence of PEO. Below $M_{\text{PEO}} \approx 1000$ (region A), the critical aggregation concentration of the surfactant corresponds to the cmc, which indicates that there is no complex formation in this molecular weight range. If the PEO molecular weight exceeds ~ 1000 , the cac appears below the cmc, and it decreases as the polymer molecular weight increases. Finally, when the polymer molecular weight becomes large enough (larger than $M_{\text{PEO}} \approx 8000$), the cac becomes practically constant (range C).

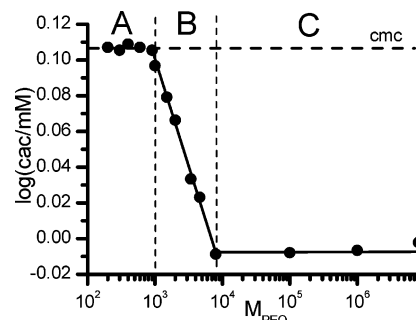


Figure 2. Critical aggregation concentration (cac) as a function of PEO molecular weight.

The cac characterizes the beginning of the surfactant binding to the polymer, that is, the formation of the first individual surfactant aggregates in the polymer coils, and it is determined by the standard free energy change of the polymer/surfactant complex formation ($\Delta G^\circ = RT \cdot \ln(x_{\text{cac}})$). Beyond a certain length of the polymer ($M_{\text{PEO}} \approx 8000$), the same surfactant aggregate with the same number of polymer segments may form in the polymer coil at the cac, regardless of the fact that the polymer contains many more segments than is necessary for the optimal interaction of the surfactant aggregate with the polymer segments. In region B below $M_{\text{PEO}} \approx 8000$, the number of segments in the polymer chain is less than would be needed optimally. Consequently, the standard free energy change of the complex formation decreases, which is reflected by the increase of the cac with decreasing M_{PEO} . The change of the cac in region B predicts that in region A (below $M_{\text{PEO}} \approx 1000$) the cac would be higher than the cmc. Since the equilibrium surfactant monomer concentration (activity) becomes almost constant at the cmc, it may not reach the cac value that would be required for complex formation in region A. As a consequence, the polymer/surfactant complex formation cannot be manifested in this region, and only free micelles form instead of polymer/surfactant aggregates.

The “Composition” of the Polymer/Surfactant Complex. The interpretation of the M_{PEO} dependence of the polymer/surfactant interaction given above is based on the underlying assumption that only one polymer molecule is involved in the polymer/surfactant complex molecule. It is well-documented in the literature that in the case of large polymers (range C) this is a valid assumption,¹ and indeed, a single polymer chain takes part in the complex formation. Furthermore, if the polymer is large enough, more than one surfactant aggregate can form in the same coil (necklace model, see Figure 3a.). However, when the polymer chain is too short to ensure the formation of an optimal composition of polymer/surfactant aggregate, in principle it is also possible that more than one polymer molecule interacts with the surfactant aggregate. Thus, the complex formation transforms from the “adsorption” of surfactant aggregates by the large polymer molecules into the “solubilization” of the small polymer molecules by the surfactant micelles or a polymer/surfactant “mixed micelle” formation (see Figure 3c).

The formation of a single polymer/surfactant aggregate can be described in general as



where x is the number of polymer molecules (P) and n is the number of the surfactants (S) in the aggregate. Equation 2 gives a possibility to determine x , the number of polymer molecules in a polymer/surfactant aggregate. By taking into account that the total polymer concentration (c_{pol} — mole polymer in unit

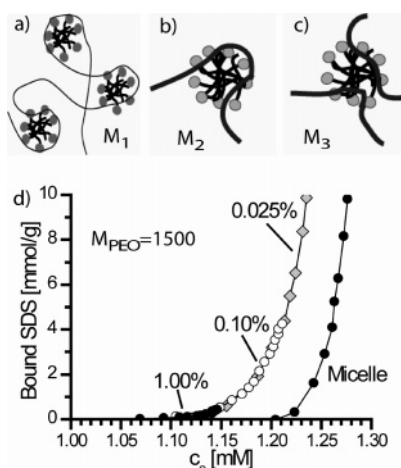


Figure 3. Schematic representation of the possible change of the polymer/surfactant complex structure with decreasing polymer molecular weight ($M_1 > M_2 > M_3$): (a) When M_{PEO} is large, several aggregates are connected by the polymer by wrapping around them (necklace model); (b) when the polymer chain length is comparable to the chain length required for the formation of an optimal composition complex, only one aggregate forms in the coil; (c) in the case of short polymer chains, in principle, more than one polymer chain could be incorporated into the complex; (d) polymer concentration dependence of SDS-binding isotherms (for explanation, see text).

volume) can be given as follows

$$c_{pol} = [P] + x \cdot [P_x S_n] \quad (3)$$

(where the brackets denote the molar concentration of the given species), it can be shown that the amount of polymer-bound surfactant ($B(c_e) \equiv n \cdot [P_x S_n]$) can be given as

$$B(c_e) = \frac{nK[S]^n[P]^{x-1}}{1 + xK[S]^n[P]^{x-1}} \quad (4)$$

where K is the equilibrium constant of the complex formation (eq 2). The above equation indicates that if only a single polymer chain takes part in the complex formation ($x = 1$) then the $B(c_e)$ function is invariant to the polymer concentration. Otherwise, if $x > 1$, then the $B(c_e)$ function is an $(x - 1)$ power function of the polymer concentration.

To clarify this aspect of the polymer/surfactant interaction, we investigated the effect of polymer concentration in a wide polymer concentration range (0.025–1.00%) for the polymers in range B. It was found that the $B(c_e)$ function does not depend on the polymer concentration, which means that $x = 1$ in the case of each investigated polymer. As an example, the surfactant-binding isotherms at different polymer concentrations are plotted in Figure 3d in the case of $M_{PEO} = 1500$. This chain length corresponds to about one-fifth of the optimal polymer length of the complex formation ($M_{PEO} = 8000$).

Surfactant-Binding Isotherms. In Figure 4a, the binding isotherms of the investigated polymers are collected. As is indicated by the figure, the polymer molecular weight has a profound effect on the binding isotherm, and practically all the characteristic features of the isotherm (the c_{ac} , the shape, and the saturation value) are modified as the polymer molecular weight changes. The isotherms can be divided into two groups. The characteristic features of the two groups will be discussed below separately.

One group of the isotherms (Figure 4b) is characteristic for the high molar mass PEOs. These polymers belong to region C

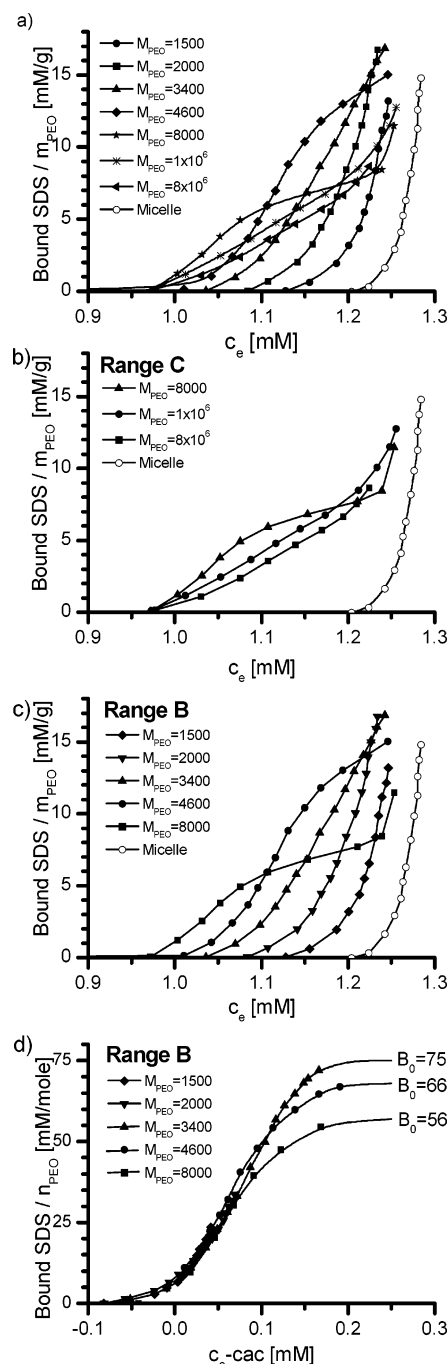


Figure 4. (a) The binding isotherm of SDS on PEO at different molecular weights of the polymer. (b) The binding isotherm of SDS on PEO in molecular weight range C (see Figure 2). (c) The binding isotherm of SDS on PEO in molecular weight range B. (d) The binding isotherm of SDS on PEO given in mmol SDS/mol PEO unit and plotted as a function of $c_e - c_{ac}$ in molecular weight range B. (The lines in the figures are guides to the eye.)

in Figure 2, and the binding isotherms of these polymers can be characterized as follows:

1. The isotherms start from the same c_{ac} (which means that the free energy of the complex formation of the first polymer/surfactant aggregate in the polymer coil is independent of the molecular weight). As has been discussed above, if the PEO molecular weight exceeds ~ 8000 , the polymer chain is long enough to form an optimal combination of the polymer segments with a surfactant aggregate.

2. The shape of the isotherms changes with M_{PEO} . As the polymer molecular weight increases, the binding isotherms

become more flat. When the molecular weight is ~ 8000 , the polymer chain is long enough to form an optimal polymer/surfactant aggregate. However, in that case, the polymer can accommodate only a single aggregate in the coil ($a_0 = 1$; where a_0 denotes the maximum number of surfactant aggregates that can form along a polymer chain). This means that the surfactant aggregates (similarly to the polymer molecules) are distributed statistically uniformly in the entire volume of the solution. As the molecular weight increases, the maximum number of aggregates in a polymer coil also increases (assuming that every $M_{\text{opt}} \approx 8000$ segment of the polymer chain can bind a surfactant aggregate, the estimated a_0 values are 125 and 1000 at $M_{\text{PEO}} = 1 \times 10^6$ and 8×10^6 , respectively). Though the polymer molecules are still distributed uniformly in the solution, the distribution of the surfactant aggregates is not uniform anymore. Several surfactant aggregates are connected by a polymer chain; thus, they are compressed in a small volume within the polymer coils. Therefore, the interaction between the aggregates becomes significant, which influences the shape of the isotherms even in the case of very dilute polymer/surfactant solutions. This effect becomes more pronounced if the polymer molar mass and consequently the number of interacting surfactant aggregates in a polymer coil increases.

3. The bound surfactant amount scaled to unit mass of the polymer (mol bound SDS/g PEO) tends to similar saturation values (B_0), regardless of the polymer molecular weight. Since as a first approximation it can be assumed that one surfactant aggregate forms along every "optimal-length chain segment" in the polymer coil, the maximum number of surfactant aggregates in a polymer/surfactant complex can be given as $a_0 = M/M_{\text{opt}}$, where M is the polymer molecular weight and M_{opt} is the "molecular weight" of the optimal-length polymer chain. If we take into account that the maximum amount of polymer-bound surfactant can be expressed as $B_0 = \bar{n}a_0c_{\text{pol}}/m_{\text{pol}}$, where \bar{n} is the average aggregation number, c_{pol} is the polymer concentration (given in moles of polymer in unit volume), and m_{pol} is the weight concentration of the polymer (grams of polymer in unit volume), it is straightforward to show that the maximum amount of the polymer-bound surfactant is determined by the aggregation number and M_{opt} ($B_0 = \bar{n}/M_{\text{opt}}$), which means that it is independent of the polymer molecular weight in accordance with the experimental results.

The other group of binding isotherms (Figure 4c) belongs to the polymers found in region B in Figure 2 ($M_{\text{PEO}} = 1500$ – 8000). The characteristic features of the binding isotherms in this group differ from the characteristics of the first group in all aspects:

1. The cac varies with the polymer molecular weight. The observed change indicates that the standard free energy change of the complex formation ($\Delta G^\circ = RT \cdot \ln(x_{\text{cac}})$) becomes less negative as the molecular weight decreases. The reason for this tendency is that the chain length of the PEO molecules belonging to this group is shorter than would be required for the formation of an optimal polymer/surfactant aggregate. As the polymer chain length decreases, the number of polymer segments interacting with the surfactant aggregate also decreases, giving rise to the formation of less favorable polymer/surfactant complexes.

2. The shapes of the isotherms are similar to each other and independent of the polymer concentration. This indicates that the aggregate/aggregate interaction is negligible even in the most concentrated solutions ($c_{\text{pol}} = 1.0\%$).

3. The saturation value of the binding isotherms (B_0) strongly increases with decreasing PEO molecular weight. As has been

discussed above, in this polymer molecular weight range only one surfactant aggregate can form in the polymer coil ($a_0 = 1$); thus, the expression given for the maximum amount of polymer-bound surfactant ($B_0 = \bar{n}a_0c_{\text{pol}}/m_{\text{pol}}$) reduces to the form $B_0 = \bar{n}/M$, which in agreement with the experimental results indicates that the maximum amount of polymer-bound surfactant is inversely proportional to the polymer molecular weight.

However, it should be noted that in this molecular weight range one polymer chain can accommodate only a single surfactant aggregate. This means that the number of surfactant aggregates is proportional to the number of polymer molecules, which means that if the bound amount is given for unit mole of the polymer (in mole SDS/mole PEO molecule), the saturation value of the binding isotherms should be similar for the polymers in range B. The recalculated binding isotherms are plotted in Figure 4d. To demonstrate the similarity of the recalculated isotherms, the cac of each isotherm is shifted to the origin. As is indicated by the figure, the isotherms coincide with each other within the experimental error up to about half-saturation (as it was stated in point 2), then they tend to similar but different saturation values at least in the case of the three higher molecular weight polymers. Figure 4d does not indicate a stepwise saturation of the bound surfactant in the function of the PEO molecular weight, as suggested by Bernazzani et al.⁵³ It should be noted, however, that the proposed binding mechanism of Bernazzani et al.⁵³ based on ITC measurements, which were performed without added salt whereas our experiments were done in a 0.1 M NaBr medium. In the case of $M_{\text{PEO}} = 1500$ and 2000, the saturation value cannot even be estimated, because the equilibrium surfactant monomer concentration reaches the cmc far below saturation. The interpretation of the different saturation values is discussed below.

Surfactant Aggregation Numbers. According to a recently developed small systems thermodynamics model of the polymer/surfactant complex formation, the amount of polymer-bound surfactant can be given with the following equation:⁵⁹

$$B = \frac{\lambda}{1 + \lambda} a_0 \bar{n} \quad (5)$$

B is given in dimensionless mol/mol unit, a_0 is the number of aggregates on a polymer coil at saturation, \bar{n} is the mean aggregation number, and

$$\lambda = \exp[(\bar{n}\mu_s - \bar{G}_{\text{sub}})/kT] \quad (6)$$

In eq 6, $\mu_s = \mu_s^0 + kT \ln x_c$ is the surfactant chemical potential, x_c is the mole fraction of the surfactant monomers in the solution, and \bar{G}_{sub} is the standard-state chemical potential of the mean surfactant aggregate (subunit) in the polymer coil. Equation 5 describes a sigmoid-type binding isotherm which is in accordance with the experimental observations (see Figure 1 or 4). Theoretically, \bar{n} and \bar{G}_{sub} may depend on x_c ; therefore, the exact evaluation of eq 5 requires the independent measurement of the $\bar{n}(x_c)$ function. In the lack of this information, we must restrict the quantitative analysis of the isotherms to the cac ($B \rightarrow 0$) and to the saturation binding ($B \rightarrow B_0$). If we take into account that if $B \rightarrow 0$ then $\lambda \ll 1$, the aggregation number at the cac can be calculated from the slope $d(\log B)/d(\log c_e)$ by extrapolating to $B = 0$. On the other hand, if $B \rightarrow B_0$, then $\lambda \gg 1$, which means that the saturation value of the binding isotherms reduces to $B_0 = a_0 \bar{n}$. Consequently, if the quantitative analysis of the binding isotherms is restricted to the polymers of range B, where the complex molecule can incorporate only one surfactant aggregate ($a_0 = 1$), then the saturation value of the

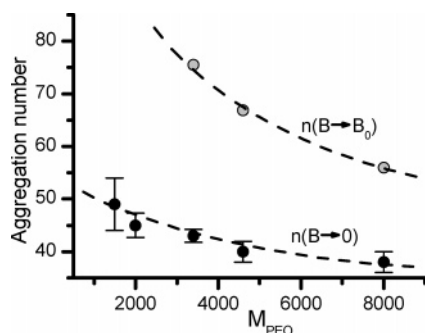


Figure 5. Aggregation number of surfactant aggregates in the function of PEO molecular weight at the cac and at saturation in the molecular weight range B.

isotherms directly gives the surfactant aggregation number at the saturation.

In Figure 5, the aggregation numbers at the beginning of the complex formation ($B \rightarrow 0$) and at saturation ($B \rightarrow B_0$) are plotted against M_{PEO} . The figure indicates two trends in the surfactant aggregation numbers. On one hand, a significant increase can be observed as the equilibrium surfactant concentration increases from the cac to the cmc (in other words, as the amount of bound surfactant increases), and on the other hand, the aggregation number also increases as the length of the polymer chain decreases.

Recent studies of the surfactant aggregation number in polymer/surfactant solutions performed by fluorescence probe^{13–15} and trace probe electrolyte methods^{16,17} also indicated that the aggregation number increases as the equilibrium surfactant concentration increases. In the case of micelle formation, small-angle neutron scattering measurements⁶⁰ also showed that the aggregation number of the free micelles increases with increasing surfactant concentration. In general, the change of the aggregation number can be interpreted in terms of three major effects:

- the decrease of the electrical free energy of the surfactant aggregate formation due to the change in the ionic strength,
- the entropy effect due to the increasing equilibrium surfactant concentration (c_e), which leads to a shift in the aggregation number distribution to higher aggregation numbers,
- the interaction between the surfactant aggregates.

Unfortunately, a detailed quantitative analysis of the contribution of these effects to the aggregation number increase has not been performed yet. However, in our case, the entropy effect seems to be the most probable reason for the observed change of the aggregation number from the cac to the cmc, because the other two effects are diminished at high ionic strength.

The interpretation of the influence of PEO molecular weight on the aggregation number is an even more complicated issue. A recent molecular interaction model of the polymer/surfactant complex formation⁶¹ suggests that there is a competition between the surfactant molecules and polymer segments to take part in the individual polymer/surfactant aggregates. If more polymer segments are involved in an aggregate, then the aggregation number is smaller, and vice versa. Though the model deals with nonionic surfactants, the situation may be similar in the case of ionic surfactants. By accepting this assumption, the following explanation can be given for the experimental results. As the polymer molecular weight (and the polymer chain length) decreases, less polymer segments are incorporated into the polymer/surfactant aggregates because of the increasing chain entropy loss of the polymer during the complex formation. The decrease in the number of incorporated polymer segments leads

to the formation of a polymer/surfactant complex with a higher surfactant aggregation number.

Summary

The binding of SDS to PEO is significantly affected by the polymer molecular weight. The polymer/surfactant interaction could be divided into three molecular weight ranges. If M_{PEO} is smaller than ~ 1000 , then polymer/surfactant complex formation does not take place, since the equilibrium monomer surfactant concentration that would be required for the formation of the polymer/surfactant complex exceeds the cmc. If the PEO molecular weight is between ~ 1000 and ~ 8000 , then complex formation takes place. In this molecular weight range, one polymer coil accommodates a single surfactant aggregate, and the cac as well as the surfactant aggregation number is decreasing as the molecular weight increases. Since a polymer/surfactant complex contains only one surfactant aggregate, the maximum amount of polymer-bound surfactant is proportional to the molar concentration of the polymer. If the polymer molecular weight is larger than ~ 8000 , then the polymer chain is long enough to form an optimal composition of polymer/surfactant complex in the polymer coil; thus, the cac becomes constant. In this molecular weight range, a polymer coil can accommodate more than one surfactant aggregate. Because of the interaction of these aggregates, the surfactant-binding isotherm becomes more and more flat as the polymer molecular weight increases. Since a polymer coil can accommodate several surfactant aggregates, the maximum amount of polymer-bound surfactant becomes proportional to the mass concentration of the polymer. Finally, independently of the polymer molecular weight, the surfactant aggregation number of the surfactant aggregate increases as the equilibrium monomer surfactant concentration increases from the cac to the cmc.

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