

Isothermal Calorimetric Investigation of the Interaction of Poly(*N*-isopropylacrylamide) and Ionic Surfactants

Watson Loh,* Luciana A. C. Teixeira, and Lay-Theng Lee†

Institute of Chemistry, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, SP, Brazil

Received: October 22, 2003; In Final Form: December 19, 2003

The interaction of poly(*N*-isopropylacrylamide) (PNIPAM) with an anionic (SDS) and three cationic (dodecyl and hexadecyltrimethylammonium bromides, DTAB and CTAB, and dodecylammonium chloride, DAC) surfactants has been studied using isothermal titration calorimetry between 17 and 29 °C. The high sensitivity of this technique allows precise determination of the parameters that characterize polymer–surfactant interactions. Based on these results, it is possible to conclude that the interaction of PNIPAM with ionic surfactants is significantly affected by temperature. This is attributed to changes in polymer hydration, which become more important near the lower critical solution temperature (≈ 32 °C). Interaction of PNIPAM with SDS is more favorable than with cationic surfactants. Surfactant hydrophobicity is also an important factor for this interaction, with CTAB displaying a more intense interaction than DTAB. The contribution from the size of the headgroup was also investigated: DAC interacts more strongly than DTAB with PNIPAM. Thus, for the same degree of hydrophobicity, a smaller headgroup favors interaction.

Introduction

Polymer–surfactant mixtures have been and still are the subject of intense investigation, mostly owing to their presence in a variety of industrial products. It is very common that, when mixed, these two components display properties different from the ones observed in their pure solutions, a result ascribed to the formation of complex structures upon their association. For mixtures of ionic surfactants and nonionic polymers, results from scattering techniques revealed that the structures of these complexes can be described by a “necklace model” of surfactant aggregates (typically smaller than the micelles formed by these surfactants in water) formed around the polymer chain.¹ These polymer-bound surfactant aggregates start to form at a concentration called the critical aggregation concentration (cac), which is lower than their critical micelle concentrations (cmc).²

Poly(*N*-isopropylacrylamide), PNIPAM, is becoming one of the most commonly studied hydrosoluble polymers. In aqueous solution, it displays an expansion–collapse transition process around 32 °C (its lower critical solution temperature, LCST).³ Below the LCST, PNIPAM is soluble in water and adopts an expanded coil conformation.^{4,5} Above the LCST, it collapses and phase separates out of water.^{3,6} Such a thermally induced transition in molecular structure has been recognized as a potential “thermosensitive switching device”.⁷ The fact that its LCST value is close to human body temperature makes PNIPAM an important candidate for biological applications in immunoassay technology, enzyme separations, and controlled drug release.⁸

Past studies have shown that PNIPAM interacts strongly with anionic surfactants (such as SDS), with important modifications in its solubility,^{3,9} molecular structure,^{5,6} and rheological proper-

ties.¹⁰ Above the LCST, interaction of the phase separated PNIPAM results in resolubilization of the polymer. Neutron scattering investigations have shown that this process is due to formation of charged polymer–surfactant complex,^{6,11} whose structure is similar to the “necklace” structure reported for PEO–SDS.^{1,2} Here a necklace consists of a macromolecule decorated with SDS micellar aggregates. Below the LCST, PNIPAM interacts with SDS, above a cac value, to form similarly charged complexes.

Although the structural properties of the PNIPAM–SDS complex have been revealed, a precise determination of the onset of their interaction (cac) has yet to be reported. From fluorescence measurements using various probes, Schild et al.³ reported a value for cac around 0.8 mmol L^{−1}, an order of magnitude lower than the cmc value for SDS. The transitions observed in those fluorescence measurements were inexplicably broader than those obtained in regular micelle formation, and the precision of the cac value thus obtained is therefore lower. Nevertheless, to our knowledge, these values remain the only ones reported for the PNIPAM–SDS complex formation. Other conventional techniques such as surface tension measurements have been shown to be unsuitable for determining these cac values, due to the low surface tension of PNIPAM solutions.¹²

Among the many techniques already used to investigate polymer–surfactant mixtures, isothermal titration calorimetry (ITC) has been increasingly employed. Its high sensitivity allows precise determination of the parameters normally used to characterize polymer–surfactant interactions, as well as provides information on the enthalpy changes of the process. These enthalpy changes can give some insight on the mechanism of the polymer–surfactant interaction, as described elsewhere.¹³

We have recently been using ITC for the investigation of surfactant interaction with different polymers, with results that confirm its suitability for these studies.^{14–16} Here, we report the results of the extension of these studies to linear PNIPAM chains. As far as we are aware, the only investigation applying

* To whom correspondence should be addressed. E-mail: wloh@iqm.unicamp.br. Fax: + 55 19 3788 3023.

† Permanent address: Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, Gif-Sur-Yvette, France.

ITC to the study of PNIPAM interaction with surfactants was reported by Wang et al.,¹⁷ using a PNIPAM microgel latex and SDS. Their results revealed quite different patterns for the calorimetric curves depending on whether the temperature was below or above the LCST for linear PNIPAM. Moreover, a critical aggregation concentration could not be clearly determined, raising doubts about its existence.

The objective of our present study is a precise determination of the cac and the enthalpy changes of the interaction process as a function of temperature up to a value just below the LCST. This allows us to investigate the effect of polymer hydration on the polymer–surfactant interaction. Additionally, by employing different ionic surfactants, we were able to assess the separate contributions from the headgroups (both from the electrical charges: SDS vs DAC or DTAB; or sizes: DTAB vs DAC) and hydrophobicity, as consequence of their different hydrocarbon chain lengths (CTAB vs DTAB).

Experimental Section

The PNIPAM sample used was purchased from Polymer Source, Inc., Canada, prepared following the procedure of Schild and Tirrell,¹⁸ displaying an average molar mass of 90 kg mol^{−1}, and $M_w/M_n = 3$, as determined by GPC analysis coupled with low-angle light scattering. Surfactants SDS, DTAB, and CTAB were purchased from Aldrich and BDH (CTAB), all of the highest purity available, and were used without further treatment. Water used throughout was of Milli-Q Plus grade. All solutions were prepared by weight, with accuracy of 0.1 mg. Dodecylammonium chloride was prepared by reacting a stoichiometric amount of aqueous HCl with dodecylamine, from Sigma, using ethanol as solvent. The product was recrystallized four times from ethanol and obtained as white crystals.

Isothermal titration calorimetry experiments were performed in a VP-ITC instrument, from MicroCal Inc., U.S.A. In these experiments, aliquots of 3–15 μ L of a more concentrated surfactant solution (2 wt. % for SDS, 5 wt. % for DTAB or DAC, and 0.5 wt. % for CTAB) were injected, at 5–10 min intervals, into the calorimeter cell (1.4 mL) containing either water or the polymer solution. As these aliquots were injected, there was an overflow of the initial solution from the cell, so that the total cell volume was kept constant throughout the experiment. Also, since the injected surfactant solution did not contain polymer, the PNIPAM concentration was not kept constant throughout the whole titration (the maximum dilution was of about 30%, but typically it was smaller than 10%), and hence, polymer concentrations are used only as reference for the discussion of the obtained results. No correction was necessary for the heat of polymer dilution since it was too small to be detected, as verified in test experiments. This overflow and the polymer dilution were taken into consideration for the calculation of the actual surfactant and polymer amounts during the experiment.

Experiments were performed at three different temperatures: 17, 25, and 29 °C, the upper limit chosen to be safely below the cloud point of the PNIPAM solution. Due to their higher Kraft temperatures, CTAB and DAC solutions were only used at higher temperatures. For the other solutions, no precipitation was observed above 15 °C. The whole calorimetric procedure was chemically calibrated, as recommended,¹⁹ by measuring the enthalpy of dilution of a propanol solution, revealing a good agreement with the reference values (observed differences were smaller than 2%).

High sensitivity DSC measurements were carried out using a VP-DSC Instrument, from MicroCal Inc., U.S.A., operating

TABLE 1: Parameters Obtained by ITC for the Micellization of SDS, DTAB, CTAB, and DAC, at Different Temperatures

surfactant	T/ °C	cmc/ mmol L ^{−1}	$\Delta_{\text{mic}}H$ / kJ mol ^{−1}	$\Delta_{\text{mic}}C_p$ / J (mol °C) ^{−1}
SDS	17	7.9 ± 0.6	3.5 ± 0.1	−490
	25	8.1 ± 0.3	−0.4 ± 0.1	
	29	7.3 ± 0.3	−2.40 ± 0.05	
DTAB	17	14.6 ± 0.3	1.50 ± 0.04	−430
	25	14.4 ± 0.2	−2.00 ± 0.02	
	29	14.2 ± 0.1	−3.60 ± 0.02	
CTAB	29	0.80 ± 0.01	−10.20 ± 0.05	
DAC	25	13.3 ± 1.0	1.5 ± 0.1	
	29	14.7 ± 0.3	−0.47 ± 0.03	

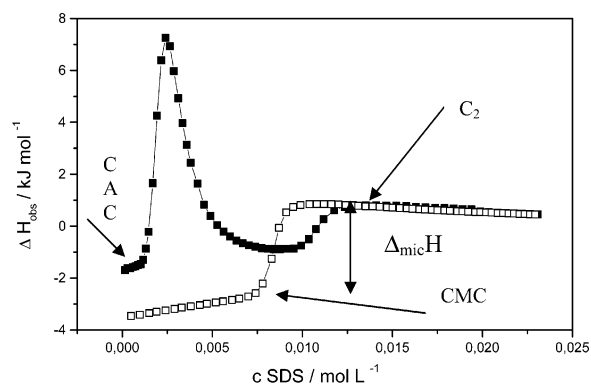


Figure 1. Calorimetric curves representing the dilution of a 2% SDS solution in water (□) and in a 0.1% PNIPAM (■) solution, at 17 °C. The enthalpy values are expressed per mole of added SDS. The parameters used to characterize this interaction are represented in the figure (see text for definitions).

at a scan rate of 15 degree h^{−1}. Slow rate scanning was used in these measurements to ensure that the calorimetric curves are independent of the scan rate, a sign that the phase transition occurs as close as possible to equilibrium conditions.

Results and Discussion

The micellization of SDS, DTAB, and CTAB in pure water were investigated by ITC, within the temperature range of 17–29 °C. The results are summarized in Table 1. All of these results agree well with the corresponding literature data.²⁰ In general, these data confirm the view that cmc values for SDS and DTAB are not significantly affected by temperature, within the studied range, while the enthalpy changes for the two micellization processes are positive at lower temperatures and become negative as temperature increases. Enthalpy change associated with the formation of CTAB micelles is significantly more negative, at ambient temperatures, than the value for DTAB. Nevertheless, all these enthalpy changes are small and these micellization processes are controlled by entropy, a feature ascribed to the well-established hydrophobic effect.²¹

Isothermal titration calorimetry, when applied to the investigation of polymer–surfactant interactions, allows the determination of the most important parameters that characterize this interaction (see, for instance, refs 13, 15, and 22), namely the cac values, the overall enthalpy change associated with the polymer–surfactant interaction, and the number of moles of bound surfactant per NIPAM unit in the polymer. The determination of these parameters can be illustrated by using the calorimetric curves shown in Figure 1 for PNIPAM and SDS at 17 °C. During the first injections, surfactant micelles present in the initial solution in the syringe are disrupted due to dilution in the calorimeter cell. For SDS, this is an exothermic process

both in pure water and in the presence of polymer. As the surfactant concentration increases, the differential enthalpy change becomes less exothermic, an indication of interaction between surfactant monomers and the polymer. At a certain surfactant concentration, ca. 1.3 mmol L^{-1} , in the case represented in Figure 1, a sudden increase in the enthalpy of dilution in PNIPAM solutions is observed. This is associated with the cooperative formation of small surfactant aggregates around the polymer chain. This concentration is called the critical aggregation concentration, c_{ac} , and is related to the capacity of the polymer in nucleating these surfactant aggregates. Hence, the value of the c_{ac} is considered as an indication of the intensity of the surfactant–polymer interaction: the more intense the interaction, the smaller the c_{ac} value, as long as the cmc of the surfactant remains fairly constant. For different surfactants with different cmc values, the more appropriate criterion is the difference between the cmc and the c_{ac} .

The observed increase in enthalpy, with respect to the reference curve for the surfactant dilution in water, is associated with the polymer dehydration caused by surfactant binding. As the surfactant binding progresses, the difference between the two dilution curves reaches a maximum and then decreases as surfactant concentration increases. This decrease in the enthalpy difference suggests a smaller extent of polymer dehydration upon surfactant binding, which continues until passing through a minimum (in the case represented in Figure 1, at ca. 10 mmol L^{-1}), followed by a new increase in enthalpy until the two dilution curves merge. Therefore, this merging point represents the concentration after which the formation of free micelles becomes more favorable than polymer-bound aggregates and is usually referred to as C_2 , the second critical or saturation concentration. At higher concentrations, only the dilution of SDS micelles takes place. The amount of surfactant bound to the polymer can be also estimated from these parameters, by subtracting the amount of free surfactant, estimated from their cmc values from the saturation concentration, as $(C_2 - \text{cmc})$.

The overall enthalpy change for the polymer–surfactant interaction can be estimated from the enthalpies of dilution of surfactant in pure water and in polymer solution.¹⁵ This is evaluated by summing up the differential enthalpies of surfactant dilution in the presence of polymer up to the point where the two curves merge and subtracting from this the sum of the corresponding values for the surfactant dilution in water. This method of estimation follows the assumption that the enthalpies of surfactant association in water and around the polymer are the same and, hence, that they cancel each other with this subtraction.

The calorimetric curves associated with the binding of SDS to PNIPAM (Figure 1) are similar to the ones reported for PPO, another hydrophobic polymer.¹³ On the other hand, curves obtained for the interaction of SDS with nonaggregated EO/PO block copolymers,²³ modified cellulose,¹³ or more hydrophilic polymers as PEO and PVP^{13,22} present a region where the enthalpies of surfactant dilution are more exothermic in polymer solution than in water. This region occurs at high surfactant concentration before the two curves merge. This more exothermic process has been ascribed to rehydration of the polymers segments that are released to the outer hydrophilic environment of the aggregate surfaces as the surfactant aggregates increase in size. This pattern suggests that a PNIPAM interaction with SDS proceeds with similar degree of polymer incorporation into the surfactant aggregates, but which remains insignificantly altered up to the saturation concentration.

The above description of the results shown in Figure 1

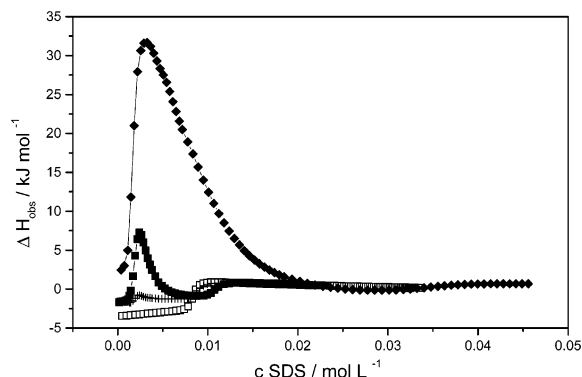


Figure 2. Calorimetric curves for the interaction of SDS with PNIPAM at 17 °C (□) 0.01, (■) 0.1, and (◆) 1 wt. %. The curve for dilution of SDS in water (□) is shown as reference.

confirms that ITC is capable of precisely detecting all of the important parameters to characterize the surfactant–PNIPAM interaction, even in case of low c_{ac} values which cannot be measured precisely by other techniques. In addition, it provides information on the energetics of this interaction, which allows inference on the mode of the surfactant–polymer interaction at different stages of the process.

The effect of increasing PNIPAM concentration on this interaction can be analyzed from the calorimetric results shown in Figure 2. By increasing polymer concentration from 0.01 to 1 wt. %, the shape of the SDS binding curves remains the same, while the enthalpy difference between SDS dilution in polymer solution and in water increases significantly remarkably. This enthalpy difference can either be due to an increase in the fraction of bound SDS or to a change in enthalpy per mole of SDS bound. Previous NMR measurements on SDS interaction with EHEC, at the concentration of 0.25 wt. %, ²⁴ suggested that the fraction of bound SDS is close to 30–40%. The results of Figure 2 suggest that the fraction of SDS bound to PNIPAM increases with the increase in polymer concentration, as expected considering that this binding may be far from completion at these low polymer concentrations. In addition, the energy difference depicted in Figure 2 allows the estimate of a lower limit for the energy of SDS–PNIPAM interaction. If all SDS molecules added were bound to PNIPAM at 1% polymer concentration, the enthalpy of binding at the maximum of the curve would correspond to ca. 30 kJ mol^{-1} . Most likely, this binding is not complete, that is, not all SDS added is bound to the polymer, and the maximum enthalpy change due to binding, expressed per mole of bound SDS, should be larger than this value.

The enthalpy values for the SDS–PNIPAM interaction are more positive than those obtained for PEO, PVP, and PPO at the same polymer concentration and temperature. Wang et al. also pointed out the same finding in their study with PNIPAM latex.¹⁷ It is not possible, however, to ascribe whether such an enthalpy difference is due to a larger fraction of SDS bound or to a more energetic (in enthalpy terms) binding. Taking c_{ac} as a criterion of the intensity of the polymer–SDS interaction, the following sequence is obtained: PNIPAM > PPO > PEO > PAM (this last value obtained from ESR measurements), ²⁵ agreeing with the sequence of decreasing hydrophobicity of these polymers.

PNIPAM is expected to display a strong temperature dependence of its aqueous solution behavior, in accordance with its low LCST, what has been investigated by a variety of techniques, including differential scanning calorimetry (DSC),^{18,26} revealing a transition that was ascribed to PNIPAM dehydration

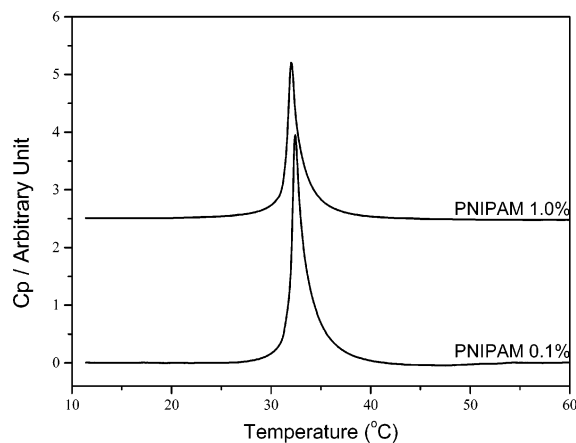


Figure 3. High sensitivity DSC curve obtained for a 0.1 wt. % PNIPAM solution. Important temperatures are 28 °C for the onset, 32 °C for the maximum, and 42 °C for the end of the transition.

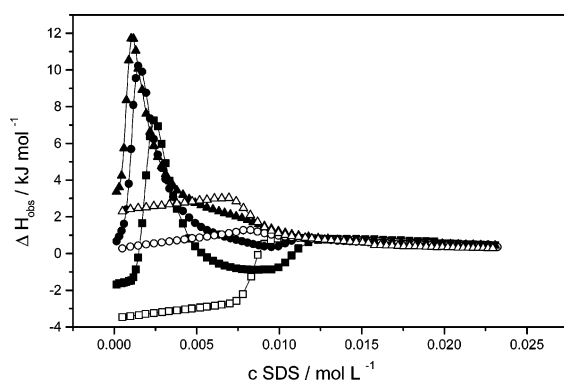


Figure 4. Effect of temperature on the interaction of SDS with PNIPAM. Calorimetric curves for the dilution of a 2% SDS solution in 0.1% PNIPAM, obtained at (■) 17, (●) 25, and (▲) 29 °C. The corresponding open symbols represent the dilution of 2% SDS in water, at the three temperatures.

accompanying the aggregation and phase separation processes. We have also performed high sensitivity DSC measurements on PNIPAM aqueous solutions at 0.1 and 1 wt. % obtaining the results shown in Figure 3. These reveal a highly cooperative endothermic process starting at ca. 28 °C, for both solutions, with transition enthalpy changes of 8.4 and 5.6 kJ (mol PNIPAM)⁻¹ respectively for 0.1 and 1% solutions (for these solutions, macroscopic phase separation was visually observed at ca. 32 °C), with all of these in agreement with previous reports.^{18,27}

Hence, it is important to notice that no significant phase transition occurs in these PNIPAM aqueous solutions within the temperature range of the present investigation (17–29 °C), confirming that we are working mainly with nonaggregated PNIPAM. SDS, on the other hand, does not display a significant difference in its tendency to self-assemble within the same temperature range, as revealed by the almost constant cmc values listed in Table 1.

The effect of temperature on the surfactant–PNIPAM interaction was also investigated in the present study and the resulting curves can be seen in Figure 4. It can be seen that the shape of the curves does not change from 17 to 29 °C, but the cac values, however, decrease as the temperature increases. This indicates a more favorable interaction as the polymer hydration becomes worse, in line with the finding that more hydrophobic polymers display more a intense interaction with ionic surfactants. The interaction of a cationic surfactant (DTAB) with PNIPAM is shown in Figure 5. In this case, the shape of the

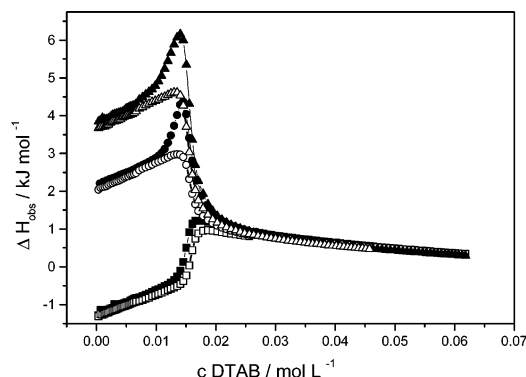


Figure 5. Effect of temperature on the interaction of DTAB with PNIPAM. Calorimetric curves for the dilution of a 5% DTAB solution in 0.1% PNIPAM, obtained at (■) 17, (●) 25, and (▲) 29 °C. The corresponding open symbols represent the dilution of 5% DTAB in water, at the three temperatures.

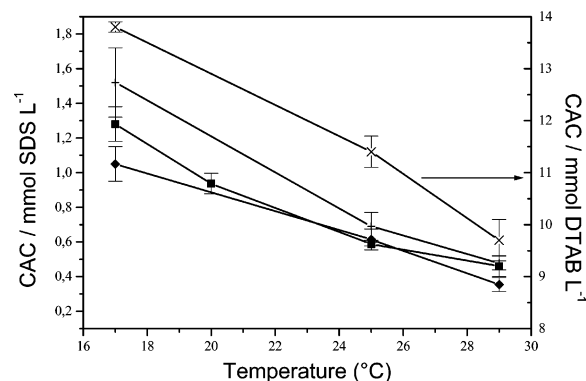


Figure 6. Variation of cac values for the interaction of SDS and DTAB with PNIPAM as a function of temperature: (○) SDS + 0.01% PNIPAM, (■) SDS + 0.1% PNIPAM, (◆) SDS + 1% PNIPAM, (×) DTAB + 0.1% PNIPAM.

dilution curves changes significantly only at 25 °C and above, revealing that the interaction becomes significant only at temperatures above 25 °C, where the PNIPAM–water interaction starts to decrease. The effects of temperature on the cac for the PNIPAM interaction with SDS and DTAB are summarized in Figure 6. In all cases, the cac values decrease as the temperature is increased.

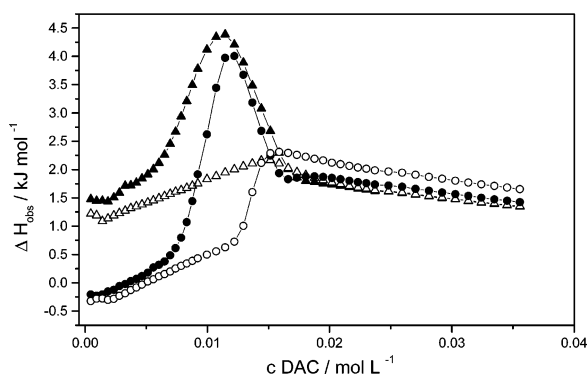
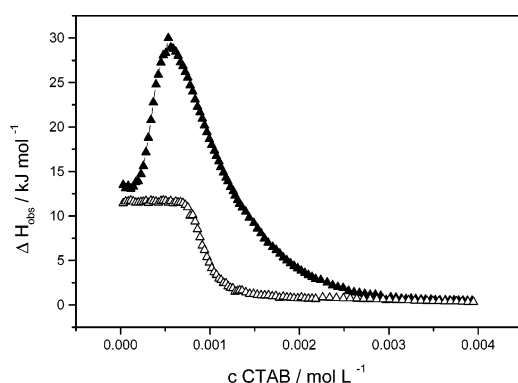
It is well established that cationic surfactants interact less strongly with nonionic polymers than do anionic surfactants, a difference that has been ascribed to steric hindrance due to the voluminous trimethylammonium headgroup.²⁸ The evidence that DAC displays a lower cac than DTAB for its interaction with PNIPAM, as shown in Figure 7, supports this hypothesis, corroborating earlier findings from another calorimetric investigation.²² It would be a better comparison if dodecylammonium bromide were used instead of DAC, but this was not possible due to the high Kraft point of the bromide surfactant. Although chloride is known to interact less intensely than bromide with cationic surfactants, the differences observed between PNIPAM interaction with DTAB and DAC are too large to be ascribed only to differences between the binding affinities of these counterions.

It has also been shown that the interaction with cationic surfactants is more effective when the polymer is more hydrophobic or less hydrated, as PPO²² or PEO at higher temperatures.²⁸ This last finding agrees with the results of Figure 6, pointing out to the influence of solvent competition with the surfactants for the interaction with these polymers. The surfactant hydrophobicity is also found to play an important role in

TABLE 2: Interaction Parameters for PNIPAM and SDS, DTAB, CTAB, and DAC Derived from the Calorimetric Curves at Different Temperatures and Polymer Concentrations (See Text for Definitions)

surfactant	polymer (wt. %)	temp./ °C	cac/ (mmol L ⁻¹)	C ₂ / (mmol L ⁻¹)	(nsurf.) _b /monomer ^a	Δ _{int} H/ ^b (kJ mol ⁻¹)
SDS	0.01	17	1.5 ± 0.2			
		25	0.69 ± 0.08			
		29	0.48 ± 0.04			
	0.1	17	1.3 ± 0.1	13–16	0.6–1.0	2.3
		25	0.59 ± 0.01	10–13	0.4–0.6	1.4
		29	0.46 ± 0.06	8–11	0.3–0.5	1.5
	1.0	17	1.1 ± 0.1	24–30	0.2–0.4	8.0
		25	0.61 ± 0.06	24–31	0.2–0.4	6.0
		29	0.35 ± 0.04	23–31	0.2–0.4	5.0
DTAB	0.1	17	13.8 ± 0.1			0.2
		25	11.4 ± 0.3			0.3
		29	9.7 ± 0.4			0.4
CTAB	0.1	29	0.23 ± 0.02	3–4	0.2–0.4	7.0
DAC	0.1	25	7.6 ± 0.7	20–24	0.4–0.9	0.7
		29	6.1 ± 0.8	17–21	0.6–1.1	0.8

^a Number of moles of bound surfactant per mole of NIPAM unit. Amount of bound surfactant calculated from (C₂ – cmc). ^b Overall enthalpy of interaction, expressed per mole of surfactant. This enthalpy change is calculated as the difference between the sums of the surfactant dilution enthalpies in the presence of polymer and in water, up to C₂.

**Figure 7.** Calorimetric curves for the dilution of 5% DAC in 0.1% PNIPAM solution at 25 °C (●) and 29 °C (▲). The corresponding open symbols represent the dilution of 5% DAC in water, at each temperature.**Figure 8.** Calorimetric curves for the dilution of 0.5% CTAB in water (Δ) and in a 0.1% PNIPAM solution (▲), at 29 °C.

such an interaction, as revealed by the interaction of CTAB with PNIPAM at 29 °C (Figure 8). The enthalpy differences for CTAB/PNIPAM binding are much more pronounced than those for DTAB, and the cac is lower. The calorimetric curves for the interaction of CTAB with PNIPAM are similar to those observed with SDS and DAC, although a more positive enthalpy change is obtained for CTAB. Another difference is that the enthalpy values for the dilution of cationic surfactants in the presence of polymer are always more positive than their enthalpies of dilution in water.

The parameters that characterize PNIPAM interaction with the different surfactants are presented in Table 2. The excess

Gibbs energy that stabilizes the polymer-bound aggregate versus free micelles can be estimated from: $\Delta G = -RT \ln(\text{cac}/\text{cmc})$.²⁹ At 29 °C (polymer concentration = 0.1 wt. %), these ΔG values for SDS, CTAB, DAC, and DTAB are 6.9, 3.1, 2.2, and 1.0 kJ mol⁻¹, respectively. These values show the intensity of the interaction in the sequence: SDS > CTAB > DAC > DTAB. Concerning the overall enthalpy of interaction with PNIPAM, CTAB causes a larger enthalpy change, followed by SDS and, with much lower values, DAC and DTAB. This energy difference is also observed to decrease slightly as temperature increases. The trend of enthalpy changes for these surfactants is different from that derived from the cac values. C.a.c. values measure polymer capacity of nucleating surfactant aggregates around its chain, whereas the enthalpy change associated with the interaction is proposed to be caused by the PNIPAM dehydration associated with the displacement of water solvation molecules due to surfactant interaction with the polymer. Although the enthalpy change is a consequence of interaction, the extent of dehydration of the polymer reflects the mode by which polymer chains interact with the surfactant aggregate.

We have recently shown for the interaction of SDS with PEO¹⁵ that the calorimetric curves change significantly between 15 and 65 °C. At the highest temperature, there were only slight differences between the dilution curves for surfactant in polymer solution and in water, but the cac values were smaller than cmc values at all of the temperatures studied. Although the intensity of interaction (measured by their cac values) did not change significantly within that temperature range, the enthalpy changes were quite distinct. This finding was ascribed to a change in the mode of PEO interaction with SDS aggregates at the different temperatures, with PEO displaying a more extensive dehydration at lower temperatures. In line with that proposition, the more pronounced enthalpy change due to PNIPAM interaction with CTAB suggests a different mode of interaction, possibly associated with a more extensive polymer dehydration upon its interaction with the surfactant, although not necessarily with a more intense interaction.

Since the chemical structure of PNIPAM displays a pendant isopropyl group, it is highly possible for this hydrophobic moiety to be incorporated into the surfactant aggregate, whereas the more hydrophilic polymer backbone helps in shielding the hydrocarbon/water interface, as has been proposed for PEO.^{15,22} Such shielding becomes more important considering that SDS aggregates formed around these polymers were found to be

considerably smaller than normal micelles,^{11,30,31} hence with a significantly larger exposition of their hydrocarbon chains to water.

The amount of bound surfactant can be also estimated from the interaction parameters listed in Table 2, as ($C_2 - \text{cmc}$). These numbers were only estimated for binding of SDS, DAC, and CTAB to 0.1 and 1% PNIPAM solutions due to the difficulty in obtaining exact C_2 values at lower polymer concentrations and, with DTAB, because the two dilution curves were too close to each other.

The intervals for the amounts of SDS bound to PNIPAM in 0.1% solutions at the three temperatures, expressed per mole of monomer are given in Table 2. These values are of the same order of magnitude as those reported for the binding of SDS to other water soluble polymers (values obtained from studies conducted at 25 °C):²² ca. 0.6 for PVP 40 000 g mol⁻¹, ca. 1 for PPO 1000, and ca. 0.5–0.7 for PEO in the molar mass range of 3350–1 000 000 g mol⁻¹. Similar values are observed for the interaction of DAC and CTAB with 0.1% PNIPAM. No significant change in the amount of bound surfactant was observed within the studied temperature range, apart from a slight decrease observed for data associated with the binding of SDS to 0.1% PNIPAM.

In summary, the present calorimetric investigation provided a general view of the processes of ionic surfactant interaction with PNIPAM. The calorimetric curves associated with this interaction process were quite similar to those reported for the corresponding interaction with other slightly hydrophobic polymers such as PPO, suggesting a similar binding mechanism. The overall enthalpy change suggests penetration of the isopropyl group in the micellar aggregate. Precise values for ΔH were determined, to our knowledge for the first time, allowing the assessment of how different conditions affect this interaction. A temperature increase was found to strengthen the polymer–surfactant interaction, owing to a decrease in the degree of PNIPAM hydration. The amount of bound surfactant and the overall energy of the interaction remained constant for all surfactants within the studied temperature range. Different surfactants displayed different binding affinities toward PNIPAM, with the intensity following the sequence: SDS > CTAB > DAC > DTAB. This sequence confirms that anionic surfactants are much more effective in binding to nonionic polymers and also that the surfactant hydrophobicity and size of its headgroup play an important role in this interaction. The enthalpy change

associated with the binding of CTAB was much greater than those observed for the other surfactants suggesting a different mode of polymer-aggregate interaction.

Acknowledgment. The authors acknowledge the Brazilian Agencies FAPESP (for financial support to this project), CNPq (for a research grant to W.L.), and CAPES (for a scholarship to L.A.C.T.). We also thank Gerd Olofsson for a series of enlightening discussions at different stages of this investigation.

References and Notes

- (1) Cabane, B.; Duplessix, J. *Phys. Chem.* **1982**, *43*, 1529.
- (2) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.
- (3) Schild, H. G.; Tirrell, D. A.; *Langmuir* **1991**, *7*, 665.
- (4) Graziano, G. *Int. J. Biol. Macromol.* **2000**, *27*, 89.
- (5) Ricka, J.; Meewes, M.; Nyffenegger, R.; Binkert, Th. *Phys. Rev. Lett.* **1990**, *65*, 657.
- (6) Lee, L. T.; Cabane, B. *Macromolecules*, **1997**, *30*, 6559.
- (7) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
- (8) Chen, G.; Hoffman, A. S. *Nature* **1995**, *373*, 49.
- (9) Eliassaf, J. *J. Appl. Polym. Sci.* **1978**, *22*, 873.
- (10) Mylonas, Y.; Karayanni, K.; Staikos, G. *Langmuir* **1998**, *14*, 6320.
- (11) Mears, S. J.; Deng, Y.; Cosgrove, T.; Pelton, R. *Langmuir*, **1997**, *13*, 1901.
- (12) Jean, B.; Lee, L. T.; Cabane, B. *Langmuir* **1999**, *15*, 7585.
- (13) Olofsson, G.; Wang, G. *Pure Appl. Chem.* **1994**, *66*, 527.
- (14) da Silva, R. C.; Olofsson, G.; Schillén, K.; Loh, W. *J. Phys. Chem. B* **2002**, *106*, 1239.
- (15) da Silva, R. C.; Loh, W.; Olofsson, G. *Thermochim. Acta.*, in press.
- (16) Jansson, J.; Schillén, K.; Olofsson, G.; da Silva, R. C.; Loh, W. *J. Phys. Chem. B* **2004**, *108*, 82.
- (17) Wang, G.; Pelton, R.; Zhang, J. *Colloids Surf. A* **1999**, *153*, 335.
- (18) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.
- (19) Olofsson, G.; Berling, D.; Markova, N.; Molund, M. *Thermochim. Acta* **2000**, *347*, 31.
- (20) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, *99*, 5588.
- (21) Evans, D. F.; Wenneström, H. *The Colloidal Domain*; Wiley-VCH: New York, 1999.
- (22) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.
- (23) Niemiec, A.; Loh, W. unpublished results.
- (24) Persson, K.; Wang, G.; Olofsson, G. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3555.
- (25) Hai, M. T.; Han, B. X.; Yan, H. K. *J. Phys. Chem. B* **2001**, *105*, 4824.
- (26) Heskins, M.; Guillet, J. E. *J. Macromol. Sci. Chem.* **1968**, *A2*, 1441.
- (27) Tiktopulo, E. I.; Bychkova, V. E.; Ricka, J.; Ptisyn, O. B. *Macromolecules*, **1994**, *27*, 2879.
- (28) Anthony, O.; Zana, R. *Langmuir* **1994**, *10*, 4048.
- (29) Chu, D.; Thomas, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6270.
- (30) van Stam, J.; Almgren, M.; Lindblad, C. *Prog. Colloid Polym. Sci.* **1991**, *84*, 13.
- (31) Mylonas, Y.; Staikos, G. *Langmuir* **1999**, *15*, 7172.