The interaction between water-soluble polymers and surfactant aggregates

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CHAPTER 2

INTERACTION BETWEEN NONIONIC SURFACTANTS AND NONIONIC POLYMERS: FACT OR FANCY?

2.1 Introduction

Nonionic surfactants form an important class of components for industrial and research purposes[89]. They are mild detergents with applications in cosmetic products and microemulsions. Their 'mildness' as surfactant has also led to applications in biochemical research, since these surfactants may solubilize proteins from cells or membranes without destroying the tertiary structure[89]. Especially surfactants based on sugar residues[90-93] enjoy a lively interest at present, both for biochemical applications[13-15] and for industrial uses[89]. Sugars are readily available as a renewable source[14,94] and biodegradable, which is of particular promise.

Nonionic surfactant are actually subdivided into two subclasses. These are (i) the true nonionics, which have a polar, hydrophilic headgroup such as a poly(ethylene glycol)ether or sugar moiety, and (ii) the zwitterionic surfactants of which the headgroups contain two opposite charges in near proximity. They bear no net charge. To avoid confusion, the term 'nonionic' will be reserved for the first subclass.

Zwitterionic surfactants sometimes behave similarly to nonionic surfactants[95] and sometimes similarly to ionic surfactants[96]. For instance, neither zwitterionic nor nonionic surfactants show a progressive decrease in free surfactant concentration above the cmc as ionic surfactants do[95]. On the other hand studies with a kinetic probe by Bunton et al.[96] revealed that micelles formed from sulfobetaine and betaine surfactants behave like cationic micelles with complete (100 %) counterion binding. Malliaris et al.[97] found that the aggregation numbers of zwitterionic and ionic micelles decrease upon

increasing temperature, whereas the nonionic surfactant, Triton X-100, showed an increase in aggregation number with increasing temperature. The latter observation is probably more characteristic for poly(ethylene glycol)ether type surfactants than for nonionic surfactants in general. The aggregation number (n) for β-D-*n*-octylglucoside, for instance, does not show a consistent increase (n = 68 (20 ^{0}C); n = 84 (30 ^{0}C); and n = 72 (50 ^{0}C))[98].

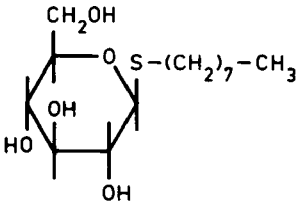
The interaction of zwitterionic surfactants with nonionic water-soluble polymers has scarcely been investigated, whereas nonionic surfactants, usually represented by the poly(ethylene glycol)ether type, have already gained a poor reputation as far as interaction with polymers is concerned[3,61,71]. They are usually considered to be totally indifferent to polymers, although *n*-nonylphenol-poly(ethylene glycol)ether interacts with PEO[99] and hydroxyethyl cellulose (HEC)[100], and in this study interaction of PPO with β-D-octylthioglucoside has been established[81]. The former complexation has been attributed to an affinity of the phenol moiety for PEO[101], since several polymers, including PEO, are known to interact with *p*-substituted phenols[102]. By contrast, viscometric measurements did not provide evidence for interaction between *n*-octylphenolethoxylate and PEO[61a].

Whether viscometry is the method of choice to detect polymer-micelle interaction with nonionic micelles, is disputable. The intermicellar repulsion between polymer-bound micelles, which lies at the origin of the polymer expansion and concomitant increase in viscosity, may well be small or insignificant for uncharged micelles. Particularly when the polymer coil in aqueous solution is already quite expanded, like that for PEO, the method is not sensitive enough. Nevertheless, viscosity and clouding point measurements have provided evidence for interactions between surfactants of the poly(ethylene glycol)ether type and some mildly hydrophobic (co)polymers and poly(carboxylic acid)s[89]. This association resembles the formation of interpolymer complexes between PEO and poly(carboxylic acid)s[103-105]. The presence of an alkyl chain in the surfactant will enhance this interaction, just as the extra methyl group in poly(methacrylic acid) enhances interaction as compared to poly(acrylic acid). This association, however, is not quite comparable with, for instance, that of PEO/SDS for which the micellar

character of SDS is decisive.

In order to explain and quantify the influence of surfactant headgroup structure on interaction with polymers, both Nagarajan[61] and Ruckenstein[71] developed detailed models. Based on different points of view, both authors stress the importance of the relative contribution of stabilization of the water-hydrophobic core interface by the polymer on the one hand and the unfavorable interaction between surfactant headgroups and polymer segments on the other. Nagarajan[61] proposes that the latter interaction stems from steric repulsion, whereas Ruckenstein[71] suggests that the interfacial tension between the headgroups and water is unfavorably influenced by polymer association. Since nonionic surfactants invariably possess bulky headgroups, the area of hydrophobic core-water contact is limited and, as a result, association with polymers is predicted to be insignificant[61,71]. However, in Nagarajan's original model the free energy of transfer of the polymer from the aqueous phase to the micellar pseudophase was not taken into account. In the most recent paper on Nagarajan's model[61e] this contribution is accounted for in the term $\mathbf{a}_{pol}$ (section 8.2), which is related to polymer properties. In Ruckenstein's treatment[71] this quantity is implicitly accounted for in the experimental method for estimating the change in interfacial tension induced by the polymer. However, this experimental method cannot be used for water-soluble polymers such as PPO[106] and HPC[53], which are soluble in nonpolar solvents. Exactly these polymers are known to show the strongest interaction with sodium dodecylsulfate (SDS)[53,67,76] and cetyltrimethylammonium bromide (CTAB)[53,67,76] and are likely candidates for favorable interactions with nonionic surfactants. A computer simulation by Balazs and Hu[107] on the effect of surfactants on the aggregation of associating polymers (polymers with a 'sticker' at each end) also revealed the importance of steric hindrance exerted by the surfactant headgroup.

In the present chapter we provide strong evidence for the association of PPO with micelles formed from the nonionic surfactant β-D-octylthioglucoside (OTG) (**1**). It is suggested that the predicted destabilizing effect of PPO on the Stern layer of the micelle is overcompensated by a favorable free energy of transfer of the polymer from water to the micelle.

1: 

After completion of our work, Winnik[108] has also provided strong evidence that interaction between HPC and OTG takes place.

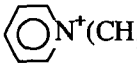
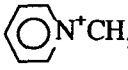
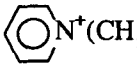
2.2 *The influence of polymers on critical micelle concentrations*

One of the most convincing indications for the formation of polymer-bound micelles has always been a reduced value of the cmc in the presence of polymer[2,3,5]. We will show that this criterion appears not to be generally valid.

The determination of the cmc of a surfactant in an aqueous polymer solution is often not a trivial matter. The very presence of polymers, in particular the rather hydrophobic ones such as PPO and HPC, excludes many techniques. For instance, several fluorescent- or UV-probes, which bind to surfactant aggregates and are used to determine the cmc, also bind to these polymers, which obscures the results. Furthermore, the presence of some of the polymers hampers the interpretation of surface tension measurements, because they are surface-active themselves. Often NMR methods cannot be used because of the overlapping resonances of the polymer. NMR resonances of polymers are usually broad and often complicated due to dyad and triad splitting[109,110]. The hydrophilic polymers, like PEO and PVA are less problematic, but they show also the weakest tendency for interaction with micelles. The problems that arise with conductivity and other techniques, used in the case of ionic surfactants, will be discussed elsewhere (sections 3.2 and 5.2).

Table 2.1 lists cmc values of several zwitterionic and nonionic surfactants in water and in the presence of various polymers. Because of the

Table 2.1 Cmc values (mM) for micelles in water and in the presence of polymers[a].

Surfactant	T,°C	H_2O	PEO	PPO	HPC	PVA-PVAc	PVP
n-$C_{10}H_{21}$ 	44	2.5[b]	2.5[b]			2.6[b]	
n-$C_{12}H_{25}$ 	45	0.32[b]	0.33[b]			0.33[b]	
n-$C_{12}H_{25}$ 	55	0.36[b]	0.38[b]			0.35[b]	
C_8E_3[g]	25	6.14[c]				6.17[c]	6.17[c]
OTG	20	10.1[d]			10.1[d]		
OTG	25	8.05[e]		8.10[e]			
		8.7[d]	8.7[d]				
		9.2[b]		8.8[b,f]			

a) Polymer concentration: 0.5 $g.dL^{-1}$ for the zwitterionic surfactants and OTG; 1.0 $g.dL^{-1}$ for C_8E_3. b) Bromophenol blue absorption method. c) Surface tension method. d) Pyrene fluorescence method. e) Microcalorimetric method. f) In D_2O: 8.2 mM. g) C_8E_3 denotes *n*-$C_8H_{17}O(CH_2CH_2O)_3H$.

high Krafft temperatures of the zwitterionic surfactants, the measurements were performed at elevated temperatures. This excluded the use of PPO and HPC because of clouding of these polymers at those temperatures. Four techniques were used to obtain the data listed in Table 2.1. (i) The bromophenol blue method, which relies on a shift in the absorption spectrum of the dye upon binding to the micelles (Figure 2.1). The probe is negatively charged but is readily stabilized in nonionic micelles. (ii) The surface tension method. This method depends on the fact that the surface tension of a solution decreases

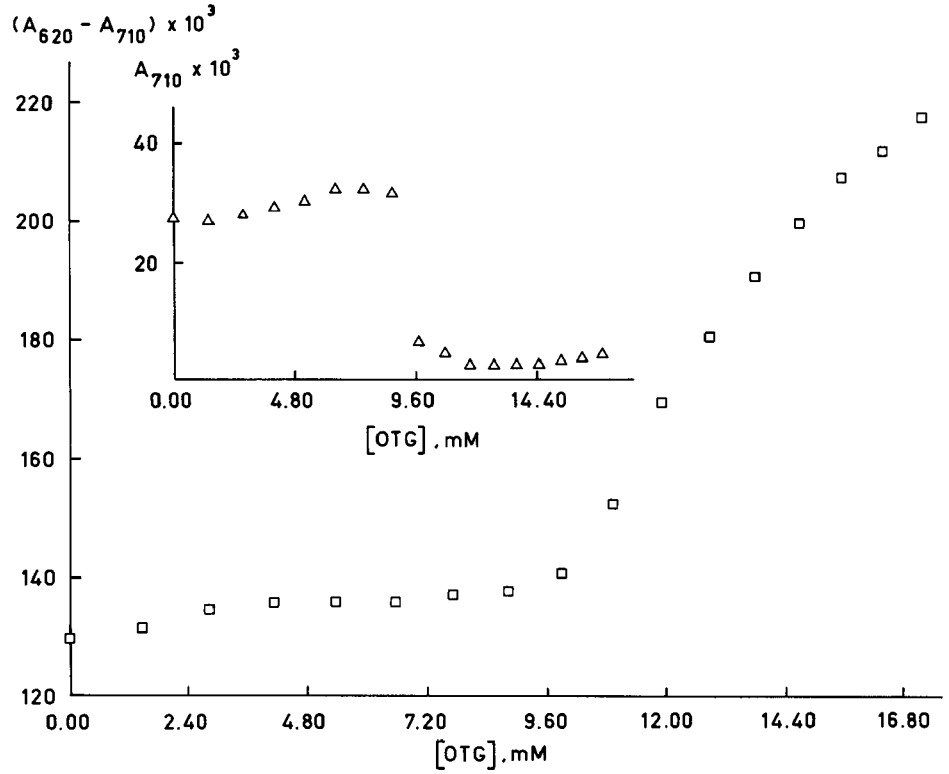


Figure 2.1 Bromophenol blue absorption and turbidity in an aqueous 0.5 g.dL^{-1} PPO solution as a function of the OTG concentration. A_{710} is a measure for the turbidity (inset); A_{620}-A_{710} denotes the 620 nm absorption of bromophenol blue corrected for the turbidity.

steadily at increasing surfactant concentrations, until, at the cmc, a constant value is reached. The presence of surface-active impurities may be detected as a minimum in the surface tension versus concentration curve. (iii) The pyrene fluorescence method[53,74], which is based on a change in the fine structure of the spectrum upon binding of the probe to the micelles (Figure 2.2). The sudden decrease in the relative peak intensities of the

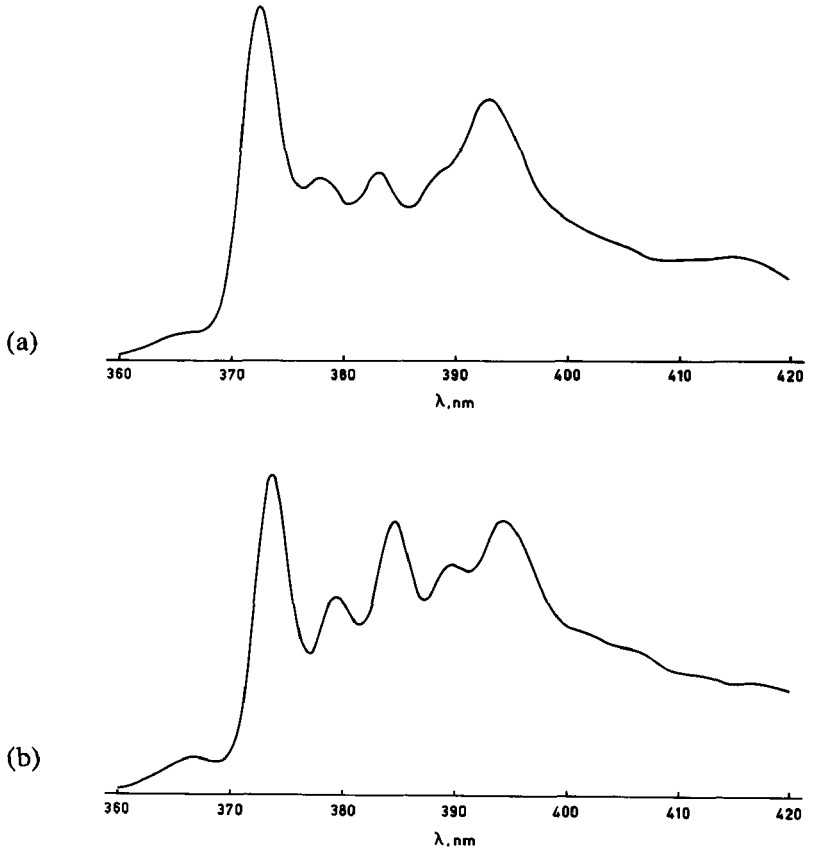


Figure 2.2 Fluoresence spectrum of pyrene dissolved in (a) water and (b) 30 mM OTG solution.

first (λ = 372 nm) and third (λ = 383 nm) peak indicates the cmc. (iv) The microcalorimetric method, which will be discussed in detail in section 2.4.

For all the surfactants listed in Table 2.1 the cmc values are virtually unchanged in the presence of polymer. Even HPC[53], which is able to lower the cmc of SDS by a factor of 15, and that of CTAB by a factor of 4, has no effect on the cmc of OTG. Although the conclusion that these nonionic and zwitterionic surfactants do not interact with the polymers would be pleasingly in accord with theories for polymer-micelle interaction (vide supra)[61,71], it is definitely not true for the combination PPO/OTG. It is known that the

rather hydrophobic PPO is folded spirally in tightly coiled discs in aqueous solution[48]. We find that even at 25 ^{0}C these discs tend to aggregate slightly, producing a slightly visible turbidity. This turbidity is, however, suddenly reduced upon addition of OTG in a concentration equal to or beyond the cmc, presumably because of interactions between the polymer and OTG micelles (Figure 2.1, inset). The change in turbidity (and, consequently, in background absorption) necessitated a correction in the analysis of the VIS-absorption data of dissolved bromophenol blue used for the cmc determination (Figure 2.1). This was the first indication that, despite the unchanged cmc, PPO/OTG interaction might take place.

Recently, interaction between HPC and OTG micelles has also been established[108], though the cmc is again not influenced.

2.3 Clouding behavior and Krafft temperatures

The decrease in turbidity of a PPO solution in the presence of OTG micelles is a result of the perturbed clouding behavior of PPO due to the presence of OTG micelles (Table 2.2). Clouding of PPO in H_2O and D_2O is a gradual process taking place in a temperature range of over 10 ^{0}C. However, in the presence of OTG clouding occurs abruptly within 2 ^{0}C, indicating a more

Table 2.2 Clouding temperatures of PPO[a].

Medium	Clouding Temperature, °C
H_2O	26-37
D_2O	26-37
H_2O + OTG (20 mM)	30
D_2O + OTG (15 mM)	25

a) 0.5 g.dL^{-1}.

cooperative process. In D_2O, OTG shifts the clouding of PPO towards lower temperatures, which is expected in view of the low solubility of OTG in D_2O below 30 ^{0}C. Probably OTG is preferentially solubilized in the polymer-rich phase. We note that the Krafft temperature of OTG in D_2O (30 ^{0}C) is shifted to a value below 20 ^{0}C by the presence of 0.5 g.dL^{-1} of PPO (Table 2.3).

It is not possible to decide whether the effect of PPO on the Krafft temperature of OTG in D_2O originates from a decrease of the cmc induced by the presence of PPO or from an increased solubility of surfactant monomers. A reduction of the cmc is not likely in view of the data shown in Table 2.1, but, unfortunately, the cmc of OTG cannot be determined at the same temperature in D_2O in the absence and presence of 0.5 g.dL^{-1} of PPO. Either the temperature is below the Krafft temperature or above the clouding point of PPO.

Comparison of the clouding behavior of Triton X-100 in H_2O and D_2O also revealed a lower cloud point in D_2O than in H_2O[111]. This means that the solubility of Triton X-100 (monomers and micelles) is lower in D_2O and a similarly decreased solubility of OTG in D_2O may cause the increase in Krafft temperature. The rationalization behind the lower solubility, suggested by Pandit and Caronia[111], is based on the enhanced structuredness of D_2O compared to H_2O[112]. Although this results in a better solubility of hydrocarbons in D_2O than in H_2O, the effect is more than compensated by the hydration of the polar headgroups, which occurs to a greater extent in H_2O.

Table 2.3 Krafft temperature of OTG.

Medium	Krafft Temperature, °C
H_2O	< 20
D_2O	30
H_2O + PPO (0.5 g.dL^{-1})	< 20
D_2O + PPO (0.5 g.dL^{-1})	< 20

2.4 *Microcalorimetry*

The remarkable association between PPO and OTG micelles is definitely confirmed by microcalorimetric measurements. In a typical experiment, 10 μL aliquots of a concentrated OTG solution ([OTG] >> cmc) were injected into the perfusion cell which contained 2 mL of the polymer solution or water. When OTG solution was injected into the PPO solution, the microcalorimetric response curve consisted of an endothermic peak followed by an exothermic peak. The endothermic peak increases in size whereas the exothermic peak diminishes and eventually disappears with increasing final OTG concentration (Figure 2.3). This phenomenon is attributed to rapid endothermic polymer-micelle association near the injection point followed by a slower disintegration of the complex and dilution of the surfactant molecules in the entire solution. The total dilution enthalpies shown in Figure 2.4 are summations of the areas of the endothermic and exothermic peaks.

The curve for OTG dilution in H_2O can be characterized by three regions. In the premicellar region I, the injected micelles disintegrate completely and the enthalpy change for demicellization and loss of intermicellar interactions is recorded. Region II is the transition region around the cmc. In the posttransition region III, the injected micelles remain intact and only a very small enthalpy change for reduction of intermicellar interaction is measured. The enthalpy of micellization calculated as the difference in dilution enthalpy between region I and III, is +4.5 $kJ.mol^{-1}$, a normal value for a nonionic surfactant[113,114].

Comparison of the curve for the PPO solution with the curve for H_2O reveals that PPO exerts only a small endothermic effect on the premicellar enthalpy of dilution. Furthermore the transition region is located in the same concentration range, indicative of an unchanged cmc. However, a clear endothermic effect, +4.3 $kJ.mol^{-1}$, is observed in the posttransition region of the PPO solution. We contend that this value represents the enthalpy of interaction between PPO and the OTG micelles. Interestingly, Shirahama[56] also found an endothermic enthalpy for interaction between PEO and SDS micelles (in a 0.1 M NaCl solution). Krescheck and Hargraves[115] found an endothermic

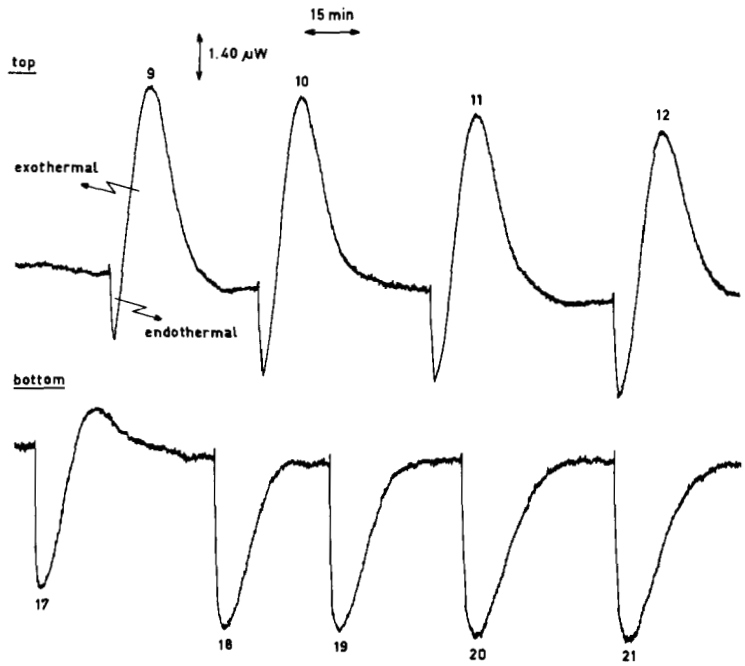


Figure 2.3 Top: Microcalorimetric response curve upon injection of a concentrated OTG solution into a PPO solution with the final OTG concentration remaining below the cmc. The numbers refer to the titration steps, i.e. 9 corresponds to the ninth titration step, see also Figure 2.4. Each response consists of an endothermic and an exothermic peak. Bottom: similar data but now the final OTG concentration is beyond the cmc. Note the increase of the endothermic signal relative to that shown in the top part. The exothermic effect has disappeared completely beyond titration step nr. 18. Signal noise is caused by the stirrer. Temp.: 25 ^{0}C.

binding of sodium octyl- and decylsulfates to PVP, but an essentially athermal binding of SDS to PVP. The dilution enthalpy curve for injection of a solution of the OTG micelles into 0.5 g.dL^{-1} of PEO equals that of water, and, therefore, there is no microcalorimetric or other evidence for interaction between PEO and OTG.

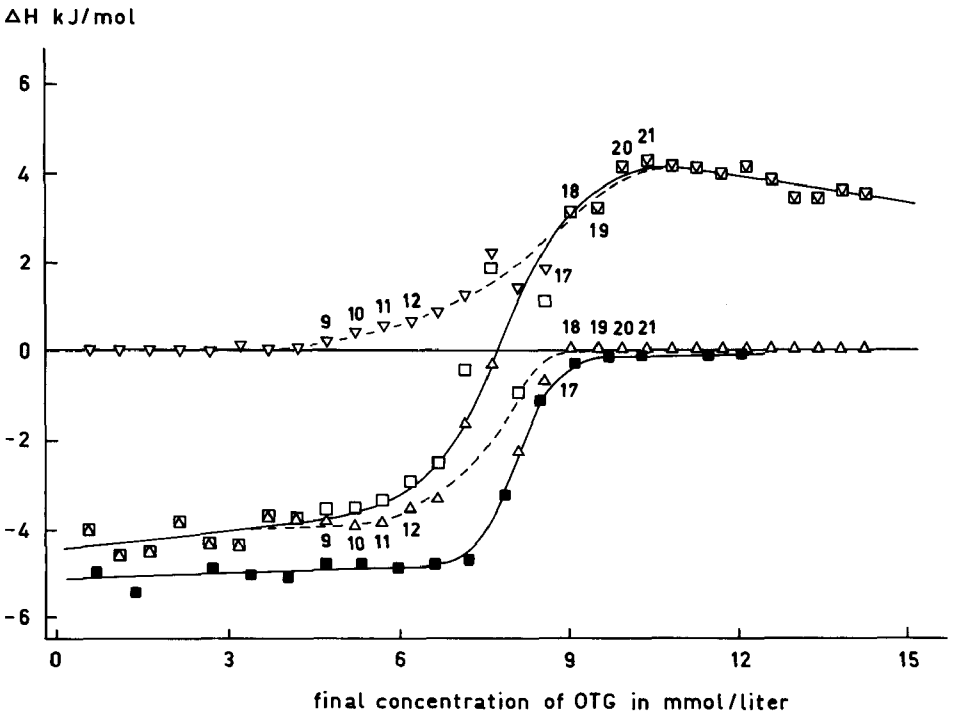


Figure 2.4 Enthalpy of dilution as a function of the final OTG concentration in water or in an aqueous solution of PPO at 25 ^{0}C.; (■) in water, cmc = 8.05 x 10^{-3}; in PPO solutions: (Δ) exothermic effect, (∇) endothermic effect, (□) summation of exothermic and endothermic effect. The numbers (9-12; 17-21) correspond with the titration steps indicated in Figure 2.3.

2.5 Discussion

Since the Gibbs energy of micellization of OTG is unchanged by the presence of PPO, the endothermic interaction enthalpy is apparently compensated by a positive entropy change. This ΔH/ΔS compensatory behavior[22] probably originates largely from the release of water molecules from the

hydrophobic hydration shells of the polymer discs upon interaction with the micelles.

The different behavior of PEO and PPO most likely reflects the difference in free energy of transfer of the polymer from water to a more apolar environment. PPO is more soluble in hydrocarbons than in water, contrary to PEO, which does not dissolve in the usual solvents other than water. PPO solubilization in or at OTG micelles may thus provide a favorable free energy that may compensate for the disturbance of the OTG Stern region. More or less the same situation applies to HPC[108]. As Ruckenstein[71] and Nagarajan[61] have pointed out, the presence of a polymer among the bulky headgroups of the nonionic surfactant will cause a destabilization of the Stern region due to polymer-headgroup repulsion.

The question arises whether PPO, interacting with OTG micelles, resides at the micellar surface like PEO in the system PEO/SDS, or deeper in the micellar core. The latter possibility is not likely for the reasons mentioned in section 1.4, but additional evidence is called for. Aggregation numbers may give a clue, because if PPO resides in the core an increase in aggregation number is expected instead of the usual decrease found in most polymer-ionic micelle complexes. We have made an attempt to measure aggregation numbers of OTG micelles in the absence and presence of PPO using quenching of the fluorescence of bis-(2,2'-bipyridyl)-mono-(4,4'-didecyl-2,2'-bipyridyl) ruthenium(II) perchlorate by 9-methylanthracene (see section 3.2). We obtain an aggregation number of 156 ± 10 for OTG micelles, which is rather high compared to the values of 68 - 84[78], or 87[116], for β-D-*n*-octylglucoside (with an ether instead of a thio linkage) determined by light scattering and sedimentation techniques. In the presence of 0.5 $g.dL^{-1}$ of PPO, we find a value of 96 ± 3. Although the exact values may be slightly in error (section 3.2), we submit that the trend is obvious, and points to location of PPO in the outer region of the micelle. Thus PPO/OTG interaction probably resembles the classical PEO/SDS association. The most important conclusion from this chapter is, however, that polymer-micelle interaction is not necessarily accompanied by a reduction in cmc.

2.6 *Experimental section*

Materials. The surfactants C_8E_3 (supplied by B. Kwant, University of Groningen) and OTG (*n*-octyl-β-D-thioglucopyranoside, Sigma) were used as received. The zwitterionic surfactants were synthesized and kindly provided by K. Hovius and A. Kuiterman[117]. PEO (weight-averaged mw 10,000, Fluka), PVP (Kolloidon-90, BASF), and PVA-PVAc (acetate content 17 %, Mowiol 3-83, Hoechst) were purified by fractionation, followed by deionization. PEO was dissolved in chloroform and precipitated in petroleum-ether (bp 40-60 ^{0}C) under rigorous stirring. PVP was dissolved in chloroform and precipitated in ether. PVA-Ac was dissolved in DMF (75 ^{0}C) and, after cooling, precipitated in ether. Aqueous solutions (5% w/w) of the respective precipitates were deionized by stirring with cationic (Dowex-50w) and anionic (Dowex -3 or -1) ion-exchange material until the specific conductivities of the solutions were below 10 $\mu\Omega^{-1}.cm^{-1}$. The deionized solutions were dialized against demineralized water in cellulose acetate tubes for 25 h. Then the solutions were freeze-dried and in the case of PVA-PVAc, dried over P_2O_5 in vacuo. PPO (weight-averaged mw 1,000 , Janssen) and HPC (weight-averaged mw 100,000, Aldrich) and the probes bromophenol blue (Merck) and pyrene (Aldrich) were used as received.

Cmc measurements. Spectrophotometric measurements of the cmc were performed by determining the absorption of bromophenol blue at a suitable wavelength between 600 and 620 nm at a probe concentration of 6 x 10^{-6} M using a Perkin-Elmer λ5 spectrophotometer. In the case of OTG in the presence of PPO (measurements at 610 nm), a small correction had to be made to account for the change in turbidity. This was done by subtraction of the absorption at 710 nm, outside the bromophenol blue absorption band (Figure 2.1). Surface tension measurements were carried out by using the Wilhelmy-plate method. Plots of surface tension vs. C_8E_3 concentration showed no minimum. Fluorometric measurements of the cmc were performed by monitoring the fine structure in the fluorescence spectrum of pyrene[53,74], using a SLM-Aminco SPF-500 C^{TM} spectrofluorometer. Sample solutions were made by adding aliquots of a

surfactant stock solution to 2 ml of pyrene-saturated water ([pyrene] ca. 10^{-7} M) or a polymer solution, prepared with pyrene-saturated water. At this concentration hardly any excimer formation occurs. Spectra were recorded from 365 nm to 400 nm in 0.05 nm steps. The emission band-width was 1 nm, and the excitation took place at 335 nm with a band-width of 5 nm. The cmc was indicated by a drop in the intensity ratio of the first (372-373 nm) and third (383 nm) peak, I_I / I_{III}, from 1.8-2.0 to 1.2-1.3. In all cases thermostated sample solutions were used.

Microcalorimetry. Microcalorimetric measurements were performed by G. Haandrikman and N.M. van Os of the Koninklijke/ Shell Laboratorium, Amsterdam, to whom we are much indebted. A LKB 2277 heat-flow microcalorimeter, described elsewhere[118], was used. Because of the long time needed to complete a dilution curve, storage of the OTG stock solution between injections in a cool atmosphere (0 - 4 ^{0}C) appeared to be necessary in order to prevent bacterial degradation.

Clouding points and Krafft temperatures. Clouding points and Krafft temperatures were determined by recording the transmission at 500 nm of vigorously stirred dispersions as a function of temperature using a Perkin-Elmer λ5 spectrophotometer. The clouding point of PPO was taken as the temperature representing the midpoint of the change in transmission in the case of a narrow transition region (1-2 ^{0}C) or as the temperature range in the case of a broad transition region (ca. 10 ^{0}C). The Krafft temperature of OTG is taken as the onset of the sudden increase in transmission in a 20 mM OTG dispersion in H_2O or a 15 mM OTG dispersion in D_2O.

Aggregation numbers. For a discussion of the method, see section 3.2. The practical aspects are described in section 3.5.