Microcalorimetric Evidence of Hydrophobic Interactions between Hydrophobically Modified Cationic Polysaccharides and Surfactants of the Same Charge

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We synthesized and characterized a series of new polymers—hydrophobically modified cationic polysaccharides—based on dextran having pendant *N*-(2-hydroxypropyl)-*N*,*N*-dimethyl-*N*-alkylammonium chloride groups randomly distributed along the polymer backbone. These polymers are good candidates for studying the hydrophobic effect on polymer/surfactant association. In previous papers we reported their interactions with oppositely charged surfactants. For further insight into the relative importance of the hydrophobic interaction in the association process now we studied the thermodynamics of the interaction of these hydrophobically modified polymers with surfactants of the same charge (DMRX/C_nTAC) by isothermal titration calorimetry (ITC). In order to try to discriminate the solution behavior of these polymer/surfactant systems, we analyzed separately the interaction of unmodified dextran with ionic surfactants and the interactions between the corresponding cationic surfactants. The interaction enthalpies for DMRX/C_nTAC systems were derived from a proposed thermodynamic model with equations that describe the polymer−surfactant interactions. The thermodynamic parameters for the DMRX/C_nTAC aggregation process as well as surfactant micellization in the presence of the polymer were also calculated. From all the results we were able to ascertain the effect on the interactions of changing the alkyl chain length of the polyelectrolyte pendant groups or the surfactant. The importance of the polymer aggregation state on the mechanism of interaction was also addressed.

1. Introduction

Interactions between polyelectrolyte and surfactants have already been the subject of several reviews.[1−6] Research in this field has been mainly devoted to oppositely charged polyelectrolyte/surfactant systems. For systems where the polyelectrolyte and surfactant have the same charge much fewer studies are available as in most cases the presence of unfavorable electrostatic repulsion leads to a very weak association. This type of interaction was observed earlier by McGlade et al.[7,8] in 1987 and 1988 by a fluorescence technique, Iliopoulos et al.[9] in 1991 by viscosity measurements, and Zana et al.[10] in 1993 by viscosity and cryo-transmission electron microscopy (cryo-TEM) experiments. If the hydrophobic interaction can overcome the electrostatic repulsion and the energy necessary to distort the polymer backbone then the polyelectrolyte will also interact with surfactants of the same charge.

In recent years, hydrophobically modified polyelectrolytes (HMPE) have attracted substantial interest. They are prepared by introduction of ionic and hydrophobic moieties on environmentally friendly nonionic polymers or polyelectrolyte precursors. Therefore, HMPE are interesting for both fundamental and applied purposes. They have been used in studies of polyelectrolyte/surfactant systems of opposite charge[11−18] as well as in systems of the same charge.[9,19−28] The difference in the interactions in mixed systems of opposite or the same charge has been studied by Philippova et al.[29]and Kästner et al.[30]

It is known that the strong association between HMPE and oppositely charged surfactants is driven by electrostatic attraction and hydrophobic interaction. As a result, a series of association processes takes place as the charge ratio of surfactant to polyelectrolyte (n_s/n_p) increases, namely, formation of polyelectrolyte−surfactant complexes, precipitation and redissolution, and micellization of surfactants in the presence of the polymer. In general, a single phase appears at low and high surfactant concentration ranges and phase separation occurs close to charge neutralization.[11,12,31−36] For mixed systems of the same charge, the association between polymer and surfactant is driven mainly by hydrophobic interactions. Hydrogen binding is an additional interaction occurring in systems containing surfactant with head groups that have the ability to form hydrogen bonds with the polymer backbone.[27] However, there is to date a lack of thorough investigations on the thermodynamic characterization of the energetics of the interactions present so as to allow a deeper understanding of their behavior. It is now well established that calorimetry is an excellent tool for providing this type of information for oppositely charged systems.[17,37a−c−39] To our knowledge, only two papers have been reported so far with calorimetric work on interactions of a polyelectrolyte with a surfactant of the same charge.[37d,40] Therefore, it is very important to provide new microcalorimetric evidence for the interaction of these types of mixed systems involving species of the same charge.

In our previous work[17] we reported a systematic thermodynamic study of the molecular self-assembling of a series of new hydrophobically modified cationic polysaccharides, DMRX (Figure 1), and their mixtures with oppositely charged surfactants in aqueous solution. The molecular structure of the studied

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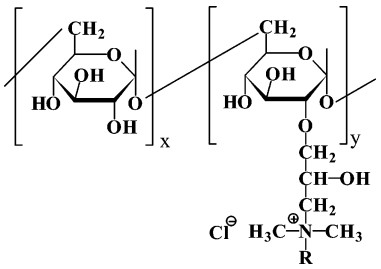

Figure 1. Chemical structure of cationic polyelectrolytes obtained by chemical modification of dextran. R = C_nH_{2n+1}, referred to as Oct (n = 8), Dod (n = 12), and Cet (n = 16). The degree of substitution is defined as DS = $100y/(x + y)$.

polymers derived from dextran by the grafting of *N*-(2-hydroxypropyl)-*N*,*N*-dimethyl-*N*-alkylammonium chloride (alkyl = octyl, dodecyl, and cetyl) pendant groups can be considered to be similar to a polymeric surfactant connected by hydrophilic spacers at the level of the head groups.[41] The restricted mobility induced by the hydrophilic dextran backbone on the pendant alkyl quaternary ammonium groups leads to various interactions being different from those in conventional surfactant systems—the van der Waals interaction between the chains, the electrostatic interaction between charged groups, the hydrophobic interaction between the alkyl side chains, and the energy of the conformational change. This results in critical micelle concentrations (cmc's) of the hydrophobically modified polymers being several orders of magnitude lower than those of the corresponding single-chain cationic surfactants (C_nTAC).[17c]

Therefore, in the present work we studied their interactions with surfactants (C_nTAC) of the same charge with the aim to characterize and ascertain the role of the hydrophobic effect on the association. It is known that the association between HMP and surfactants is similar to surfactants' mixed micellization.[42] It is to be expected that the interaction between the studied polymers and CTAC or DTAC shares some characteristics with the interactions observed between the two cationic surfactants. Some studies are available concerning formation of mixed micelles with surfactants of the same charge,[43−53] but very few use microcalorimetry.[49−52] Malliaris et al.[45] studied formation of mixed micelles between DTAC and CTAC using conductivity and fluorescence methods, but so far no energy information on the interaction is available, which would enable a better understanding of the more complex enthalpy curves that we observe for the DMRX/surfactant systems.

Thermodynamic characterization of the interactions was obtained from isothermal titration calorimetry (ITC). In order to discriminate the importance of the various components of the interaction, we studied (i) the interaction of DMRX with alkyltrimethylammonium salts of the same charge as the pendant groups, (ii) the interaction of unmodified dextran with ionic surfactants, and (iii) the interaction between the corresponding surfactants of the same charge. The thermodynamic information obtained from ii and iii is used to provide further understanding of the mixed solution behavior of these hydrophobically modified polyelectrolytes (DMRX) with surfactants of the same charge as well as about the importance of the change in alkyl chain length of polyelectrolyte pendant groups and surfactants on the interactions and thus to unravel the complex patterns displayed by these mixed systems.

2. Experimental Methods

2.1. Materials. The studied polyelectrolytes were a series of polymers based on dextran having pendant *N*-(2-hydroxypropyl)-*N*,*N*-dimethyl-*N*-alkylammonium chloride groups randomly distributed along the polymer backbone. They were synthesized according to previously described methods[17a,c] by chemical modification of one dextran sample: D40 (Sicomed S.A. Bucharest) with M_w = 40 000 g/mol. In the code used hereafter for the different substituted polymers DMRX, D stands for dextran, M (in kDa) for the weight-averaged molecular weight of the unmodified dextran, R the length of the pendant group, and X the degree of substitution (DS = X = $100[y/(x + y)]$, in mol %). The studied polyelectrolytes can therefore be denoted as D40Oct30, D40Dod30, and D40Cet15 (Figure 1).

Dodecyltrimethylammonium chloride (DTAC or C_{12}TAC) (TCI, >98%), cetyltrimethylammonium chloride (CTAC or C_{16}TAC) (Fluka, >98%), and cetyltrimethylammonium bromide (C_{16}TAB or CTAB) (Sigma, 99%) were used without further purification. All solutions were prepared using water produced by a Milli-Q filtration system either by weight or by volume and stabilized at room temperature for 2 days before use.

2.2. Isothermal Titration Microcalorimetry (ITC). The microcalorimetric unit used in this work as well as the experimental procedure have been described in detail in our previous work.[17a] A twin microcalorimetric channel (Thermometric AB, Sweden) equipped with a 3 mL titration cell (Lund University, Sweden) was used throughout. The polymer solution or water volume in the calorimetric vessel was 2.6 mL. The calorimetric titration experiments consisted of a series of consecutive additions of concentrated surfactant solution into water or concentrated surfactant + polymer solutions into polymer solution of the same polymer concentration. Polymer was used in the syringe in order to maintain a constant polymer concentration throughout the titration.[17a,40] The titrating solution was added automatically, in aliquots of 4−8 μL, from a modified gastight Hamilton syringe through a thin stainless-steel capillary until the desired concentration range was covered. A special Kel-F turbine, made at a Lund University workshop (Sweden), was used throughout as it proved to promote very good mixing. All experiments were performed at 308.15 ± 0.01 K.

3. Results and Discussion

3.1. Interaction between Cationic Surfactants (C_nTAC). Previously we studied by ITC the dilution of concentrated solutions of DTAC and CTAC into water at 308.15 K. The process of demicellization of these two surfactants into pure water was found to be endothermic, indicating that the enthalpies of micelle formation (ΔH_{mic}) in the absence of polymer are in all cases negative.[17c]

Microcalorimetric results for the mixed micellization of C_nTAC surfactants were now obtained in two experiments, where the position of both surfactants was exchanged: (i) a DTAC solution in the vessel was titrated with CTAC and (ii) a CTAC solution in the vessel was titrated with DTAC. These experiments were performed in order to make a direct parallel between the calorimetric tracing of the titration of D40Dod30 with CTAC and D40Cet15 with DTAC.

The variation of ΔH_{obs} with C_{CTAC} (or C_{DTAC}) is shown in Figure 2. The curves for case i (Figure 2a) (C_{DTAC} (in the vessel) < cmc; cmc (DTAC)[17c] = 24 mmol/dm^3) show a pattern similar to the CTAC dilution curve in pure water. It is observed that there is a break in each curve that depends on the molar fraction and represents the onset of mixed micelle formation.

According to the ideal mixing approximation for two-component surfactant solutions the critical mixed micelle concentration (cmc_{mix}) as expressed by total surfactant concentrations can be calculated from their individual cmc and the

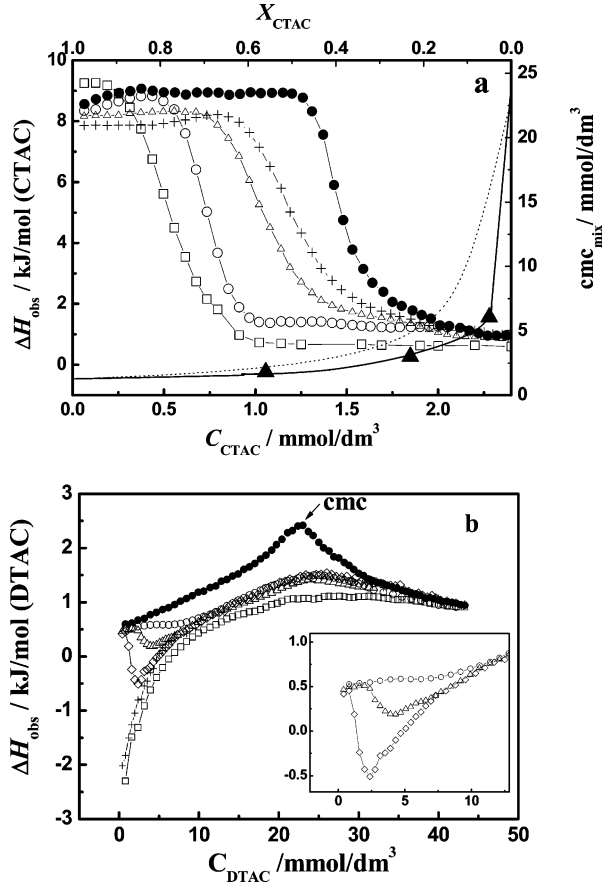

Figure 2. Microcalorimetric titration curves for the mixed systems of surfactants of the same charge. (a) ΔH_{obs} vs C_{CTAC} with CTAC in the syringe (0.02 mol/dm^3) and DTAC concentrations in the vessel: 0.6 (+), 1.2 (△), 3.0 (○), and 5.9 mmol/dm^3 (□). For the representation of cmc$_{mix}$ vs X_{CTAC}, the solid line corresponds to the values calculated from our calorimetric results and the dotted line to the results calculated from the ideal mixing approximation (see text). (b) ΔH_{obs} vs C_{DTAC} with DTAC in the syringe (0.25 mol/dm^3) and CTAC concentrations in the vessel: 0.35 (○), 0.69 (△), 1.0 (◇), 1.7 (+), and 3.5 mmol/dm^3 (□). In b the inserted plot shows an enlargement of the beginning of the titration curves for the cases where C_{CTAC}(in the vessel) < cmc. The total surfactant concentrations at the break are represented in Figure 2a by solid triangles ▲. Curves (●) in a and b are for dilution of the concentrated surfactant solution into water.

molar fraction of one component, i.e., by use of equation: $1/\text{cmc}_{mix} = X_1/\text{cmc}_1 + (1 - X_1)/\text{cmc}_2$, where subscripts 1 and 2 represent each surfactant. It is very interesting to examine the difference between the results from this calculation and from our experiments. The cmc$_{mix}$ can be calculated from our calorimetric measurements as the sum of C_{DTAC} and C_{CTAC} when mixed micelles start to form. These values are plotted as a function of the molar fraction of CTAC (X_{CTAC}), as shown in Figure 2a, where a solid line shows the values obtained from our experimental results and a dotted line represents the results that can be calculated from the ideal mixing approximation. A small deviation of cmc$_{mix}$ from the ideal approximation is observed as X_{CTAC} decreases, which must arise from the asymmetry of the two surfactant's chains.[50]

For case ii, the calorimetric tracings for titration of DTAC into CTAC (Figure 2b) exhibit a very different profile when C_{CTAC} (in the vessel) < cmc or when C_{CTAC} (in the vessel) > cmc (cmc(CTAC)[17c] = 1.26 mmol/dm^3). For the curves where C_{CTAC} is below cmc, we can see a break at a concentration much smaller than the cmc of pure DTAC (insert in Figure 2b). The total surfactant concentration at the onset of the break was also calculated in this case as described above, and the values are added to the plot (solid line) in Figure 2a as solid triangles. It can be seen that these values fit perfectly to the curve of cmc$_{mix}$ vs X_{CTAC} (solid line), as they should, showing that we are in fact observing the onset of mixed micelle formation. For the curves where C_{CTAC} in the vessel is above cmc, no break is observed, i.e., in this case we do not detect the onset of mixed micelle formation. The continuing addition of DTAC monomers induces an increase in aggregation number of the CTAC/DTAC mixed micelles with DTAC insertion.[45] Therefore, the shape of the calorimetric titration curves must reflect the structural rearrangements that occur in the mixed micelles upon increasing DTAC concentration, as suggested before.[50−53] An ill-defined maximum at a concentration similar to the cmc of pure DTAC appears, suggesting formation of pure DTAC micelles thereof.

3.2. Thermodynamic Description of the Polymer−Surfactant Interaction of the Studied Systems. We should keep in mind that by having polymer in the syringe with the same concentration as in the vessel the polymer concentration is constant throughout the experiment. In this case, a detailed analysis of the various processes taking place is needed for a correct assignment of the interaction enthalpies.

We can assume that the reaction takes place in two steps: (1) PS complex (or PS complex + surfactant micelles) dissociates into surfactant monomers and polymer molecules and (2) the surfactant monomers associate again with the polymer (considering all polymer molecules present in the cell). For process 1, the equations can be written as follows

$$(n - x)\text{S(mic)} + \text{S}_x\text{P}_q \rightarrow n\text{S(mon)} + q\text{P} \quad \Delta H(1) \quad (1)$$

$$(n - x)\text{S(mic)} \rightarrow (n - x)\text{S(mon)} \qquad \Delta H(2) = (n - x)\Delta H_{\text{demic}} \quad (2)$$

In the two equations the symbols n, x, and q express the amount of the added surfactant, the surfactant bound to polymer, and the polymer added in each injection (mol), respectively. The molar enthalpy of dissociation of surfactant micelles is $\Delta H_{\text{demic}} = -\Delta H_{\text{mic}}$ (in kJ/mol).

Subtracting eq 2 from eq 1 will give

$$\text{S}_x\text{P}_q \rightarrow x\text{S(mon)} + q\text{P} \quad \Delta H(3) = x[-\Delta H_{\text{complex}}] \quad (3)$$

In eq 3 $\Delta H_{\text{complex}}$ is expressed as the molar enthalpy of formation of polymer−surfactant complex (in kJ/mol).

From this we can see that

$$\Delta H(1) = \Delta H(2) + \Delta H(3), \text{ i.e.,}$$
$$\Delta H(1) = (n - x)\Delta H_{\text{demic}} + x[-\Delta H_{\text{complex}}]$$

Or if we want to express it per mol of added surfactant

$$\Delta H(1)/n = [(n - x)/n]\Delta H_{\text{demic}} + [x/n][-\Delta H_{\text{complex}}] \text{ (in kJ/mol)}$$

Considering process 2, addition of a mixed titrant solution (polymer + surfactant) into polymer solution in the cell

$$\{(n - x)\text{ S(mic)} + \text{S}_x\text{P}_q\} + r\text{P} \rightarrow \text{S}_n\text{P}_{(r+q)} \quad \Delta H(4) \quad (4)$$

In eq 4 the symbol r represents the amount of polymer in the cell. Considering now the result of subtracting eq 1 from eq 4, we have

$$n\text{S(mon)} + q\text{P} + r\text{P} \rightarrow \text{S}_n\text{P}_{(r+q)} \quad \Delta H(5) \quad (5)$$

where $\Delta H(5)$ is the interaction enthalpy of surfactant with polymer. Therefore, it can be calculated as $\Delta H(5) = \Delta H(4) - \Delta H(1)$ or

$$\Delta H(5) = \Delta H(4) - (n - x)\Delta H_{\text{demic}} - x[-\Delta H_{\text{complex}}]$$

When calculated per mole of added surfactant, the above equation will become

$$\Delta H(5)/n = \Delta H(4)/n - [(n - x)/n]\Delta H_{\text{demic}} - [x/n][-\Delta H_{\text{complex}}]$$

We can see that the interaction enthalpy ($\Delta H_{\text{int}} = \Delta H(5)/n$) between surfactant and polymer can be calculated per mole of surfactant with infinitely dilute solution as the reference state. It is worth noting that we cannot obtain the parameter x only from calorimetric experiments, but when the polymer concentration is low the x value is negligible, i.e., we can calculate the interaction enthalpy directly from the calorimetric results as

$$\Delta H_{\text{int}} = \Delta H(5)/n = \Delta H(4)/n - \Delta H_{\text{demic}}$$

In practice, this means that the ΔH_{int} can be calculated from the difference between the observed enthalpy values in the presence of polymer ($\Delta H(4)/n$) and the enthalpy of demicellization in water (ΔH_{obs} in the absence of polymer) as in the titrations without polymer in the syringe.[54]

For higher polymer concentrations (0.5%) the lack of parameter x makes it impossible for us to calculate accurately the interaction enthalpy. Previously, we did address this problem experimentally, so that we had data to support our model. The study was done with an oppositely charged surfactant/polymer system SDS/D40Oct30. We did perform two types of experiments: (i) titrating concentrated surfactant + polymer solutions into polymer solution of the same polymer concentration[17a] and (ii) titrating concentrated surfactant solution into polymer solution (to be published elsewhere). For this system we only have a significant difference in the calorimetric curves for the two setups, i.e., a significant difference in the observed enthalpy values in the initial stage of the titration, when the polymer concentration is above 0.75%. Therefore, it is reasonable to assume that for the present studied systems, where polymer and surfactant are of the same charge and therefore the interactions are smaller, x is negligible for the polymer with octyl pendant groups for concentrations up to 1% and for polymers with dodecyl and cetyl groups up to 0.25%. Thus, ΔH_{int} and ΔH_{agg} for D40Dod30 and D40Cet15 are only provided for concentrations up to 0.25%. Nevertheless, just for comparative purposes, the calorimetric tracings for polymer concentration 0.5% are depicted in Figure 4.

3.3. Interaction of Unmodified Dextran with Ionic Surfactants. In the case of DTAC the presence of dextran has little effect on the observed enthalpies and the cmc (results not shown), whereas an obvious effect was observed for CTAC. This difference can be rationalized considering the different alkyl chain length in DTAC (dodecyl) and CTAC (cetyl).

The microcalorimetric curves of the variation of the observed enthalpies (ΔH_{obs}) with the CTAC concentration (C_{CTAC}) are shown in Figure 3, where the corresponding dilution curve of CTAC into water is also included for comparison. By analogy with the notation used in other uncharged polymer−surfactant systems,[54,55] in this case we refer to the break in these curves as the critical aggregation concentration (cac), the concentration at which aggregation occurs in the presence of the polymer. The enthalpy of aggregation (ΔH_{agg}) in the presence of dextran

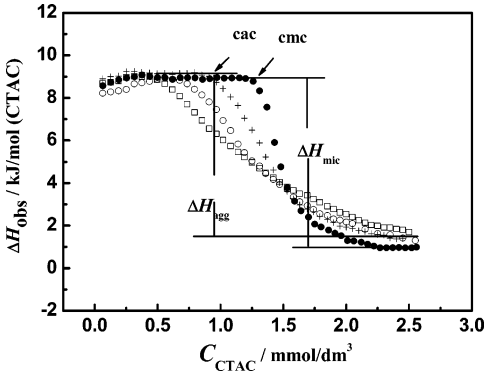

Figure 3. Microcalorimetric curves for the titration of dextran with CTAC at different dextran concentrations in (w/v)%: 0.1% (+), 0.25% (○), and 0.5% (□) at 308.15 K. The curve (●) represents dilution of the concentrated CTAC solution (0.02 mol/dm^3) into water.

can be obtained from the difference between the observed enthalpies at the two linear segments as shown in Figure 3. The ΔH_{agg} values under different dextran concentrations are similar but somewhat smaller than the ΔH_{mic} (−8.1 kJ/mol)[17c] of the CTAC. The cac and cooperativity of the aggregation process, on the other hand, decrease as the dextran concentration increases. It is clear that any difference between the observed curves with and without polymer must result from polymer−surfactant interactions. The decrease in cooperativity implies that the concentration range corresponding to the micellization process in the presence of dextran is larger than in pure water. This means that the micelle aggregate is changing as the CTAC concentration increases, probably due to a change in aggregation number.

3.4. Interaction between Cationic DMRX and CTAC (or CTAB). The above analysis has shown that the cationic surfactant CTAC can interact both with the dextran backbone and with the cationic surfactant DTAC. It is tempting to infer that it will also do so with the cationic hydrophobic pendant groups of DMRX polymers. Nevertheless, it is to be expected that the interaction of DMRX having both polysaccharide backbone and pendant side chain with the surfactants (C_nTAC) of the same charge will be more complex.

A. Observed Enthalpy Patterns (cac and ΔH_{agg}). The obtained enthalpy curves (ΔH_{obs} vs $C_{\text{surfactant}}$) at constant polymer concentrations for DMRX/CTAC and D40Cet15/CTAB systems and the corresponding dilution curves for CTAC and CTAB solutions in pure water are presented in Figure 4a−d, where the surfactant concentration is the final concentration in the calorimetric vessel after each injection. The solution behavior is different from what we observed when we had an oppositely charged surfactant/polymer system.[17] In the systems we studied previously the thermodynamics represented the contributions of both hydrophobic interaction and attractive electrostatic interaction, whereas now we have repulsive electrostatic interaction. One consequence of this is that obviously no phase separation occurs in these mixed systems.

If we compare the results obtained before for DMRX with oppositely charged surfactants[17] with the systems DMRX/CTAC or CTAB presented here we can say that the observed enthalpy patterns are definitely less complex and only a break is observed in the enthalpy vs concentration curves. They are indeed more similar to those of uncharged polymer/ionic surfactant systems.[54−56] The CTAC concentration at which the break occurs is well defined and referred to as the critical aggregation concentration (cac), i.e., in this case the concentration at which surfactant molecules start to form mixed micelles with the alkyl side chains

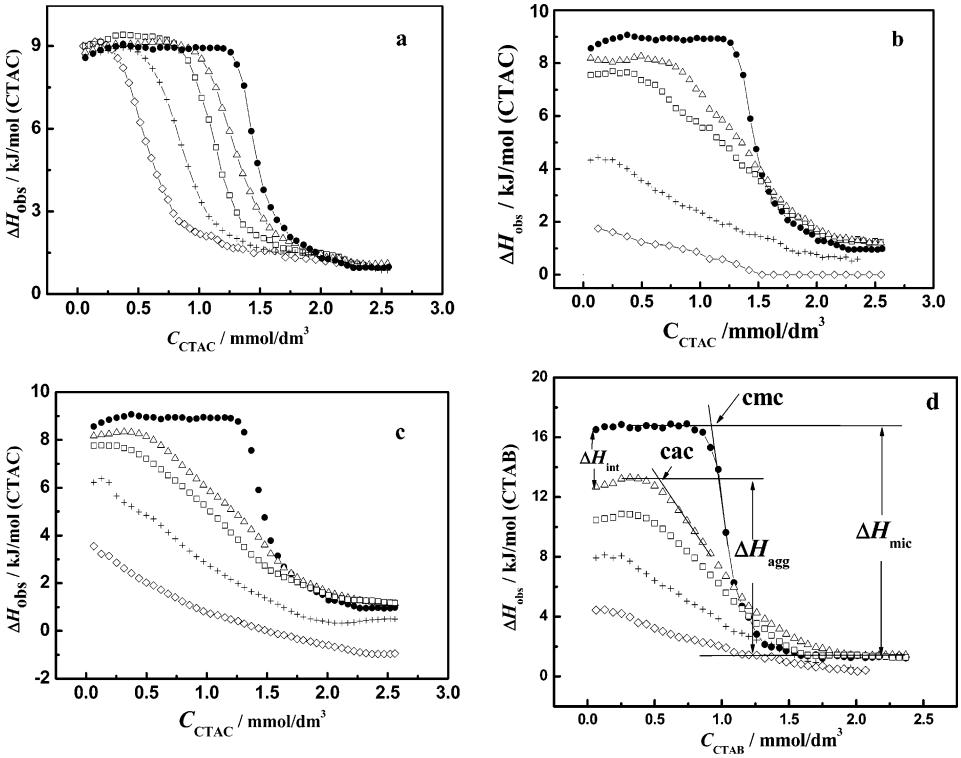

Figure 4. Microcalorimetric titration curves for DMRX/CTAC or DMRX/CTAB systems and dilution enthalpy curves (●) of CTAC or CTAB (0.02 mol/dm^3) into water: (a) D40Oct30/CTAC, (b) D40Dod30/CTAC, (c) D40Cet15/CTAC, and (d) D40Cet15/CTAB. The polymer concentrations for all systems are 0.05% (△), 0.1% (□), 0.25% (+), and 0.5% (◇).

TABLE 1: cac and ΔH_{agg} Values for Mixed Systems of DMRX (D40Oct30, D40Dod30, and D40Cet15) with CTAC at 308.15 K

Systems	$C_{polymer}$[a]	cac[b] (mmol/dm^3)	ΔH_{agg}[b] (kJ/mol)	Δ[c] (%)
D40Cet15/CTAC	0.05 (0.35)	0.48	−7.1	11
	0.1 (0.69)	0.37	−6.5	19
D40Cet15/CTAB	0.05 (0.35)	0.47	−11.9	25
	0.1 (0.69)	0.38	−9.3	41
	0.25 (1.73)	0.25	−7.5	52
D40Dod30/CTAC	0.05 (0.59)	0.76	−7.0	12
	0.1 (1.18)	0.51	−6.3	21
	0.25 (2.96)	0.25	−3.6	55
D40Oct30/CTAC	0.05 (0.61)	1.00	−8.1	∼0
	0.1 (1.21)	0.88	−8.1	∼0
	0.25 (3.03)	0.58	−8.1	∼0
	0.5 (6.05)	0.31	−8.1	∼0

[a] The concentration, $C_{polymer}$, is expressed in polymer mass percentage ((w/v)%) and in parentheses as the polymer side group concentration, $C_{side\ group}$ (mmol/dm^3). [b] The estimated errors for cac and ΔH_{agg} are less than 4%. [c] $\Delta = [(\Delta H_{agg} - \Delta H_{mic})100]/\Delta H_{mic}$.

of the polymer. The corresponding enthalpy of aggregation (ΔH_{agg}) in the presence of polymer can be derived as shown in Figure 4d. All obtained values of cac and ΔH_{agg} are given in Table 1.

According to Colby et al.[23] the concentration at which the binding of surfactant to HMPE of the same charge starts should be called the critical incorporation concentration (CIC), characterized by a noncooperative inclusion of the surfactant tail in the hydrophobic microdomains of the polymer. We believe that the aggregation of surfactant in the presence of HMPE is the result of two simultaneous processes: a noncooperative inclusion in the polymer hydrophobic microdomains that can be described by CIC, where the mixed micelles formed do not significantly change the properties of already existent hydrophobic microdomains and a cooperative self-aggregation of the bound surfactant, described by cac, where the properties of the system can change. The balance between these two processes depends very much on the number and polarity of the hydrophobic microdomains already present in the polymer solution and therefore on the polymer concentration. In previous studies[17c,57] we reported two critical concentrations for each pure polymer in water. For the present mixed systems, the break points sensed by ITC, which we will call cac, are probably a combination of the two processes mentioned above. These break points occur when the polymer concentration is below the second critical concentration (for which the values we obtained before are $C_{polymer} = 0.5\%$ for D40Oct30, $C_{polymer} = 0.37\%$ for D40Dod30, and $C_{polymer} = 0.15\%$ for D40Cet15).[17c] For D40Cet15, when the polymer concentration is 0.25% (only slightly above the second critical concentration) the presence of the break is not clear. Above this concentration (0.25%), for D40Cet15 and D40Dod30 no breaks are found in the curves (0.5% as well as 1% (data not shown)).

For all studied DMRX/CTAC or CTAB the cac's are lower than the cmc's of the corresponding free surfactant and clearly decrease as the polymer concentration increases. To get a clear comparison among these mixed systems the dependence of the ratio of cac to cmc (cac/cmc) on polymer concentration, $C_{polymer}$ (or hydrophobe concentration, $C_{side\ group}$) is plotted in Figure 5a and b. Figure 5a shows a plot of cac/cmc ratios as a function of $C_{polymer}$ for unmodified dextran/CTAC and D40Oct30/CTAC. It is seen that both the dextran backbone and the polyelectrolyte pendant group play an important role on the cac decrease. Figure 5b shows the comparison between mixed surfactant systems (DTAC/CTAC) and DMRX/CTAC systems, where cac/cmc ratios are plotted as a function of polymer side group or surfactant concentrations in the vessel. We found that the longer the alkyl side chains the lower the cac for the same hydrophobe concentration. Additionally, the effect observed for the polymer/surfactant system is stronger than the one for free surfactants

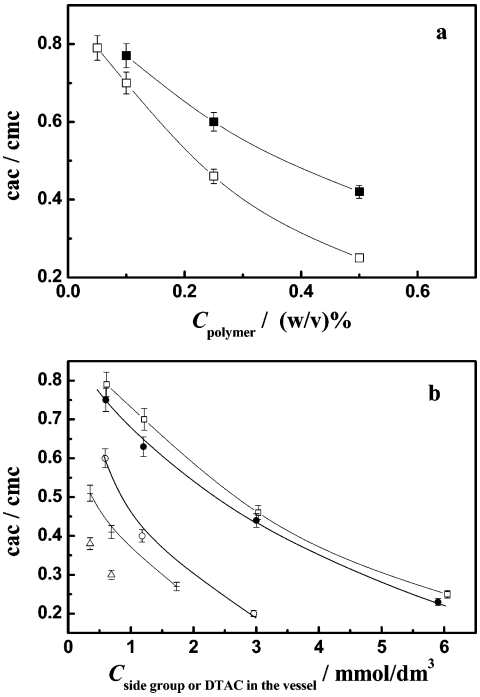

Figure 5. Comparison between calorimetric results for the studied systems: (a) comparison between D40Oct30/CTAC (□) and dextran/CTAC (■) (cac/cmc vs $C_{polymer}$); (b) effect of the alkyl chain length of the polyelectrolyte's side group on the interaction between similarly charged systems. D40Oct30/CTAC (□); D40Dod30/CTAC (○); D40Cet15/CTAB (+), and D40Cet15/CTAC (△) (cac/cmc vs hydrophobe concentration, $C_{side\ group}$). For comparison, a similar ratio is also ploted for DTAC/CTAC (●)—the points represent the ratio of C_{CTAC} at the break to the cmc of CTAC and are plotted against C_{DTAC} in the vessel. The error bars represent an estimated 4% error.

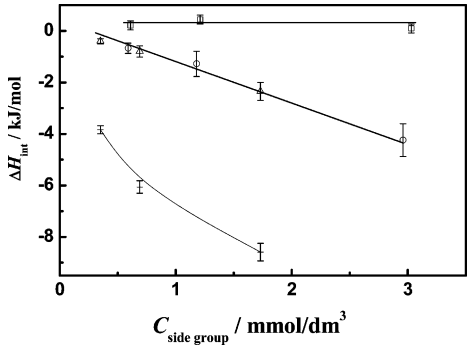

Figure 6. Effect of the alkyl chain length of the polyelectrolyte's side groups on the interaction enthalpy (ΔH_{int}). ΔH_{int} was calculated based on the first injection: D40Oct30/CTAC (□) D40Dod30/CTAC (○) D40Cet15/CTAC (△), and D40Cet15/CTAB (+). The error bars represent an estimated 4% error.

of the same alkyl chain lengths as the pendant groups of the polymer (like when comparing the system D40Dod30/CTAC with free DTAC/CTAC (with no "stereo block spacers"), see curves ○ and ● in Figure 5b). This implies that the conformational constraint of the polyelectrolyte backbone has an important effect on the aggregation process.

On the other hand, the enthalpies of aggregation (ΔH_{agg}) at cac are exothermic, and their absolute values are lower than the ΔH_{mic} of CTAC (−8.1kJ/mol).[17c] We can evaluate the extent of enthalpy change by calculating $\Delta = [(\Delta H_{agg} - \Delta H_{mic})100]/\Delta H_{mic}$ (Table 1). The extent of decrease of ΔH_{agg} increases with polymer concentration increasing—for the system D40Oct30/CTAC ΔH_{agg} is similar to ΔH_{mic} of CTAC, whereas for D40Dod30/CTAC and D40Cet15/CTAC absolute ΔH_{agg} values are smaller than ΔH_{mic} of CTAC. For DMRX/CTAC systems when the $C_{polymer}$ is above the second critical concentration we cannot obtain the ΔH_{agg} values from their observed enthalpy curves as no break is observed.

B. Interaction Enthalpies. All enthalpies reported here are calculated on the basis of total surfactant concentration in the calorimetric vessel. Determination of binding isotherms for HMPE/surfactant systems is not straightforward as a HMPE sticks to the surfactant-selective electrode membrane which impairs the measurements. Even in cases where binding experiments were performed together with microcalorimetric ones for the same system, this was done only as a support for the microcalorimetric findings, and the authors also refer their enthalpies to the total surfactant concentration.[37d]

The observed enthalpy curves shown in Figure 4a−d in the presence of DMRX deviate in the initial stage of titration to different extents from the dilution curves of the surfactant in water. In particular, in the presence of D40Dod30 and D40Cet15 the endothermic effect has a pronounced decrease with increasing polymer concentration. According to the above thermodynamic description (section 3.2) the difference between the observed enthalpy curves with and without polymer can be ascribed to the interaction between surfactant and polymer, as shown in Figure 4d. We did observe that for the mixed systems with CTAC the interaction enthalpy remains almost constant before cac. For D40Oct30/CTAC (Figure 4a), in the studied concentration range, no difference between ΔH_{obs} values in the presence and absence of polymer before cac is detected in the studied concentration range ($\Delta H_{int} \approx 0$) as a result of a weak interaction due to the shorter hydrophobic pendant chain. We should refer to fluorescence measurements made previously with this polymer that indicated that a significant hydrophobicity of its aggregates only occurs at concentrations higher than 0.3%.[57] For D40Dod30/CTAC (Figure 4b), D40Cet15/CTAC (Figure 4c), or D40Cet15/CTAB (Figure 4d) the interaction is stronger as we have a longer alkyl chain in the pendant groups and negative ΔH_{int} values will increase with increasing polymer concentration ($C_{polymer}$ or $C_{side\ group}$). In Figure 6 the obtained ΔH_{int} values are plotted as a function of the hydrophobic side group concentration as we have different degrees of substitution.

The observed enthalpy curves of DMRX/CTAC systems exhibit a stronger dependence on polymer concentration than the ones observed when we had dextran/surfactant (Figure 3). The fact that the interaction enthalpy between CTAC and unmodified dextran is about zero before cac and small after micellization (Figure 3) indicates that the observed change for the hydrophobically modified polymer/CTAC must arise mainly from interactions between CTAC molecules and the pendant side chains of polyelectrolyte.

In the studied polymer concentration range the polymer concentration in the calorimeter vessel is always above its first critical concentration (cmc) but in some cases below the second critical concentration (see above). In the case of Figure 4b, the D40Dod30 concentration is above the second critical concentration (0.37%) only in one case, and that is the only curve where no break is observed. Regarding Figure 4c, the D40Cet15 concentration is above the second critical concentration (0.15%) for two of the plotted curves, where again no break is observed. This is similar to the calorimetric pattern described above when we discussed the surfactant/surfactant interactions (section 3.1, Figure 2b). The polymer aggregation morphology is different at the first and second critical concentrations. At the first critical concentration intramolecular hydrophobic interactions lead to hydrophobic microdomain formation inside the same polymer

chain. After this "micellization" intermolecular cross-linking clusters can form, grow, and eventually reach a kind of stable network structure (at the second critical concentration).[17a,c,57] Then in the cases where CTAC is added to already formed hydrophobic microdomains it leads to a morphological change of polyelectrolyte induced by the surfactant.

The differences in ΔH_{int} between D40Dod30/CTAC and D40Oct30/CTAC (Figure 6) are believed to reflect the effect of the alkyl side chain length of polyelectrolyte, where hydrophobic interactions of the cetyl chain of CTAC with the dodecyl side chain of D40Dod30 are much stronger than with the octyl side chain of D40Oct30. D40Dod30 and D40Cet15 have larger and more hydrophobic microdomains than D40Oct30, and thus, inclusion of CTAC tails is much more favorable.[57] Therefore, the increase in the exothermic ΔH_{int} with an increase in polymer concentration can be assigned to the increase in the number, size, and hydrophobicity of the polymer microdomains, which have an increased ability to bind CTAC.

The degree of substitution (DS) of D40Cet15 is one-half that for D40Oct30, but the length of its alkyl side chain is twice as much. In other words, both hydrophobically modified polymers have the same total carbon number considering all pendant groups, but the differences in ΔH_{int} between D40Oct30/CTAC and D40Cet15/CTAC are quite large. We can therefore conclude that the effective hydrophobicity that results from increasing the alkyl side chain length has a larger impact on the interaction than an increase in the DS. It is also worth noting that when we plot ΔH_{int} as a function of side group concentration ($C_{side\ group}$), the curves for D40Cet15/CTAC and D40Dod30/CTAC almost coincide (Figure 6) as this representation takes into account the difference in the degree of substitution. This result shows that the distances between alkyl side chains are not very important when the polyelectrolyte in solution already exists in the aggregated state.

C. Effect of Counterions. It is well known that surfactant solutions containing the same amphiphilic backbone but different counterions present differences in cmc, ΔH_{mic}, aggregation number, and size and shape of the aggregates[58−65] due to a different counterion binding. In the present work, the counterion effect can be seen when we compare calorimetric results for CTAC and CTAB in the presence and absence of D40Cet15. The cmc (0.93 mmol/dm^3) and ΔH_{mic} (−15.8 kJ/mol) of CTAB are derived from the dilution enthalpy curves of CTAB in water (Figure 4d), showing that by changing the counterion from Cl^- to Br^- the cmc decreases and the exothermic magnitude of ΔH_{mic} increases (for CTAC, cmc = 1.26 mmol/dm^3 and ΔH_{mic} = −8.1 kJ/mol). The differences in cmc and ΔH_{mic} are ascribed to the fact that the two counterions bind to the micellar interface to a different extent and with different energy depending on the counterions' dehydration and location in the Stern layer.[58,59] The counterion Br^- is larger than Cl^-, and thus, its ionic hydration is weaker. As a result, the weakly hydrated Br^- ions can be more readily adsorbed on the micellar surface, decreasing the charge repulsion between the polar groups. On the heavily hydrated ions the charge is partially screened by the surrounding polar water molecules, and these counterions are less effective at reducing the charge repulsion between the head groups. Therefore, the smaller the counterions the larger the entropic driving force for them to bind to micelles.

For the mixed systems with polymer the solution behavior is essentially determined by the inherent properties of amphiphilic ions and counterions. When we have D40Cet15 the interaction enthalpies (ΔH_{int}) are different for CTAB and CTAC for the same polymer concentration (Figures 4c,d and 6). The interaction of D40Cet15 with CTAB is stronger than that with CTAC. The difference in ΔH_{int} is ascribed to the effect of the counterions on the interactions between polyelectrolyte and surfactant of the same charge.

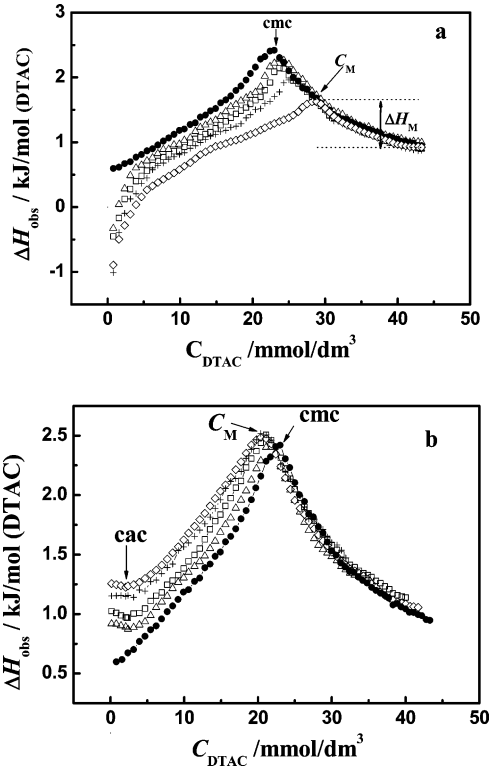

Figure 7. Microcalorimetric titration curves for the systems D40Dod30/DTAC (a) and D40Oct30/DTAC (b) at different polymer concentrations: 0.05% (△), 0.1% (□), 0.25% (+), and 0.5% (◇). The curve (●) is for dilution of the concentrated DTAC solution (0.25 mol/dm^3) into water.

In addition, the cac values at the same polymer concentration ($C_{polymer}$ = 0.05−0.1% < the second critical concentration) do not change within the estimated errors with the change of counterion (Table 1) and the cac/cmc ratios decrease in both cases as the polymer concentration increases (Figure 5b). The corresponding absolute values of ΔH_{agg} decrease with the polymer concentration, and the extent of decrease for D40Cet15/CTAC is smaller than that for D40Cet15/CTAB (Table 1). These results imply that the aggregation process of these mixed systems is entropy and enthalpy driven and in the mixed systems with smaller counterions (Cl^-) the entropic factor plays a more significant role. This conclusion is similar to what can be deduced for the case of the binding of counterions to micelles in the absence of polymer.[59]

3.5. Interaction between Cationic DMRX and DTAC. Figure 7a and b shows typical enthalpy curves for mixed systems of DMRX with DTAC. The titration curves for D40Dod30/DTAC (Figure 7a) and D40Cet15/DTAC (not shown) present a similar pattern for the observed enthalpy change as a function of DTAC concentration, to some extent being similar to the curves corresponding to surfactant/surfactant systems of the same charge (Figure 2b).

For D40Dod30/DTAC (Figure 7a) in the initial stage of the titration ΔH_{obs} deviates quite significantly from the dilution curve of the surfactant in water and depends on polymer concentration, indicating that binding of surfactant to polyelectrolyte takes place at very low concentration. Note that this behavior is very similar to the one found when we titrated DTAC solution into CTAC solutions above its own cmc (Figure

TABLE 2: C_M and ΔH_M Values for Mixed Systems of DMRX (D40Oct30, D40Dod30, and D40Cet15) with DTAC at 308.15 K

Systems	$C_{polymer}$[a]	C_M[b] (mmol/dm^3)	ΔH_M[b] (kJ/mol)
D40Cet15/DTAC	0.05 (0.35)	24	−1.3
	0.1 (0.69)	24	−1.2
	0.25 (1.73)	26	−0.9
	0.5 (3.47)	29	−0.5
D40Dod30/DTAC	0.05 (0.59)	24	−1.4
	0.1 (1.18)	24	−1.2
	0.25 (2.96)	26	−1.0
	0.5 (5.91)	29	−0.7
D40Oct30/DTAC	0.05 (0.61)	22	−1.5
	0.1 (1.21)	21	−1.6
	0.25 (3.03)	21	−1.6
	0.5 (6.05)	20	−1.5

[a] The concentration, $C_{polymer}$, is expressed in polymer mass percentage ((w/v)%) and in parentheses as polymer side group concentration, $C_{side\ group}$ (mmol/dm^3). [b] The estimated errors for C_M and ΔH_M are less than 4%.

2b). This profile of observed enthalpy curves was also found in the same charge systems of HM-alginate/SDS, where SDS molecules bind noncooperatively to the hydrophobic pendant groups of the polymer.[40] With this less hydrophobic surfactant (DTAC) we could not distinguish as clearly as with CTAC the calorimetric patterns when $C_{polymer}$ was above or below the second critical concentration, probably because the interaction is weaker here due to the shorter alkyl chain of the surfactant.

However, cac values were easily detected for mixtures of DTAC and D40Oct30, which has a shorter alkyl side chain (Figure 7b). The cac values appear at an approximately constant DTAC concentration (about 3.0 mmol/dm^3) for the different polymer concentrations.

The concentration, C_M, at which surfactant micelles start to form is referred to as the critical micelle concentration of DTAC in the presence of polymer. The systems with DTAC and D40Dod30 or D40Cet15 show C_M values that are larger than the cmc of pure DTAC and increase with increasing polymer concentration; further, when considered as a function of side group concentration ($C_{side\ group}$), the C_M values for D40Cet15/DTAC show a larger increase with the $C_{side\ group}$ than the ones observed for D40Dod30/DTAC (Table 2). For D40Oct30 the decrease in C_M values with increasing polymer concentration is not significant. In this system the interactions are very weak (the shape of the enthalpy curves in Figure 7b is very similar to that of DTAC into water), and therefore, the presence of the cationic polymer is mainly producing an increase in the ionic strength of the solution, which in turn leads to a very small decrease in cmc of DTAC.

In summary, we can say that for DMRX/DTAC systems the mixed micelles that form between surfactant and the cross-linking structure of the polymer have an important effect on the micellization process of DTAC. Before C_M we have the coexistence of free DTAC monomers and mixed micelles with the cross-linking structures; at C_M, DTAC micelles start to form. One possible explanation for the different effects of D40Dod30 (or D40Cet15) and D40Oct30 on DTAC aggregation behavior is the following: if the cross-linking structures of the mixed micelle are broken at or before C_M, the pendant alkyl chains tend to and promote micellization of the surfactant against the thermal motion, leading to a slight decrease in C_M as compared to the cmc of DTAC in water, as happens with D40Oct30/DTAC. However, if the cross-linking structures coexist with the surfactant micelles at C_M, micellization of free DTAC is retarded, leading to a C_M larger than the cmc of DTAC. Therefore, it all depends on the hydrophobicity of the polymer.

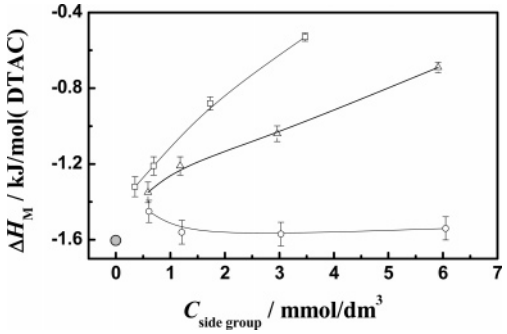

Figure 8. Variation of ΔH_M with $C_{side\ group}$ for DMRX/DTAC systems: D40Oct30/DTAC (○), D40Dod30/DTAC (△), and D40Cet15/DTAC (□). Note: the symbol (●) on the plot is the ΔH_{mic} value of DTAC. The error bars represent an estimated 4% error.

Regarding the enthalpy, we did observe that in the initial stage of titration the interaction enthalpies (ΔH_{int}) between DTAC and D40Dod30 or D40Cet15 are exothermic whereas ΔH_{int} between DTAC and D40Oct30 are endothermic. This suggests that the interaction of the added DTAC molecules with the D40Oct30's octyl side chains is controlled by entropy. Before C_M the large difference in ΔH_{obs} values between D40Dod30/DTAC and the dilution enthalpy curve of DTAC in water suggests that besides the increase of free DTAC monomers we probably also have changes in cross-linking micelles—changes in the aggregation number, cross-linking degree, and maybe even in shape. Further, ΔH_{obs} becomes less endothermic with increasing polymer concentration, which can be ascribed to the increase in the number of hydrophobic moieties.[40] The corresponding enthalpy of micellization (ΔH_M) in the presence of the polymer can be derived from the observed enthalpy curves, as shown in Figure 7a. The obtained results can also be found in Table 2. The variation of ΔH_M with hydrophobic side group concentration for DMRX/DTAC systems shows the same trend as the C_M (Table 2 and Figure 8). The increase in the deviation of ΔH_M from ΔH_{mic} of pure surfactant also reflects the complexity of the mixed solution behavior at C_M. In the case of D40Oct30 very little change in enthalpy with polymer concentration is observed, probably because the polymer/surfactant interaction is not very strong. The values of ΔH_M for all studied systems are negative, suggesting that the process is either enthalpy-driven or enthalpy- and entropy-driven, depending on the relative magnitude of the two thermodynamic properties.

4. Conclusion

These hydrophobically modified cationic polyelectrolytes proved to be very useful for the study of the hydrophobic effect on polymer/surfactant association as we observed that these HMPE can associate not only with surfactants of opposite charge but also of the same charge despite the unfavorable electrostatic repulsion in the later case. These results taken together give detailed insight into the effects of both the conformational constraint of the polyelectrolyte backbone and the alkyl side chain length on the polymer/surfactant interactions.

As pointed out above, the existence of breaks in microcalorimetric curves for DMRX/CTAC systems correlates with the aggregation state of the polymer. When the polymer concentration is between polymer cmc and its second critical concentration, the ITC curves show a break, which we interpret as indicating the onset of mixed aggregate formation.

Further, the increase in polymer concentration and length of the R substituent determines a decrease in ΔH_{obs} at the start of the titration as well as a change in the slope of the curves. The decrease in the slope is an indication of less cooperativity in the assembling process. An important thermodynamic equation was derived for polymer−surfactant interactions in the studied systems. Hence, ΔH_{int} values for DMRX/CTAC systems were directly obtained from the difference between the observed enthalpy values in the presence and absence of polymer.

The hydrophobic interaction in D40Dod30/CTAC is stronger than that in DTAC/CTAC (with no "stereoblock spacers") and can overcome the electrostatic repulsive interaction and the energy necessary to distort the polymer backbone, resulting in mixed micelle formation. On the other hand, the longer the pendant alkyl side chain the stronger the interactions with the surfactant.

In the case of DTAC, it is found that in the initial stage of the titration ΔH_{obs} deviates quite significantly from the dilution curve of the surfactant in water and depends on polymer concentration, indicating that the binding of surfactant to polyelectrolyte takes place at very low DTAC concentration. We could not detect a difference in behavior depending on polymer concentration. This less discriminating behavior is a consequence of the shorter alkyl chain of this surfactant, which implies a weaker hydrophobic interaction. Therefore, the interactions observed in both systems (DTAC and CTAC with polymers of the same charge) are clearly driven by hydrophobicity.

Finally, we would like to stress that the ITC technique could be very successfully used to show that the hydrophobic interaction can overcome the repulsive electrostatic interactions and promote association; further, the results suggest that the interaction mechanism depends on the hydrophobicity of both the surfactant and the pendant groups of the polymer.

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