

## Interactions between surfactants and uncharged polymers in aqueous solution studied by microcalorimetry

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### Abstract

The interaction between ionic surfactants and uncharged polymers in dilute aqueous solution has been studied by titration microcalorimetry. The resulting enthalpic titration curves give detailed information about polymer - surfactant interactions. While sodium dodecylsulfate interacts strongly with poly(ethylene oxide) and poly(vinyl-pyrrolidone), the micelle formation of the cationic surfactants dodecyl-, tetradecyl-, and hexadecyl-trimethylammonium bromide is not measurably perturbed by the presence of these polymers. However, there is no significant difference between the interaction of the anionic and cationic surfactants with ethyl(hydroxyethyl)cellulose ethers. The aggregation of surfactants in polymer solutions shows clear similarities to the solubilization of small, polar molecules in ionic micelles. Preaggregation between surfactant monomers and polymers can be significant as indicated by sizeable endothermic enthalpy contributions from hydrophobic pair-wise interaction.

Systems containing surfactants and water-soluble polymers are of great interest both for their widespread applications and for their inherently interesting properties. Polymer - surfactant complexes are used for instance in paints and coatings, in laundry detergents, cosmetic products, and in tertiary oil recovery. Systems containing nonionic polymers and ionic surfactants have been studied quite extensively during the last couple of decades so much is known about them. The various studies are summarized and discussed in several review articles (ref 1-5). However, fundamental questions such as why and how surfactants form aggregates in the presence of polymers and how the polymer is involved in the aggregate formation are still unanswered. We became interested to see if results of calorimetric measurements could help to answer these questions and therefore, we started a study of some typical polymer - surfactant systems by titration microcalorimetry.

### EXPERIMENTAL

**Materials.** Sodium dodecylsulfate SDS (BDH, 99%), dodecyltrimethylammonium bromide DoTAB (Aldrich, 99%), tetradecyltrimethylammonium bromide TTAB (Sigma, 99%), and hexadecyl-trimethylammonium bromide CTAB (Sigma, 99%) were used as received. Samples of poly(ethylene oxide) PEO with nominal molar masses of 4 000, 8 000 (two different samples), 20 000, 100 000, and 1 500 000 were used without further treatment. Poly(N-vinylpyrrolidone) PVP with an average molar mass of 40 000 (Aldrich, special grade) and poly(propylene oxide) PPO with molar mass of 1 000 (Aldrich) were used as received. Samples of ethyl (hydroxy-ethyl)cellulose EHEC E230G and EHEC CST 103 (Berol Nobel AB, Sweden) were dialyzed before use.

The *calorimetric measurements* were made using the commercial microcalorimetric measuring channel of the 2277 TAM Thermal Activity Monitor system (ThermoMetric AB, Järfälla, Sweden) in a home-built high-precision thermostat bath (ref 6). The calorimetric titration experiments consisted of series of consecutive additions of concentrated surfactant solution to the calorimeter vessel initially containing 2.7 g of polymer solution. In some of the experiments concentrated polymer solution was added to surfactant solution in the vessel. The liquid samples were added in portions of 7 - 15 mg from a gas-tight Hamilton syringe through a thin stainless-steel capillary tube. A microprocessor-controlled motor-driven syringe drive was used for the injections. The fast titration procedure was used with six minutes between each injection (ref 7). The dynamic correction method used to deconvolute the potential signals was based on the simple Tian equation.

## RESULTS AND DISCUSSION

The SDS - PEO system is the most extensively studied polymer - surfactant system. Various types of measurements have shown that dilute SDS - PEO solutions are characterized by two critical concentrations. Such results were summarized by Cabane and Duplessix in the form of a phase diagram (ref 8). The first critical concentration, often denoted c.a.c., is nearly independent of polymer content and indicates the start of formation of polymer bound aggregates of SDS. The second critical concentration, often denoted c2, varies with polymer content and indicates where the polymer has become saturated and free SDS micelles start to form.

We have made measurements of additions of concentrated (10 or 5 mass per cent) solution of SDS to solutions of PEO of varying concentration and chain length. The calorimetric titration curve for 0.100 mass % PEO 8000 solution at 25 °C is shown in Fig. 1. The curve for dilution of the SDS solution in water is included in the figure. Below the c.m.c., 0.0080 mol/kg in water, the added micelles break up to give monomers in solution while above the c.m.c., the added micelles are only diluted. The enthalpy curve in water is almost linear as the enthalpy of micelle formation  $\Delta H(\text{mic})$  is only - 0.2 kJ/mol at the c.m.c. at this temperature. The difference between the two curves can be ascribed to SDS - PEO interactions. They are surprisingly complex, giving one fairly large endothermic peak and two small exothermic peaks. After the last peak, the observed enthalpy changes  $\Delta H(\text{obs})$  are, within errors of measurements, the same in the two solutions indicating only dilution of the concentrated micellar solution. We identify the start of the first peak with the c.a.c., that is the concentration at which SDS starts to aggregate in the presence of PEO. Figure 2 summarizes results of titrations of PEO solutions containing between 0.050 and 1.00 mass % of PEO. This figure shows that the c.a.c. is independent of polymer content and from these results and additional measurements on solutions containing 0.0100 and 0.0050 mass % PEO the value of c.a.c. = (4.1 ± 0.1) mmol/kg was derived. This is in good agreement with previously reported values derived by other methods (ref 8-10). It can be noted that also the maximum of the peak is almost independent of polymer content. The extent of the first peak and the location of the following two exothermic peaks are directly related to the polymer concentration so that the peak minima appear at about constant PEO monomer-to-SDS ratio, R(EO/SDS). The maximum between the two exothermic peaks where  $\Delta H(\text{obs})$  coincides with  $\Delta H(\text{obs})$  in water is found to be located at c2, the concentration where free micelles start to form. Thus the second small peak lies in the region where polymer bound aggregates are in equilibrium with free micelles.

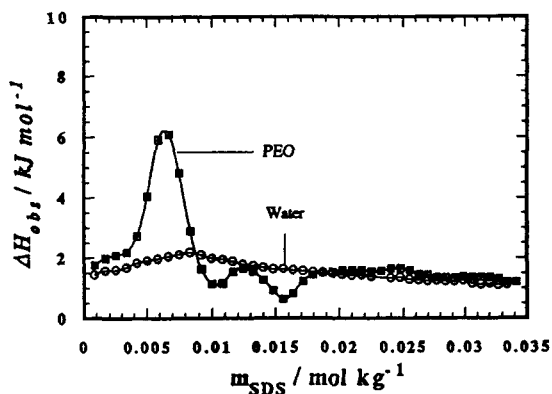


Fig. 1. Calorimetric titration curves from additions of 10 mass % SDS to 0.100 mass % solution of PEO 8000 in water at 25 °C.

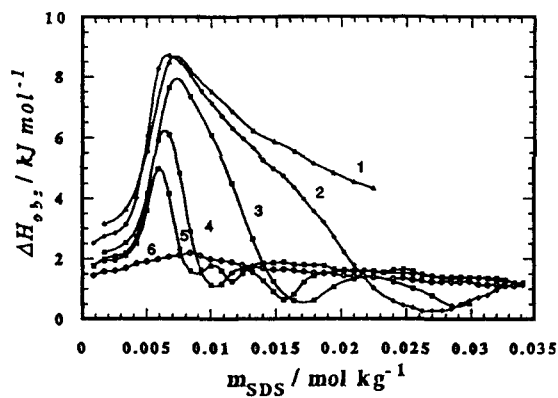


Fig. 2. Addition of 10 mass % SDS to solutions of PEO 8000

1. 1.000 %
2. 0.500 %
3. 0.250 %
4. 0.100 %
5. 0.050 %
6. pure water

According to the eximer formation study by Zana *et al.* (ref 11) and the dynamic fluorescence quenching study by van Stam *et al.* (ref 12), the aggregation number of the SDS clusters formed on the PEO chain increases in a regular manner with SDS concentration from about 30 just above the c.a.c. to about 60 when the saturation concentration c2 is reached. The aggregation number of the saturated polymer bound aggregates is considered to be somewhat lower than that of free micelles.

The events during the titration of PEO 8000 with micellar SDS solution can be summarized in the following way. In additions giving final molalities below the c.a.c., the added micelles are diluted and break up to give monomers in solution. These monomers interact with the PEO chains giving an endothermal contribution which increases with the polymer content. This interaction is probably of the same nature as the hydrophobic interaction between hydrocarbon chains observed in premicellar solutions of surfactants, see ref 13-14. As the c.a.c. is reached, SDS aggregates start to form on the PEO chains. The c.a.c. is independent of the PEO content indicating that it is the local concentration of

ethylene oxide groups that is important. Initially, the average aggregation number is small but as the SDS content increases, the number of SDS molecules in the clusters increases and when the polymer has become saturated, the aggregation number is about the same as for free micelles. The enthalpy change for addition of SDS micelles to give polymer bound aggregates becomes gradually less endothermic as the aggregation number increases. This change in the interaction enthalpy may arise from changes in the solubilization of ethylene oxide groups in the clusters as the SDS content increases. The first peak in the titration curves for addition of SDS to PEO solutions resemble the curves observed for similar titrations of pentanol solutions (ref 14). The shape of these curves could be rationalized in terms of enthalpy changes accompanying changes in the composition of the mixed SDS-pentanol micelles with increasing SDS concentration. As  $\Delta H(\text{mic})$  is close to zero at 25 °C, the curve shapes were dominated by the enthalpy contribution from changes in the hydration of pentanol. When the SDS content has increased to c2, corresponding to R(EO/SDS) of about 2.8, the added micelles are only diluted. As the amount of free micelles increases a second, small exothermic peak is observed. The minimum of the peak lies at R(EO/SDS) between 1.4 and 1.7. The location and the size of the peak are not significantly affected by a change in temperature or the presence of 0.100 m NaCl. The first part of the titration curves was unchanged when SDS was added to solutions of PEO of varying chain length (4000, 20 000 to 1 500 000) which is in accordance with previous observations that c.a.c. is independent of chain length for molar masses above 4000. However, the two small exothermic peaks were not resolved any longer but instead a broad exothermic hump was seen. The  $\Delta H(\text{obs})$  in the PEO solutions joined the water curve at about the same monomer-to-SDS ratio as in the PEO 8000 experiments. The unusual resolution of PEO 8000 curves may be due to the fact that for this chain length there will be on the average one SDS aggregate per chain at saturation (ref 9,12).

When PEO 8000 solution was added to (micellar) SDS solutions there was an initial phase extending up to R(EO/SDS) of about 0.8 where the observed enthalpy change (calculated per mol of monomer)  $\Delta H(\text{obs})$  varied only little and was in fact close to the dilution enthalpy in water. This is somewhat surprising because according to the NMR study by Kwak and coworkers (ref 15), the binding of PEO to SDS micelles is almost complete at low R(EO/SDS). The enthalpy change for the interaction of ethylene oxide groups with fully grown SDS aggregates is accordingly small. At higher polymer concentrations there is a steep rise in  $\Delta H(\text{obs})$  giving a well defined peak which reaches maximum at R(EO/SDS) of 1.8 in water and 1.5 in 0.100 m NaCl. This peak reflects the same phenomenon as the last endothermic peak in the curves from additions of SDS to PEO solutions. The nature of the transition is unknown but a conformational change of the polymer - SDS complex is a possible explanation.

After a valley with a minimum at R(EO/SDS) of about 2.8 which is the composition corresponding to c2, a second broad endothermic peak is seen. In this region all SDS is polymer-bound and with increasing polymer concentration the aggregation number will decrease and the endothermic hump reflects the changing aggregate size. With PEO samples of higher molar mass, the two peaks are not well resolved.

**SDS - PVP** This polymer is more hydrophobic and interacts stronger with SDS than PEO as indicated by the significantly lower c.a.c., 2.0 mmol/l determined by surface tension measurements (ref 11,16) or 2.6 mmol/l from conductometric experiments (ref 17).

The calorimetric titration curve resulting from additions of 10 mass % SDS solution to 1.00 mass % PVP solution at 25 °C is shown in Fig. 3a. The upper left corner was extended by measurements using a microcalorimeter with a 25 ml reaction vessel and the resulting titration curve is shown in Fig. 3b. Below the c.a.c. there is a fairly strong endothermic interaction between SDS monomers and the PVP chains. At an SDS molality of 0.5 mmol/kg this excess dilution enthalpy amounts to 2.0 kJ/(mol SDS). The effect probably stems from hydrophobic interaction between the hydrocarbon chain of SDS and the

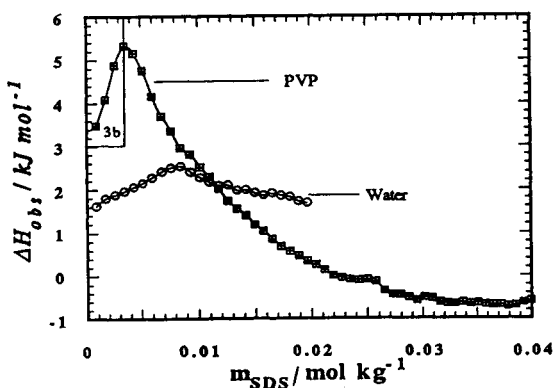


Fig. 3a. Addition of 10 % SDS to 1.00 % PVP solution at 25 °C.

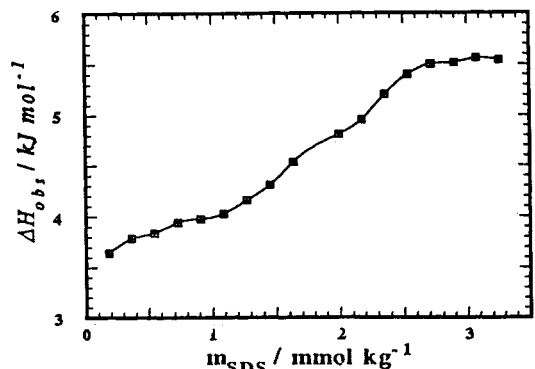


Fig. 3b. Additional measurements at low SDS molality by additions of 5 mass % SDS to 20 ml PVP solution.

hydrophobic polymer backbone, see ref 13,14. Due to the strong preaggregation effect there is no clear break in the titration curve indicating the c.a.c. Instead there is a steady increase to a well defined maximum. The location of this maximum is independent of polymer content. After the maximum,  $\Delta H(\text{obs})$  drops to a pronounced minimum relative to the dilution curve in water. The extension of the broad, exothermic peak is proportional to the polymer concentration. Excepting the initial part, the PVP titration curves resemble the curves from the titrations of PEO 20 000.

The titration curve resulting from additions of 20 % PVP solution to 0.050 mol/kg SDS at 25 °C is shown in Fig. 4. The initial part of the curve lies well below the dilution curve in water indicating an exothermal interaction between PVP and SDS micelles amounting to - 0.8 kJ/(mol repeat unit). This value is the same for titration into 0.100 mol/kg SDS. Like in PEO solutions there is then a steep increase in  $\Delta H(\text{obs})$  to a maximum but in the PVP system the peak is broad and  $\Delta H(\text{obs})$  decreases only slowly. The steep rise occurs at a repeat unit-to-SDS ratio of about 1.5 which is about the same as for PEO - SDS. The rise is also about the same, 1.4 kJ/(mol repeat unit). The only significant change in the curve when 0.100 mol/kg NaCl was added is a shift of the rise to a monomol-to-SDS ratio of about 1.

To summarize: the titration curves from the SDS-PEO and SDS-PVP systems show strong resemblance indicating similar interactions between SDS and the two polymers.

Preliminary results indicate that interactions between the anionic surfactant *sodium poctylbenzene-sulfonate* (SOBS) and PEO are closely similar to interactions in the SDS - PEO system. The c.m.c. for SOBS in water at 25 °C is 11 mmol/l (ref 18) and c.a.c. in PEO solutions 7 mmol/l (present work). Fig. 5 shows a plot of  $\Delta H(\text{obs})$  against PEO content expressed as monomol/kg from additions of 10 % PEO solution to 0.050 mol/kg SOBS at 25 °C. The dilution curve in water is included in the figure. Also in this system there appears an endothermic peak in the region where polymer bound complexes are expected to be in equilibrium with excess surfactant micelles.

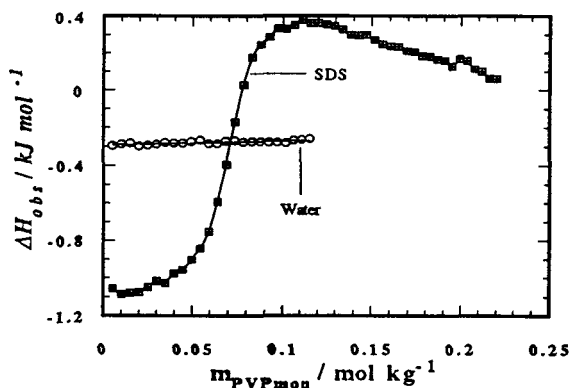


Fig. 4. Addition of 20 % PVP to 0.05 m SDS and water at 25 °C.

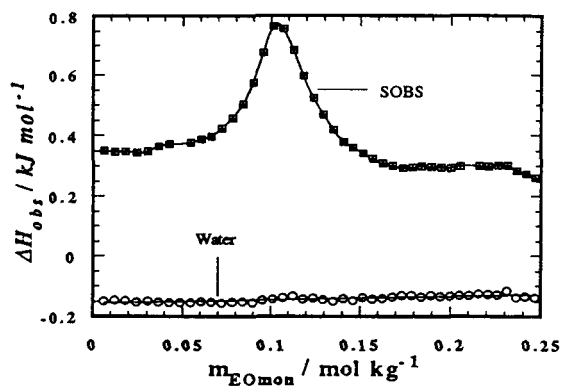


Fig. 5. Titration curves from additions of 10 % PEO to 0.050 m SOBS and water.

**RTAB - PEO and RTAB - PVP** In accordance with previous findings, the calorimetric titration curves derived from additions of the alkyltrimethylammonium bromides to PEO and PVP solutions showed no indications of measurable polymer-surfactant interactions. The reason for this difference between anionic and cationic surfactants in the reaction towards PEO and PVP is obscure. Towards other polymers like poly(propylene oxide) PPO and EHEC, the two types of surfactants behave in a similar manner (see below).

**Ethyl(hydroxyethyl)cellulose EHEC** is a versatile water-soluble polymer with many practical applications and interesting physicochemical properties. Aqueous solutions show a liquid-liquid phase separation when the temperature is increased. The cloud point CP, normally in the range 35 to 70 °C, depends on the degree and on the type of substitution. In the presence of small amounts of ionic surfactants, an anomalous change of the rheological properties with temperature has been observed (ref. 19). When the dilute EHEC solution containing surfactant is heated, it changes from a low-viscous solution to a clear and stiff gel. The transformation is reversible.

The titration curves from additions of SDS to 0.250 mass % solution of two different samples of EHEC are shown in Fig. 6. Sample I is EHEC E230G with a CP of 70 °C and sample II is EHEC CST 103 with a CP of 35 °C. From measurements at lower concentrations than shown in the figure, the c.a.c. for sample I was determined to 3.4 mmol/kg and for the more hydrophobic sample II to 1.5 mmol/kg. Although the interaction between SDS and EHEC is strong, particularly with the more hydrophobic sample, the interaction between SDS monomers and the polymer is weak as indicated by the observed small enthalpies of dilution below c.a.c. The curve for sample I closely resembles the curve from the titration of the long chain PEO 1 500 000, which gave a broad, exothermic peak without structure.

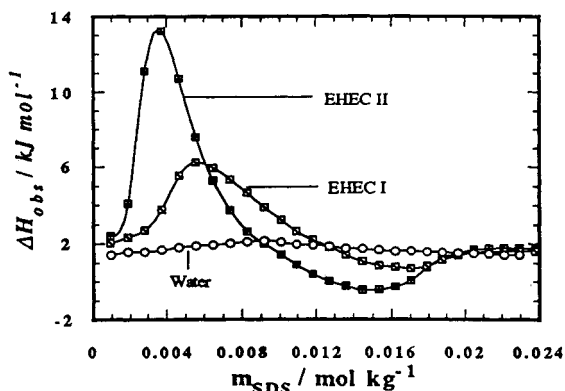


Fig. 6 Titration of 0.25 % EHEC I (CP 70 °C) and EHEC II (CP 35 °C) with 10 % SDS.

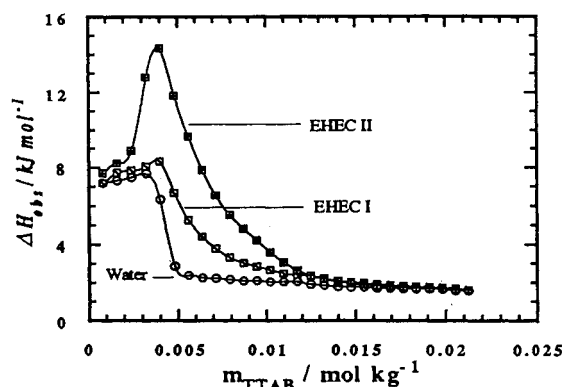


Fig. 7. Addition of 10 % TTAB to 0.25 % EHEC solutions.

Figure 7 shows the titration curves from additions of the cationic surfactant TTAB to the two EHEC samples. For TTAB in water at 25 °C, the c.m.c. is 3.5 mmol/l (ref 20) and  $\Delta H(\text{mic})$  equal to -5.2 kJ/mol determined at the c.m.c. from the jump in the curve of  $\Delta H(\text{obs})$  against TTAB concentration from titrations in water, cf Fig. 7. The curve from the titration of the less hydrophobic EHEC shows no easily recognizable c.a.c. but it deviates significantly from the dilution curve in water which shows that the polymer has a significant influence on the micelle formation of TTAB. The interaction between TTAB and the more hydrophobic EHEC gives pronounced changes in the titration curve with an endothermic peak at the onset of formation of polymer bound aggregates like for SDS with a c.a.c. of 2 mmol/kg. The curves from the two EHEC titrations join the water curve at the same TTAB concentration without the exothermal hump seen in the SDS curves. If it is assumed that there are no changes giving enthalpic contributions in the region with excess micelles, the concentration where the curves merge can be considered to indicate  $c_2$ , the concentration where free micelles start to form. From Fig. 7 this concentration can be estimated to about 15 mmol/kg for the 0.25 % polymer solutions. Clear is that the significant difference between SDS and RTAB observed in the reaction with PEO or PVP is not present in the EHEC systems. The reason for the difference between the polymers in the reaction towards the anionic and cationic surfactants is surprising and unclear.

## CONCLUSIONS

Detailed information about polymer - surfactant interactions can be obtained by titration microcalorimetry.

Surfactant aggregation in polymer solutions shows clear similarities to the solubilization of small uncharged molecules in ionic micelles.

There is no clear difference between anionic and cationic surfactants in their interaction with nonionic cellulose ethers, EHEC, while there was no measurable interaction between alkyltrimethylammonium bromides and PEO and PVP which interact strongly with SDS. Preaggregation between surfactant monomers and the polymer can be significant as indicated by substantial endothermic enthalpy contribution from hydrophobic, pair-wise interaction.

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