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Thermodynamics of Self-Assembling of Hydrophobically Modified Cationic Polysaccharides and Their Mixtures with Oppositely Charged Surfactants in Aqueous Solution

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Microcalorimetric techniques, combined with turbidity measurements, were used to study the thermodynamics of self-assembling of hydrophobically modified cationic polysaccharides and their mixtures with oppositely charged surfactants in aqueous solution. 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. The parameters for their micellization process are evaluated from the results of the observed dilution enthalpy curves and compared with those of the related cationic surfactants (DTAC and CTAC). The microcalorimetric results for the mixed systems (polyelectrolytes with oppositely charged surfactants) are used along with turbidity measurements to characterize systematically the thermodynamics of their interaction. The phase behavior is described and the interaction enthalpies are derived from the differences between the observed enthalpy curves with and without polyelectrolyte. Therefore, we discuss in detail the effect of changing the alkyl chain length of polyelectrolyte pendant groups, the molecular weight of the dextran backbone, and the temperature of the measurements on the interactions between polyelectrolyte and surfactant.

Introduction

During the last two decades, research in the field of polyelectrolyte–surfactant interactions has made impressive progress.^{1–5} Considerable efforts have been made to explore the unusual physicochemical characteristics of oppositely charged polyelectrolyte/surfactant systems (PES). In the reported studies, much interest has been focused on the interactions between hydrophobically modified polyelectrolytes (HMPEs) and surfactants.^{6–14} HMPEs have a strong tendency to self-associate and/or to associate with surfactants, leading to intricate phase behavior and rich self-assembling morphologies in aqueous solution, which exhibit a great potential in drug/gene delivery research and in other biomedical applications. The strong association between HMPEs and oppositely charged surfactants is driven by electrostatic attraction and hydrophobic interaction. The mechanism and strength of the interactions depend on the characteristics of the surfactants and polyelectrolytes, that is, the structure of the surfactant's hydrophobic part,^{15–26} as well as the charge density, degree of substitution, chain conformation, hydrophobicity, and molecular weight of the polyelectrolyte chains.^{13,18,27–34} In particular, the effect of these factors on the solution behavior of PES systems changes with the system's composition, that is, it depends on the molar ratio of surfactant to polyion unit (n_s/n_p).^{7,25,29,35} A desired aggregation behavior can thus be obtained by controlling the ratio n_s/n_p . These mixed systems often go through a series of complicated association processes as n_s/n_p increases: the formation of PES complexes, their aggregation, precipitation,

and redissolution, the micellization of free surfactants. These events are accompanied by the variation of physicochemical properties (e.g., rheological and thermodynamic). Therefore it is very important for the understanding of mixed systems to investigate the dependence of their solution behavior on n_s/n_p .

HMPEs are usually based on the introduction of ionic and hydrophobic moieties on environmentally friendly nonionic polymer or polyelectrolyte precursors. The mixed systems based on polysaccharides with ionized pendant groups have attracted much attention due to their hydrophilicity, biodegradability, and antibacterial properties.^{7,13,17,18,22,36–38} These types of HMPEs present a very interesting solution behavior when mixed with oppositely charged surfactants. Thus, the understanding of the interactions of this special group of polyelectrolytes with oppositely charged surfactants has particular importance. We have synthesized a series of new hydrophobically modified cationic polysaccharides (Figure 1), where the pendant *N*-(2-hydroxypropyl)-*N,N*-dimethyl-*N*-alkylammonium chloride groups are randomly distributed along the dextran backbone. The self-assembly of these new HMPEs has been studied by fluorescent and viscosity techniques.³⁹ Further, the thermodynamic characterization of the interactions between one of them (D40Oct30) and sodium alkyl sulfates (SC_nS , $n = 8, 12$, and 14) was made by isothermal titration calorimetry (ITC), combined with UV–vis spectrophotometry, conductivity, and kinematic viscosity measurements.^{40,41}

In this work, we report a systematic thermodynamic study of the self-assembling of some hydrophobically modified cationic polysaccharides and their mixtures with oppositely charged surfactants in aqueous solution. Our first studies are now extended to three other polymers of the same series as the previous one (D40Oct30), hereby denoted as D40Dod30, D40Cet15, and D465Oct30. We used high-sensitivity ITC,

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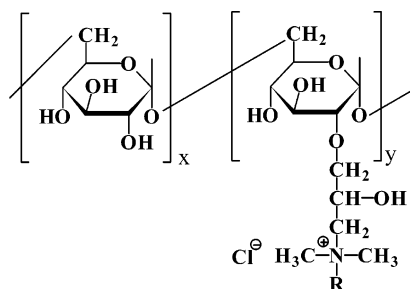


Figure 1. Chemical structure of cationic polyelectrolytes obtained by chemical modification of dextran: R = C_nH_{2n+1}⁺, referred to as Oct (*n* = 8), Dod (*n* = 12), and Cet (*n* = 16). DS = 100*y*/(*x* + *y*).

TABLE 1: Information about the Studied Cationic Polyelectrolytes

polymers	D40Oct30	D40Dod30	D40Cet15	D465Oct30
<i>M</i> _w ^a	57350	62675	53412	680278
DS ^b	28	30	15	30
<i>N</i> ^c	69	74	37	861

^a Molecular weight calculated by adding the weight of pendant groups to the molecular weight of unmodified dextran. ^b Degree of substitution for hydrophobic modification, DS = 100*y*/(*x* + *y*). The estimated error is ±2–3 mol %. ^c Number of positive charges per mol polymer chain.

combined with turbidity measurements. Recently published papers dealing with the thermodynamics of interactions between polyelectrolyte and surfactant have shown that ITC has distinct advantages over other experimental techniques as both the energetic information and accurate critical concentrations for the interactions in PES systems are derived simultaneously from a single calorimetric titration run.^{28,40–45} Our aim is to analyze the effect of changing the alkyl chain length of the polyelectrolyte pendant groups, the molecular weight of dextran backbone, and the system temperature on the interactions and thus to reveal the complex patterns displayed by these systems. We have performed detailed experiments and will put forward reasonable explanations for the new results and very interesting phenomena found in these mixed systems.

Experimental Methods

Materials. Synthesis of the studied polyelectrolytes has been done according to previously described methods.^{39,40} They were synthesized by the chemical modification for two dextran samples: D40 (Sicomed S. A. Bucharest) with *M*_w = 40 000 and *M*_w/*M*_n = 1.12 and D465 (Sigma) with *M*_w = 465 000. As shown in Figure 1, the hydrophobically modified cationic polysaccharides have pendant quaternary ammonium groups, where the DS (degree of substitution) is the content in pendant groups, calculated as 100[*y*/(*x* + *y*)] mol %. The code of the polymer (DMRX) indicates the weight-averaged molecular weight of the unmodified dextran (*M*, in kDa), the length of the substituent R (according to Figure 1), and the degree of substitution (*X*). The main characteristics of the polymers are included in Table 1.

The surfactants, sodium octyl sulfate (SOS) (MERCK, 99%), sodium dodecyl sulfate (SDS) (SIGMA, 99%), dodecyltrimethylammonium chloride (DTAC) (TCI, >98%) and cetyltrimethylammonium chloride (CTAC) (Fluka, >98%) were used without further purification. All the solutions were prepared using water produced by a Milli-Q filtration system, either by weight or by volume, and were stabilized at room temperature for two days before use.

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.⁴⁰ Briefly, the volume of polymer solution or water in the calorimetric vessel was 2.6 mL. The titrating solution was added to the vessel automatically, in aliquots of 4–8 μL, from a modified gastight Hamilton syringe, through a thin stainless steel capillary, until the desired range of concentration had been covered. A special Kel-F turbine, made at Lund University workshop (Sweden), was used throughout, as it proved to promote very good mixing. This is a very important experimental detail, as in parts of the titration curve there is a two-phase system. All experiments were performed at 308.15 and 298.15 (±0.01) K.

Turbidity Measurements. Parallel turbidity measurements with the same polymer/surfactant solutions used for ITC were performed on an 845x UV–vis spectrophotometer, at a wavelength of 400 nm in a quartz sample cell with a light path of 10 mm, thermostated at 308.15 and 298.15 K with a water bath (Julabo, F25-HP). The measured values of turbidity were corrected with the polymer-free blank.

Results and Discussion

Part I. Thermodynamic Characterization of Self-Assembling of the Studied Amphiphilic Polyelectrolytes. Thermodynamics of surfactant solutions provides the basis for understanding and predicting the solution behavior of amphiphilic polyelectrolytes. In this study, two cationic surfactants (DTAC and CTAC) that closely resemble the hydrophobic pendant groups of the studied amphiphilic polyelectrolytes were used to carry out an interesting comparison between the solution behavior of amphiphilic polyelectrolytes and surfactants. The provided information can give good insight into the analysis of the micellization process of amphiphilic polyelectrolytes in aqueous solution.

Micellization of Alkyltrimethylammonium Chloride (C_n-TAC) in Aqueous Solution. Microcalorimetric measurements have been made on cationic surfactants, DTAC and CTAC, at two different temperatures (298.15 and 308.15 K). The calorimetric curves of change of the observed enthalpies of dilution (Δ*H*_{obs}) with the surfactant concentration are shown in Figure 2. The critical micelle concentrations (cmc's), the enthalpies of micellization (Δ*H*_{mic}) at 298.15 and 308.15 K as well as the heat capacity of micellization (Δ*C*_{p,mic}) for the two surfactants are summarized in Table 2. The cmc values for DTAC and CTAC available from the literature, mainly from noncalorimetric methods,^{46–48} are in good agreement with our values (the cmc's obtained from fluorescence by Roelants et al.⁴⁶ are 17 mM for DTAC and 1.3 mM for CTAC, and the cmc's obtained from fluorescence by Asakawa et al.⁴⁷ are 24.4 mM for DTAC and 1.31 mM for CTAC). The values of both cmc and Δ*H*_{mic} at 298.15 and 308.15 K are in good agreement with those obtained from calorimetric methods by Wang et al.⁴⁹ their values for CTAC are cmc = 1.25 mM and Δ*H*_{mic} = −1.7 kJ/mol at 298.15 K and −8.2 kJ/mol at 308.15 K. For DTAC, the agreement with the value obtained by Różycka-Roszak et al.^{50,51} from calorimetry is only fair, with Δ*H*_{mic} = 2.7 kJ/mol at 298.15 K.

As seen in Table 2, the cmc values of the cationic surfactants decrease as expected with increasing alkyl chain length (*n*). The magnitude of exothermic Δ*H*_{mic} at 308.15 K increases with increasing *n*, and the values of Δ*H*_{mic} at 298.15 K change with *n* from a positive to a negative value. Thus, for DTAC, the entropy is the driving force for micellization at 298.15 K. As the temperature increases, an increasingly negative enthalpy will

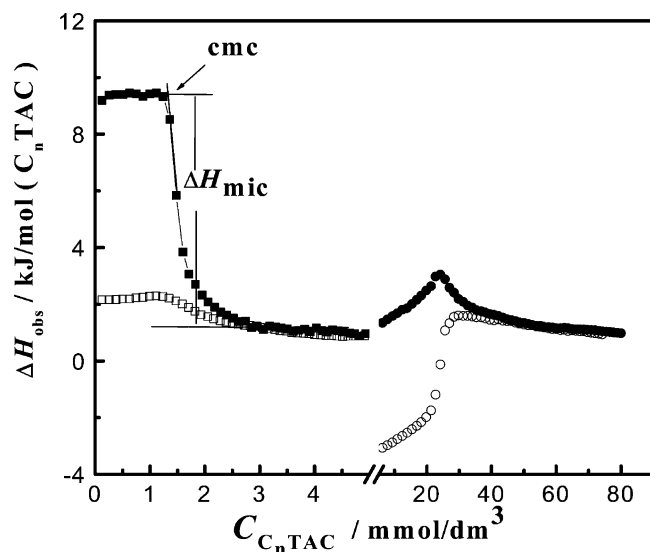


Figure 2. Microcalorimetric titration curves for dilution of 0.04 M CTAC (■□) and 0.5 M DTAC (●○) into water, where the solid symbols refer to the measurement at 308.15 K and the hollow symbols to 298.15 K.

TABLE 2: Enthalpies of Micellization (ΔH_{mic}) and Critical Micelle Concentrations (cmc's) for the Studied Amphiphiles at 298.15 and 308.15 K

amphiphilic compounds	cmc ^a (mmol/dm ³)		ΔH_{mic} ^b (kJ/mol)		$\Delta C_{p,\text{mic}}$ ^b (J/(K mol))
	298.15 K	308.15 K	298.15 K	308.15 K	
C ₁₂ TAC ^c	22.2	24.2	3.33	-1.60	-493
C ₁₆ TAC ^c	1.26	1.26	-1.50	-8.10	-660
D40Oct30 ^d	0.07	0.07 ^e	1.3	0.8 ^e	-47
D465Oct30 ^d		0.07		0.9	
D40Dod30 ^d	0.01 ^f		-0.8	-1.3	-52
D40Cet15 ^d	0.007 ^f		-4.1	-5.7	-157

^a For amphiphilic polyelectrolytes, the cmc's were expressed in terms of the concentration of their side chains. ^b The ΔH_{mic} and $\Delta C_{p,\text{mic}}$ values of polymers are expressed in kJ/mol of side group and J/(K mol) of side group, respectively. ^c The estimated error for surfactants' cmc and ΔH_{mic} is less than 2%. ^d The estimated error for polymers' cmc is 4% and for ΔH_{mic} is 15%. ^e From our previous work⁴⁰ (the cmc is 0.006 g/dL if expressed as polymer concentration). ^f From fluorescent measurements,³⁹ where both D40Dod30 and D40Cet15 have the same cmc if expressed as polymer concentration, 0.001 g/dL.

also play a role. The change in $\Delta C_{p,\text{mic}}$ is calculated as

$$\Delta C_{p,\text{mic}} = [\Delta H_{\text{mic}}(308.15 \text{ K}) - \Delta H_{\text{mic}}(298.15 \text{ K})]/\Delta T$$

by assuming a linear dependence of ΔH_{mic} on temperature in this small interval. The difference in $\Delta C_{p,\text{mic}}$ between DTAC and CTAC can be attributed to their different alkyl chain lengths. The heat capacity change per CH₂ group for the transfer of an alkyl chain from an aqueous to a hydrocarbon environment can be estimated from our results to be about -42 J/(K mol). This value is in good agreement with the CH₂ increment derived by Gill and Wadsö⁵² for the transfer of a CH₂ group from water to a pure organic media, -49.2 J/(K mol). The results of DTAC and CTAC are typical for the micellization of single chain surfactants. They are similar to the pattern of variation of ΔH_{mic} with the number (*n*) of CH₂ group found for the alkyltrimethylammonium bromide series (C_{*n*}TAB). Bashford et al.⁵³ and Mosquera et al.⁵⁴ found that ΔH_{mic} values were positive for *n* ≤ 10 at low temperature (*T* ≤ 298.15 K) and changed linearly from a small positive value to a negative value with increasing *n*. Bashford et al.⁵³ also obtained negative $\Delta C_{p,\text{mic}}$ values for

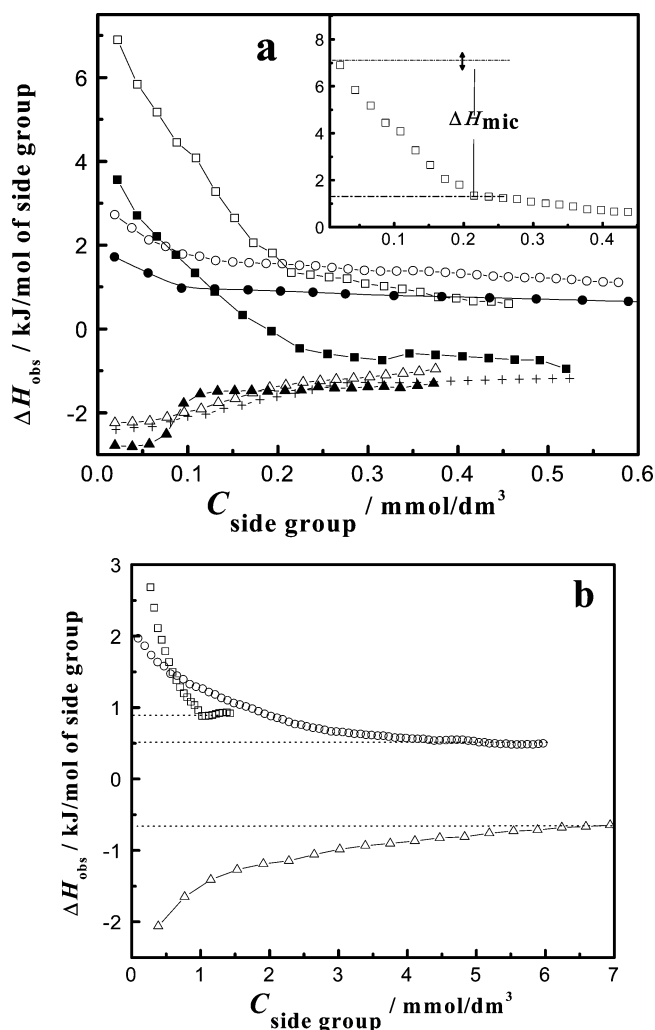


Figure 3. Microcalorimetric titration curves for dilution of concentrated polymer solutions (1.0% and 5.0%) into water. (a) The polymer concentration in the syringe is 1.0%: curve (+) is for D465Oct30 at *T* = 308.15 K; (▲) D40Oct30, (●) D40Dod30, and (■) D40Cet15 at *T* = 298.15 K (solid symbols) and 308.15 K (hollow symbols). The inserted plot shows how we determined ΔH_{mic} for D40Cet15 and D40Dod30, where the vertical double-headed arrow denotes an estimated error for the extrapolation. (b) The polymer concentration in the syringe is 5.0% for D40Cet15 (□) and D40Dod30 (○) at 308.15 K and 10 (w/v)% for D40Oct30 (Δ) at 308.15 K.⁴⁰

C_{*n*}TAB, which increased in absolute magnitude with increasing *n* but the increase *per* CH₂ group decreased slightly as *n* increased. Their value for the CH₂ increment can be obtained by taking the slope of $\Delta C_{p,\text{mic}}$ as a function of *n*: the obtained value is -45 J/(K mol) (for the range C₁₀ to C₁₆), in very good agreement with our value for the same increment.

Self-Aggregation of Amphiphilic Polyelectrolytes in Aqueous Solution. The molecular structure of our polymers, as shown in Figure 1, is similar to a polysurfactant connected by hydrophilic spacers at the level of the headgroups. Therefore, the hydrophobic tails can self-assemble to form micellelike clusters or hydrophobic microdomains at very low concentration. As explained in our previous work,⁴⁰ two kinds of aggregate morphologies can be inferred from the dilution patterns of D40Oct30—intramolecular micellelike clusters and intermolecular cross-linking clusters, depending on the polymer concentration. The previous work is now extended to the thermodynamic properties of other polymers with different chain lengths in the hydrophobic pendant groups as well as for different molecular weights of the dextran backbone. Figure 3

shows microcalorimetric titration curves for the dilution of concentrated polymer solutions (1.0% or 5.0%) into water. The polymers have octyl, dodecyl, and cetyl chains. In this graph, the observed enthalpies (ΔH_{obs}) for each injection are plotted against the concentrations of polyelectrolyte side groups ($C_{\text{side group}}$) in the calorimetric vessel, for an easy comparison with the corresponding cationic surfactant. The calculation of ΔH_{mic} of these amphiphilic polyelectrolytes is made in accordance with Raju et al.⁵⁵ and our previous study on D40Oct30 micellization.⁴⁰ The curves of ΔH_{obs} as a function of $C_{\text{side group}}$ for D465Oct30 and D40Oct30 in Figure 3a at 298.15 or 308.15 K have an obvious break that corresponds to the micellization process, allowing a determination of the cmc and ΔH_{mic} . For D40Dod30 and D40Cet15, on the other hand, we cannot detect their cmc's by calorimetry, due to the sensitivity limit of our instrument. We can only identify the concentrations at the end of the micellization process ($C_{\text{side group}} = 0.12$ mM for D40Dod30 and $C_{\text{side group}} = 0.21$ mM for D40Cet15). We have to mention that pyrene fluorescence intensity ratio (I_3/I_1) variation with polymer concentration gave two critical values for the aggregation of these polymers, one as the start of the aggregation process, called cac_1 , and the second as the end of pyrene fluorescence change, called cac_2 .³⁹ The values of cac_2 so obtained (namely, 0.13 mM for D40Dod30 and 0.15 mM for D40Cet15) are in good agreement with the values referred to above for the concentrations at the end of the micellization process as obtained here by ITC. Therefore, the cmc's for D40Dod30 and D40Cet15 are taken here as the cac_1 values obtained from fluorescence measurements.³⁹ Both D40Dod30 and D40Cet15 have the same cmc when expressed in terms of polymer concentration, but they are quite different when expressed in terms of polyelectrolyte side chain concentration, namely, $C_{\text{side group}} = 0.01$ mM for D40Dod30 and $C_{\text{side group}} = 0.007$ mM for D40Cet15. From these values, we can calculate approximately the ΔH_{mic} values for D40Dod30 and D40Cet15, where the observed enthalpy values corresponding to the cmc are estimated by extrapolating their respective enthalpy curves to the cmc obtained by fluorescence, as shown in the insert plot of Figure 3a. Although the enthalpy of micellization thus obtained has a larger uncertainty, it is useful for comparison purposes. All the results for the studied amphiphilic polyelectrolytes are listed in Table 2.

D465Oct30 and D40Oct30 have the same pendant groups and the same degree of hydrophobic modification; they only differ in the molecular weight of the dextran backbone. It is clearly observed that the dilution curves of D465Oct30 and D40Oct30 are superimposable at 308.15 K (Figure 3a). This implies that when the DS is kept constant, changing dramatically the length of the dextran backbone (i.e., changing the number of monomers of dextran from 247 to 2870) has no significant effect on the dilution processes. However, for the polymers based on dextran of the same M_w , when the alkyl side chain length (n) of the pendant groups changes from $n = 8$ to $n = 12$ or 16, the dilution processes change very significantly—the values of ΔH_{obs} are exothermic for D40Oct30 and become endothermic for D40Dod30 and D40Cet15 at the same temperature, indicating that their respective ΔH_{mic} values should have opposite signs. A similar trend was observed with the corresponding cationic surfactants, $C_n\text{TAC}$ or $C_n\text{TAB}$.^{53,54} Therefore, in this temperature range, the positive ΔH_{mic} value for D40Oct30 indicates that the micellization process is entropy driven, whereas for D40Dod30 and D40Cet15 the micellization is also favored by an increasingly negative enthalpy with increasing n . Correspondingly, their cmc's decrease with increasing n , due to the strengthening of

hydrophobic interactions between intra- or intermolecular alkyl chains. Further, the cmc's are several orders of magnitude lower than the ones of the corresponding cationic surfactants. The differences in ΔH_{mic} and cmc between the studied amphiphilic polyelectrolytes and the related cationic surfactants are attributed to the restriction that the hydrophilic dextran backbone (with moderate flexibility) imposes on the position of alkyl side chains, leading to various interactions being different from those in surfactant systems—the van der Waals interaction between the chains, charged group repulsion, hydrophobic interaction between the alkyl side chains, and the energy of the conformational change. A subtle thermodynamic balance between the various interaction factors controls the magnitude and sign of ΔH_{mic} . For the studied polyelectrolytes, the interaction that favors micelle formation, mainly the hydrophobic interaction, can overcome the electrostatic repulsive interaction and the energy necessary to distort the polymer backbone, resulting in the formation of small and stable micellelike clusters. It is worth noting that the concentration range of micellization for D40Cet15 is larger than that of D40Dod30. The DS of D40Cet15 is half the one of D40Dod30, which means that the distances between alkyl side chains are larger in D40Cet15 than those in D40Dod30. Therefore, the net interactions between intramolecular alkyl chains are less likely for the former polymer, due to lower coverage, whereas the intermolecular interactions are stronger due to its longer alkyl side chains.

Another interesting comparison can be made between D40Oct30 and D40Cet15. The DS of D40Cet15 is half that of D40Oct30, but the length of its alkyl side chain is twice that of D40Oct30. As a result, its cmc is 10 times lower than that of D40Oct30. The ΔH_{mic} is exothermic for D40Cet15 but is endothermic for D40Oct30. As analyzed above, the sign of ΔH_{mic} should be the result of the balance between various inter- or intramolecular interactions, both attractive and repulsive. We can therefore conclude that the effective hydrophobicity that results from increasing the length of the alkyl side chain has a larger impact than that of increasing the DS. From D40Cet15 to D40Oct30, the charged group repulsion increases, whereas the attraction between the side chains decreases.

The temperature, on the other hand, has an important effect on the dilution processes of the studied polyelectrolytes. From Figure 3a, where a comparison can be found between the dilution curves at two different temperatures, it is apparent that the magnitude of ΔH_{obs} increases with increasing temperature in the studied concentration range, indicating that the hydrophobic interactions become weaker with increasing temperature.⁵⁶ The difference in ΔH_{mic} values at two different temperatures allows us to roughly estimate the change in heat capacity of micellization ($\Delta C_{p,\text{mic}}$). $\Delta C_{p,\text{mic}}$ values were obtained for the three polymers (D40Oct30, D40Dod30, and D40Cet15) assuming a linear dependence of ΔH_{mic} on temperature for this small temperature interval. It is known that, for surfactant systems, $\Delta C_{p,\text{mic}}$ is a useful thermodynamic function for the understanding of the micellization process. Therefore, analyzing the behavior of $\Delta C_{p,\text{mic}}$ should also be of great value for amphiphilic polyelectrolytes. Even though we have large uncertainties, as we only did determinations at two temperatures, some interesting points can be raised. The difference (-5 J/(K mol) of side group) in $\Delta C_{p,\text{mic}}$ between D40Dod30 and D40Oct30 is too small (within the experimental error) to allow any comparison, but the difference in $\Delta C_{p,\text{mic}}$ between D40Cet15 and D40Dod30 is large, -105 J/(K mol) of side group. The increment in $\Delta C_{p,\text{mic}}$ per CH_2 group can be roughly estimated to be about -26 J/(K mol) of side group, which is lower than the increment we found

for the cationic surfactant's case (-42 J/(K mol)), as mentioned above. The factors affecting the heat capacity change for micellization in the polyelectrolyte system are very complex, but such a difference can be tentatively rationalized in terms of a difference in their molecular structures. The alkyl side chains are fixed by the hydrophilic dextran backbone, and therefore, as the temperature increases, the observed changes in interaction energies as compared to the surfactant's micellization are smaller. As has been proposed before,⁵⁶ $\Delta C_{p,\text{mic}}$ values reflect hydration/dehydration of alkyl chains. Therefore, our estimates suggest a more open structure for the alkyl chains in the aggregates formed by pendant groups (more hydrated) as compared to those of normal surfactants. Further, our previous fluorescence measurements³⁹ have shown that the variation of pyrene emission intensity ratio, I_3/I_1 (a parameter related to the polarity of the aggregates), depends on the length of the alkyl chain and DS, and increases from 0.6 (D40Oct30) to 0.76 (D40Cet30), showing a similar polarity of the aggregates to that of the corresponding surfactants $C_n\text{TAC}$, which also decreases as the alkyl chain length increases. For amphiphilic polyelectrolyte systems, there have been so far few comparable measurements at different temperatures and little or no interpretation of the data has been provided. As far as direct calorimetry studies are concerned, the scarcity of data is at least in part due to their quite low cmc's and consequent difficulty in determining ΔH_{mic} .

It should be stressed that in the case of HMPEs, contrary to surfactant systems where the increase in concentration determines mainly the increase in micelle number, the variation in polymer concentration can have different effects on its self-assembly. At low polymer concentration, intramolecular hydrophobic interactions lead to a 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. The pattern of the dilution enthalpy curves that we found supports the occurrence of such a gradual cross-linking process in the high concentration range.⁴⁰ The dilution enthalpy curves for D40Dod30, D40Cet15, and D40Oct30 in the high concentration region are shown in Figure 3b. The three polyelectrolytes show basically the same trend, with the change in ΔH_{obs} (absolute value) with concentration slowly decreasing and eventually approaching a constant ΔH_{obs} value—for D40Oct30, above 6.1 mM ($C_{\text{polymer}} = 0.5\%$), for D40Dod30, above 4.4 mM ($C_{\text{polymer}} = 0.37\%$), and for D40Cet15, above 1.0 mM ($C_{\text{polymer}} = 0.15\%$). This behavior can be ascribed to the difference in alkyl side chain length, that is, the longer the alkyl chains, the lower the concentration at which stable cross-linking structures can form and the more clear the observed break. It is worth mentioning that the fluorescence and viscosity measurements performed with the same polymers revealed the presence of weak intermolecular aggregation (cross-linking) in the case of D40Oct30. No evidence for such interactions was found in the case of D40Dod30 and D40Cet15, perhaps due to the predominance of intramolecular processes in these cases.³⁹ These results could be assigned to the lack of sensibility of the above-mentioned methods to the intimate aggregation processes, showing that ITC could be a more useful technique in the discrimination between these two types of interactions.

Part II. Interactions of the Series of Amphiphilic Polyelectrolytes with Oppositely Charged Surfactants. In general, a series of association processes between polyelectrolyte and oppositely charged surfactant take place when they are brought to contact, namely, the formation, precipitation, and redissolution

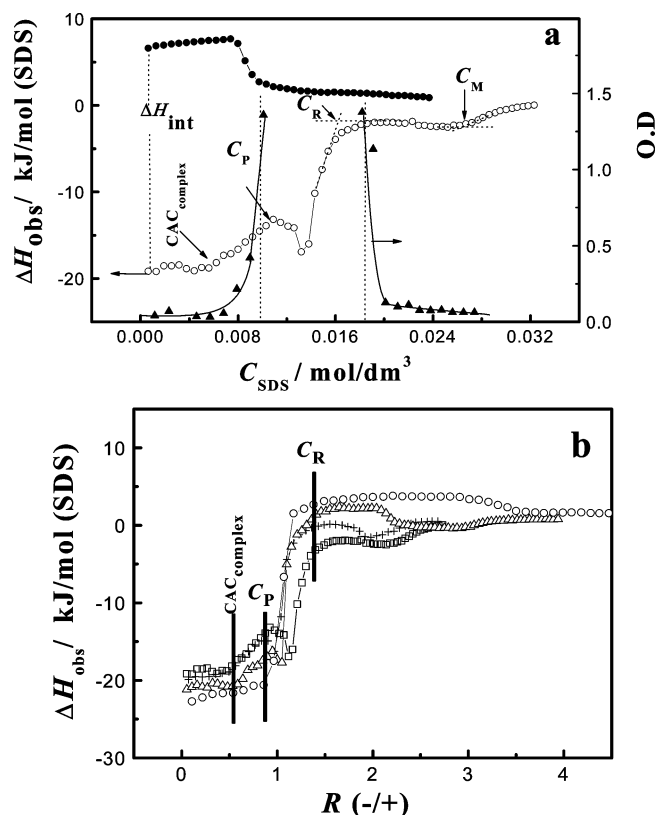


Figure 4. Microcalorimetric titration curves for D40Dod30/SDS systems at $T = 308.15 \text{ K}$. (a) Curve (\circ) is the observed enthalpy curve (ΔH_{obs} vs C_{SDS}) for the D40Dod30(1.0%)/SDS, curve (\blacktriangle) is the corresponding turbidity curve (optical dispersion, $\lambda = 400 \text{ nm}$, $T = 308.15 \text{ K}$), and curve (\bullet) is for the dilution of the concentrated SDS solution (0.2 mol/dm^3) into water. (b) Variation of the observed enthalpies with charge ratios $R(-/+)$ for these systems at different D40Dod30 concentrations: (\square) 1.0%, ($+$) 0.75%, (Δ) 0.5%, and (\circ) 0.25%.

of the PES complexes. These events occur at different charge ratios, $R(-/+)$. The association mechanism depends to a great extent on the molecular structure of polyelectrolyte and surfactant. For D40Oct30/sodium alkyl sulfates (SOS, SDS, or STS) systems, the thermodynamic characterization and phase behaviors have been reported in our previous work.⁴¹ This provided us with information that allowed the choice of the best surfactant for the present study. The system D40Oct30/SOS exhibits a large insolubility region due to the large cmc value of SOS ($\text{cmc} = 138 \text{ mmol/dm}^3$); whereas D40Oct30/STS exhibits a narrow precipitation region, but a large increase in viscosity after redissolution, leading to the difficulties for the calorimetric measurements. Therefore, we chose SDS as the surfactant for the present study with the series of polyelectrolytes with different side chain lengths and different molecular weights of dextran backbone. Besides these systems, we have also made a few measurements with D40Dod30 (0.25%)/SOS, to get a cross comparison with the previously studied D40Oct30/SOS or D40Oct30/SDS.

Evaluation on Phase Behaviors for the Studied Mixed Systems. Figures 4 and 5 show the results for the mixed systems of SDS and the polyelectrolytes having dodecyl or cetyl pendant side chains. Two typical examples are shown, with the observed enthalpy and OD curves plotted as a function of C_{SDS} for the D40Dod30/SDS and D40Cet15/SDS systems (Figures 4a and 5a) and in Figures 4b and 5b, the observed enthalpy curves at different polymer concentrations are plotted as a function of the charge ratio of SDS to polyelectrolyte, $R(-/+)$. By plotting

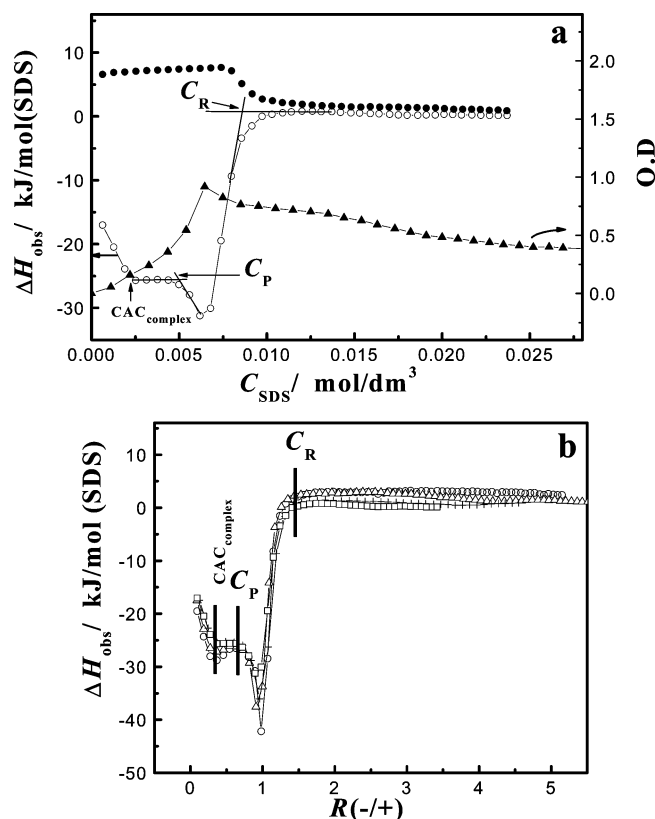


Figure 5. Microcalorimetric titration curves for D40Cet15/SDS systems at 308.15 K. (a) Curve (○) is the observed enthalpy curve (ΔH_{obs} vs C_{SDS}) for D40Cet15 (1.0%)/SDS, curve (▲) is the corresponding turbidity curve (optical dispersion, $\lambda = 400$ nm, $T = 308.15$ K), and curve (●) is for the dilution of the concentrated SDS solution (0.2 mol/dm³) into water. (b) Variation of the observed enthalpies with charge ratios, $R(-/+)$ for these systems at different D40Cet15 concentrations: (□) 1.0%; (+) 0.75%; (Δ) 0.5%, and (○) 0.25%.

ΔH_{obs} vs $R(-/+)$, a reasonable comparison can be made between different mixed systems and, hence, extract the common factors as well as the differences in the various association processes. All these mixed systems go through a series of morphological changes, like polymer side-chain-rich clusters, cross-linking mixed aggregates, precipitation, redissolution, and SDS-rich mixed micelles and free micelles. Critical concentrations or phase boundaries related to the aggregation of the polyelectrolyte–SDS complex ($\text{CAC}_{\text{complex}}$), onset of precipitation (C_P), and redissolution (C_R) can all be identified from ITC titration curves combined with turbidity measurements (Figures 4a and 5a). It is found that the charge ratios at $\text{CAC}_{\text{complex}}$ (for D40Oct30/SDS, $R(-/+) = 0.8$,⁴¹ for D40Dod30/SDS, $R(-/+) = 0.6$, and for D40Cet15/SDS, $R(-/+) = 0.4$) decrease with an increasing length of grafted alkyl chain, similarly to the corresponding variation of cmc's of cationic surfactants with the alkyl chain length. At C_P , the hydration of the headgroups in ion pairs composed of a surfactant molecule and a cationic surfactant-like side chain of the polymer decreases significantly due to charge neutralization and the coacervate morphology (precipitation) starts to form. The exact positions of the points corresponding to maximum precipitate formation (negative minima between C_P and C_R) are subject to large uncertainties and present low reproducibility between different repetitions. Charge ratios at C_P and C_R are almost independent of the grafted alkyl chain length (the obtained mean charge ratios were $R(-/+) = 0.9$ at C_P and $R(-/+) = 1.3$ at C_R). After C_R , cross-linking mixed micelles with net negative charges do form and enlarge gradually upon further insertion of SDS molecules,

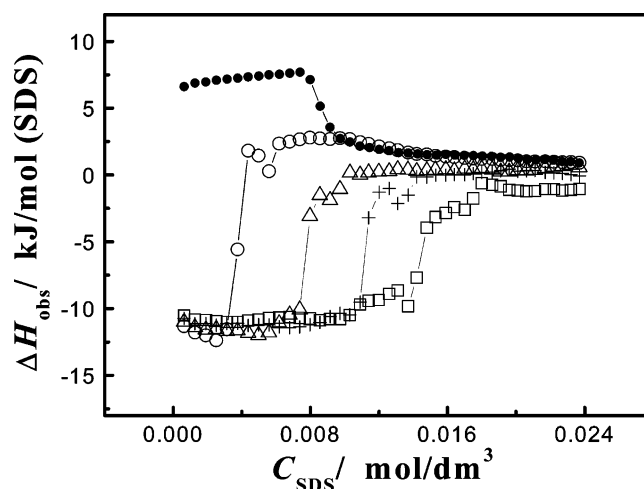
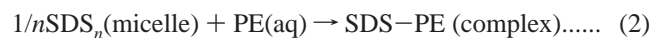
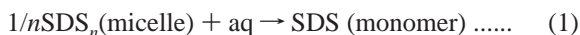


Figure 6. Variation of the observed enthalpies with surfactant concentration for D465Oct30/SDS systems at $T = 308.15$ K. D465Oct30 concentrations are (□) 1.0%, (+) 0.75%, (Δ) 0.5%, and (○) 0.25%; the initial SDS concentration in the syringe is always 0.2 mol/dm³. Curve (●) is for the dilution of the concentrated SDS solution into water.

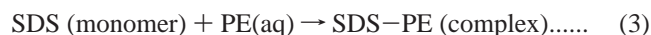
with increasing SDS concentration. C_M (Figure 4a) can be viewed as the cmc of SDS in the presence of a polymer, where SDS micelles are built around the charged sites of the backbone.⁴¹ For D40Dod30/SDS, the charge ratios at C_M seem to decrease as the polymer concentration increases, when analyzed as a function of $R(-/+)$. On the other hand, it is clearly observed from plots of ΔH_{obs} as a function of total SDS concentration (not shown) that C_M increases with increasing polymer concentration, presenting a value higher than the pure surfactant's cmc (7.78 mmol/dm³).⁴¹ The difference between C_M and cmc increases with an increase in polymer concentration –1.1, 1.5, 2.3, and 3.3 times cmc for the polymer concentrations 0.25, 0.5, 0.75, and 1.0%, respectively. Therefore, we can say that $\text{CAC}_{\text{complex}}$, C_P , and C_R are correctly and more clearly compared as a function of $R(-/+)$, whereas C_M depends on free SDS concentration. For D40Cet15/SDS, we cannot detect any break in the titration curve after C_R that would allow the determination of C_M . The system keeps a semitransparent appearance of bluish color, which usually corresponds to the presence of large aggregates, without any precipitation in a large concentration range (Figure 5a). This could mean that the longer cetyl side chains and SDS self-aggregate to form large SDS-rich mixed micelles or even vesicles.

Comparing the microcalorimetric results of D465Oct30 (Figure 6) and D40Oct30⁴⁰ having the same DS, we could see that the calorimetric curve shapes and phase boundaries of the two systems are almost the same. This means that the dextran molecular weight does not affect significantly the thermodynamics of the interaction with SDS and the phase behavior. This conclusion is in agreement with published results for other oppositely charged polyelectrolyte/surfactant mixed systems.^{18,32,33}

Interaction Enthalpies in the Studied Mixed Systems. As described in the previous section, all curves present a similar pattern for the observed enthalpy change. Before $\text{CAC}_{\text{complex}}$, ΔH_{obs} deviates largely from the dilution curve of the surfactant in the absence of polyelectrolyte, showing a pronounced exothermic effect, and after C_R , they gradually approach it. Therefore differences between the observed enthalpy curves with and without polyelectrolytes are ascribed to SDS–polyelectrolyte interactions. We can derive the interaction enthalpies (ΔH_{int}) in the initial stage of the titration for the process from the eqs



where reaction 1 corresponds to the dilution of SDS into water, including the enthalpy of dilution of concentrated SDS solution and the enthalpy of demicellization ($\Delta H_{\text{obs}}(1)$), and reaction 2 corresponds to the total process—dilution of SDS into polymer solution, including not only the energies pertaining to reaction 1 but also the enthalpy of formation of the SDS–polyelectrolyte complex ($\Delta H_{\text{obs}}(2)$). By subtracting the two equations, we obtain



Thus, from the differences in observed enthalpy values with and without polyelectrolytes, the interaction enthalpies (ΔH_{int}) of SDS with polyelectrolyte can be calculated as

$$\Delta H_{\text{int}} = \Delta H_{\text{obs}}(2) - \Delta H_{\text{obs}}(1)$$

This is depicted in Figure 4a. Defined and calculated in this way, ΔH_{int} reflects the net interaction between SDS and the polyelectrolyte in the initial stage of the titration.

Calorimetric results from the SDS/dextran system show that there is no interaction between SDS and the dextran backbone, as we observed no difference between the two enthalpy dilution curves for the titration of concentrated SDS into water or into the dextran solution (results not shown). This suggests that SDS interacts only with the cationic surfactant attached to the dextran backbone as side chains but not with the backbone itself. The segments grafted have almost the same chemical structure (hydrophilic head and hydrophobic tail) as the cationic surfactants also reported here. Therefore, any difference between the interaction enthalpies for the polyelectrolytes/SDS systems must arise from the interactions of the alkyl side chains of polyelectrolyte with SDS or from morphological changes of the polyelectrolyte induced by the surfactant. For the systems with D40Oct30 and D40Dod30, the observed exothermic enthalpies remain almost constant for charge ratios before $\text{CAC}_{\text{complex}}$, which allows us to estimate the interaction enthalpies—for example, at 308.15 K, $\Delta H_{\text{int}}(\text{D40Oct30/SDS}) = -17.1$ kJ/mol of side group and $\Delta H_{\text{int}}(\text{D40Dod30/SDS}) = -25.8$ kJ/mol of side group (Table 3). This difference in ΔH_{int} is believed to reflect the effect of the alkyl side chain length, the mean exothermic magnitude of ΔH_{int} increasing about 2.2 kJ/mol per CH_2 group, suggesting that the longer the alkyl side chains the stronger the hydrophobic interaction with SDS. When we studied the effect of increasing the alkyl chain length of anionic surfactants, we found a similar effect with D40Oct30/STS or SDS:⁴¹ the value of ΔH_{int} for D40Oct30/STS at 308.15 K can be estimated to be about -21.9 kJ/mol, thus ΔH_{int} increases by about 2.4 kJ/mol for each CH_2 group of the surfactant alkyl chain.

Figure 7 shows that the observed enthalpy curve of the D40Dod30/SOS system exhibits a similar trend to D40Oct30/SOS.⁴¹ Both systems have a wide two-phase region, which means that, in the studied concentration range, the precipitate does not dissolve after C_S , where all charged sites of the polymer are saturated with SOS molecules. The charge ratios at critical concentrations (C_P and C_S) are independent of the alkyl side chain length of the polymer. However, there is a large difference in the exothermic magnitude of ΔH_{int} in the starting stage of the titration; if we calculate ΔH_{int} from the first injection at 308.15 K, $\Delta H_{\text{int}}(\text{D40Oct30/SOS}) = -5.1$ kJ/mol of side group

TABLE 3: Enthalpies (ΔH_{int}) and Heat Capacity ($\Delta C_{p,\text{int}}$) of Interaction between the Studied Amphiphiles and SDS at $T = 298.15$ K and $T = 308.15$ K

systems $C_{\text{polymer}} = 1.0\%$	ΔH_{int}^a (kJ/mol of side group)		$\Delta C_{p,\text{int}}$ (J/(K mol) of side group)
	298.15 K	308.15 K	
D40Oct30+SDS	−7.2	−17.1	−990
D40Dod30+SDS	−16.0	−25.8	−980
D40Cet15+SDS	−16.5 ^b	−23.6 ^b	−710 ^b
	−21.6 ^c	−32.7 ^c	−1110 ^c

^a The estimated error for ΔH_{int} is 4%. ^b Calculation based on the first injection. ^c Calculation based on the fourth injection.

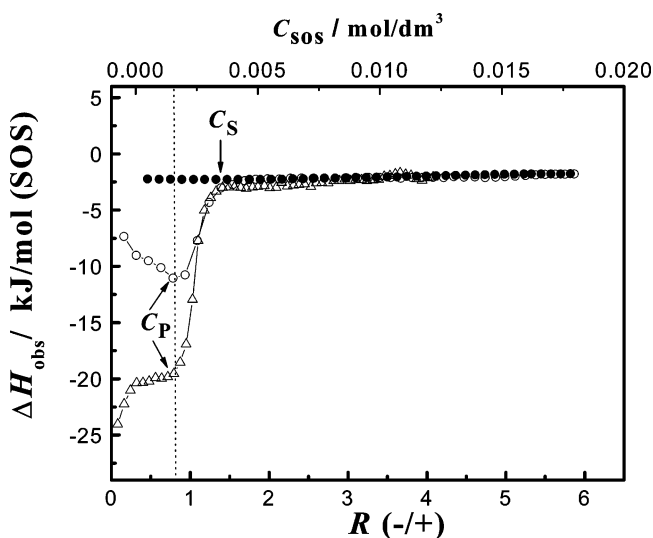


Figure 7. Variation of the observed enthalpies with charge ratios—a comparison between D40Dod30 (0.25%)/SOS (Δ) and D40Oct30 (0.25%)/SOS (\circ)⁴¹ at $T = 308.15$ K. Curve (\bullet) is for the dilution of the concentrated SOS solution (0.3 mol/dm³) into water.

but $\Delta H_{\text{int}}(\text{D40Dod30/SOS}) = -21.8$ kJ/mol of side group. The larger negative values for D40Dod30/SOS can be rationalized as the result of an enhanced hydrophobic interaction due to longer alkyl side chains in D40Dod30. An interesting comparison can also be made between the interaction enthalpies of D40Oct30/SDS (-17.1 kJ/mol of side group) and D40Dod30/SOS (-21.8 kJ/mol of side group), where we are cross-comparing the different changes in the alkyl chain either in the polymer or in the surfactant. Before cnc, the clusters of the former consist of rich-octyl side chains, while the latter consist of rich-dodecyl side chains. Therefore, the difference of the observed enthalpies reflects the hydrophobic interaction relative to the cluster size induced by the surfactant. Longer side-chain-rich clusters exhibit stronger hydrophobic interaction energy than shorter ones.

Comparison between Oppositely Charged D40Cet15/SDS and CTAC/SDS. Unlike D40Oct30 or D40Dod30/SDS systems, for D40Cet15/SDS, the initial observed enthalpies show a large negative slope as SDS concentration increases. We think that this is a consequence of the progressive enlargement of the mixed hydrophobic clusters, induced by SDS. Therefore, we thought it would be very interesting to compare the behavior of D40Cet15/SDS with CTAC/SDS, as these two systems involve the interaction of a similar surfactant (quaternary ammonium group with cetyl chain) in one case bound to the polymer (D40Cet15) and in the other to the free form (CTAC).

A comparable result is obtained for the interactions between the corresponding cationic surfactant (CTAC) and SDS. As mentioned above, the structure of the polyelectrolytes can be

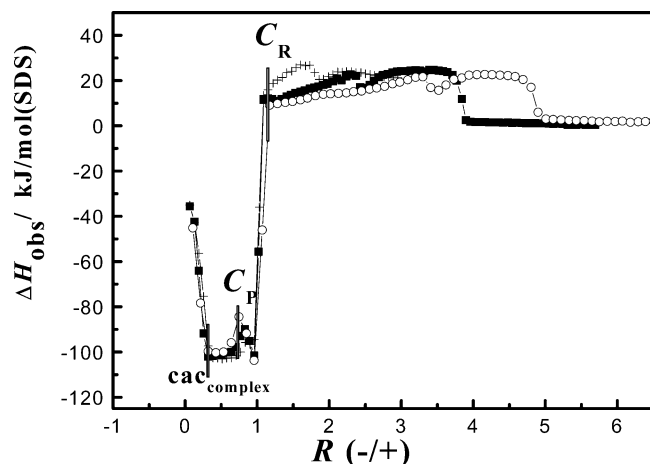


Figure 8. Variation of the observed enthalpies with charge ratios, $R(-/+)$ for CTAC/SDS systems at $T = 308.15$ K. The CTAC concentrations in the cell are (+) 10 mmol/dm^3 , (■) 5 mmol/dm^3 , and (○) 3 mmol/dm^3 . The initial SDS concentration in the syringe is always 0.2 mol/dm^3 .

considered as a “poly-Gemini surfactant” connected by the same repeated spacer. So, the thermodynamics and phase behavior of their mixtures with SDS must be comparable to some extent with the ones observed for mixtures of their parent surfactants with SDS. In Figure 8, we plot the observed enthalpy curves for the titration of SDS into CTAC solutions of different concentrations ($C_{\text{CTAC}} > \text{cmc}$). All curves present a pattern similar to the ones observed for DC40Cet15/SDS, including similar curve shapes and approximately the same charge ratios at $\text{CAC}_{\text{complex}}$, C_P , and C_R . Note, however, that we are naming these critical concentrations according to the nomenclature above, although in these systems, they might represent different phase events. Below C_R , the magnitude of the observed enthalpy change is quite different in the two types of mixed systems. It is evident that the interaction energy between SDS and CTAC is much larger than the one observed between SDS and D40Cet15. This gives an important insight into the effects of the conformational constraints of the polyelectrolyte backbone on the interactions. The oppositely charged surfactants with no “stereoblock of spacers” must have a more compact arrangement of molecules in the micelles or other aggregates, most likely a crystalline precipitate of $\text{CTA}^+ \text{DS}^-$ forms, due to an electrostatic attraction of the headgroups. Therefore, the mixed micelles must have a larger aggregation number and a larger interaction enthalpy. Above C_R , the mixed surfactant system probably goes through different aggregate morphologies, maybe vesicles or deformed micelles,^{57–59} while the systems with DC40Cet15 stay in a semitransparent morphology, maybe partly because of large cross-linking morphologies, due to the moderate rigidity of the backbone. Further interpretation needs to be combined with information obtained from other methods.

Effect of Temperature on the Interactions. The temperature has an important influence on the interactions between this series of polyelectrolytes and SDS, as one would expect for interactions that are at least partly driven by hydrophobicity. Figure 9 shows the observed enthalpy curves for three systems ($C_{\text{polymer}} = 1.0\%$), D40Oct30/SDS, D40Dod30/SDS, and D40Cet15/SDS at 298.15 and 308.15 K, where the corresponding SDS dilution curves in water are also included for comparison. It is observed that the differences in ΔH_{obs} with temperature take place mainly in the initial stage of the titration (at $C_{\text{SDS}} < \text{CAC}_{\text{complex}}$). We can derive the ΔH_{int} values in this concentration range for the two different temperatures according to the method and equations described above. The values can be found in Table 3. For

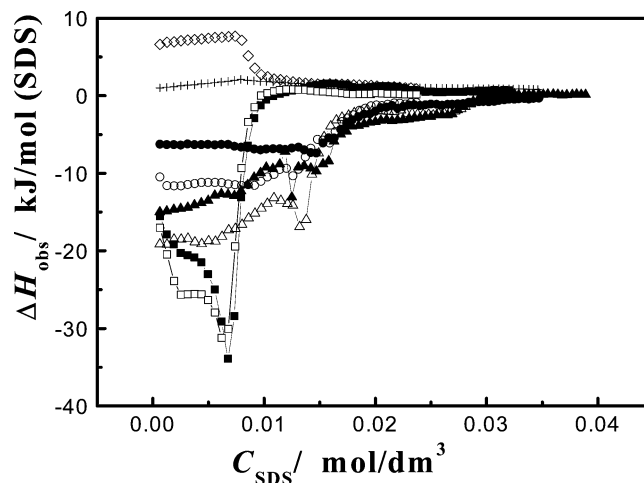


Figure 9. Variation of the observed enthalpies with SDS concentration for polyelectrolyte/SDS systems at $T = 298.15$ K (solid symbols) and 308.15 K (hollow symbols), (●○) D40Oct30, (▲△) D40Dod30, and (■□) D40Cet15. The polymer concentration is 1.0% in all cases. Curve (◇) is for the dilution of the concentrated SDS solution (0.2 mol/dm^3) into water at $T = 308.15$ K and (+) at $T = 298.15$ K.

D40Oct30/SDS and D40Dod30/SDS, when SDS concentration is below the $\text{CAC}_{\text{complex}}$, ΔH_{int} values are almost constant (compared with the same temperature), but for D40Cet15/SDS, ΔH_{int} values vary largely with SDS concentration—for example, at 298.15 K, $\Delta H_{\text{int}} = -16.5 \text{ kJ/mol}$ of side group for the first injection and $\Delta H_{\text{int}} = -21.6 \text{ kJ/mol}$ of side group for the fourth injection (at $\text{CAC}_{\text{complex}}$). This is the result of the pronounced slope found in this system for the initial stage of the titration that we discussed above. This implies that the mixed hydrophobic clusters with the longer cetyl chains are progressively enlarging. The absolute values of ΔH_{int} always decrease as the temperature decreases, indicating a negative change in heat capacity ($\Delta C_{p,\text{int}}$) for the process. The obtained $\Delta C_{p,\text{int}}$ values for D40Oct30/SDS and D40Dod30/SDS are approximately the same, and $\Delta C_{p,\text{int}}$ values for D40Cet15/SDS are between -710 and -1110 kJ/(K mol) of side group (Table 3). It is therefore difficult to estimate precisely the effect of alkyl side chain length on $\Delta C_{p,\text{int}}$. We can say at this stage that there seems to be a trend that is to some extent similar to the change in heat capacity observed for the dilution of the polyelectrolytes into water. We will not attempt to give any interpretation of the $\Delta C_{p,\text{int}}$ values obtained in the present study.

It is worth noting that both $\text{CAC}_{\text{complex}}$ and C_P are almost temperature independent, but not C_R , therefore, the two-phase region at lower temperature is larger for both D40Dod30/SDS and D40Oct30/SDS systems, as shown in Figure 10 for D40Dod30/SDS (turbidity results). This result could be related to the variation of the hydrophobic interaction strength with temperature.

In summary, the micellization process of hydrophobically modified cationic polysaccharides can be evaluated from the results of ITC and fluorescence measurements. The positive ΔH_{mic} value for D40Oct30 indicates that the micellization process is entropy driven, whereas for D40Dod30 and D40Cet15 it is also favored by an increasingly negative enthalpy with increasing n . The polyelectrolyte cmc's are several orders of magnitude lower than the corresponding ones for the cationic surfactants ($C_n\text{TAC}$).

Their interaction with oppositely charged surfactants in aqueous solution was also studied by high-sensitivity ITC, combined with turbidity measurements. The results reveal a

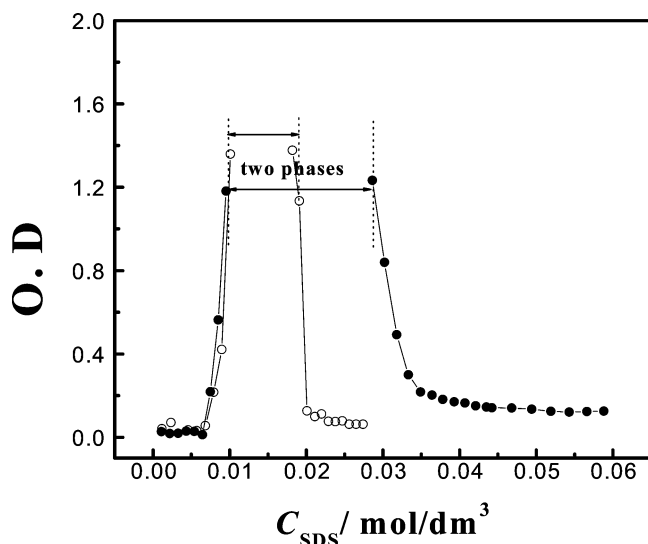


Figure 10. Turbidity (optical dispersion) of mixed solutions of D40Dod30 and SDS as a function of total SDS concentration ($\lambda = 400$ nm) at $T = 298.15$ K and $T = 308.15$ K. D40Dod30 concentration is 1.0%. Solid symbols refer to $T = 298.15$ K and hollow ones to $T = 308.15$ K.

complex thermodynamic behavior for these systems, which we characterized with the results from the present study.

The alkyl chain length of polyelectrolyte pendant groups and the temperature have a strong influence both on pure polymer behavior and on the interactions with SDS, while the molecular weight of the dextran backbone does not affect significantly either the thermodynamics of the pure polymer or the interaction with SDS or the phase behavior.

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