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Interaction of cationic hydroxyethylcellulose (JR400) and cationic hydrophobically modified hydroxyethylcellulose (LM200) with the amino-acid based anionic amphiphile Sodium N-Dodecanoyl Sarcosinate (SDDS) in aqueous medium

Abhijit Dan, Soumen Ghosh, Satya P. Moulik *

Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata 700032, India

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ABSTRACT

Interaction of an ionic amphiphile with an oppositely charged polyelectrolyte may dramatically alter the physicochemistry of the polymer in solution. Exploration of the macro and microscopic details of such processes is a topic of contemporary interest. In this study, results of interaction of the anionic amphiphile, Sodium N-Dodecanoyl Sarcosinate (SDDS) with the cationic hydroxyethylcellulose, JR400 and hydrophobically modified cationic hydroxyethylcellulose, LM400 at the air/water interface and in the bulk over a fair range of concentration in the absence and presence of salt are presented. At a very low concentration, SDDS monomers interact with the polymer; above the critical aggregation concentration (CAC), small micelle like aggregates form complexes with the polymer. The complex, thereafter, self-associates to form a turbid coacervate phase. At increased [SDDS], the turbidity decreases by way of disintegration of the coacervates, and the solution becomes clear. The salt, NaCl affects the SDDS–polymer interaction. The amphiphile interaction with mixed JR400 and LM200 also produces characteristic interfacial and bulk features. Different physical methods are employed to probe the interaction process and an attempt for correlation of the results has been made.

1. Introduction

The polymer–surfactant interaction is an important topic of research in modern surface, biophysical and pharmaceutical science (Goddard, 1986a, 1986b). A variety of combinations arise in practice, and their possible uses and applications are diverse (Antunes, Thuresson, Lindman, & Miguel, 2003; Meier, Hotz, & Gunther-Ausborn, 1996). In the realm of biology, the interaction process can be explored to immobilize enzymes to form polyelectrolyte complexes, and to purify proteins by selective coacervation (Margolin, Sherstyuk, Izumrudov, Zezin, & Kabanov, 1985). Different types of interaction are possible viz., between neutral polymer and nonionic surfactant (Feitosa, Wyn Brown, & Hansson, 1996), neutral polymer and anionic surfactant (Dai & Tam, 2001; Dan, Chakraborty, Ghosh, & Moulik, 2007; Griffiths et al., 2004), polyelectrolyte and surfactant of opposite charges (Exerowa, Kashchiev, & Platikanov, 1992; Sokolov, Yeh, Kohkhlov, Grinberg, & Chu, 1998; Tsekov & Ruckenstein, 1993), etc. In this discipline, interaction of biopolymers (polysaccharides, proteins, enzymes and DNA) with amphiphiles and lipids constitute a special category (Chatterjee, Moulik, Majhi, & Sanyal, 2002; Maulik, Dutta, Chattoraj, & Moulik, 1998; Mun, Rho, & Kim, 2009).

The complexes formed in such interacting systems raise fundamental questions about the process mechanism that still remains to be clearly understood (Deo et al., 2003; Sen, Sukul, Dutta, & Bhattacharyya, 2002). The interaction features are considered to be the combined manifestations of electrostatic and hydrophobic forces (Goddard, 1986a, 1986b). It generally depends on the types of polymer and the surfactant. The charge density on the ionic polymer chain and the aggregating amphiphile ion decide the physicochemical features of the process. The presence of salt can strikingly influence the process. Monomer binding to the polymer chain followed by aggregate formation of the amphiphilic ions and their binding to specific centers on the polymer to form cross-linked type complex may also arise. The complex can be weakly to strongly soluble in water, and can form a different phase (coacervate) by self-association. The net charge on the polymer reduces with addition of the amphiphile ions in solution and passes through a point of neutrality and become oppositely charged with excess addition of the amphiphile. Then the associated complex coacervate gets dissociated or disintegrated and becomes soluble making the solution clear. Depending on the nature of the polymer and the amphiphile, formation of turbid, viscous and even gel-like

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* Corresponding author. Fax: +91 33 2414 6266.
E-mail address: spmcss@yahoo.com (S.P. Moulik).

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consistencies may arise in solution. Addition of salt may either assist the association process or retard it (Bai, Nichifor, Lopes, & Bastos, 2005; Dan, Ghosh, & Moulik, 2009b; Wang, Kimura, Huang, & Dubin, 1999).

Carbohydrate based and other polymers containing moderate number of fairly hydrophobic substituents can strongly interact with surfactants (Goldraich, Schwartz, Burns, & Talmon, 1997; Li & Dubin, 1994; Regismond, Winnik, & Goddard, 1996). Due to unfavorable contact between the hydrophobic groups and water, these polymers have a tendency for self-aggregation and association with surfactants. Water soluble cationic celluloses and other biopolymers have been used in such studies (Burke & Palepu, 2001; Burke, Palepu, Hait, & Moulik, 2003; Dan, Ghosh, & Moulik, 2009a; Guillemet & Piculell, 1995; Hait, Majhi, Blume, & Moulik, 2003; Winnik & Regismond, 1996).

Sodium N-Dodecanoyl Sarcosinate (SDDS), a novel amino-acid based surfactant, has several biological and commercial uses (Lanigan, 2001). It is added in tooth pastes for the control of dental caries (Fosdick, 1956). It does not affect acid dissolution of tooth enamel or the inhibitory effect of fluoride on the dissolution process (Rajstein, Fuks, Markitziu, & Gedalia, 2007). It is a foaming and cleansing agent used in shampoo, shaving and wash products. It is also used in formulating textile treatment agent. In a recent report (Basu Ray, Ghosh, & Moulik, 2009), detailed interfacial and bulk behaviors of SDDS have been documented. In view of its varied application potential, interaction studies between SDDS and water soluble polymers need to be explored.

In the present study, we have investigated the interaction of SDDS with cationic hydroxyethylcellulose, JR400 and hydrophobically modified cationic hydroxyethylcellulose, LM400 in aqueous medium without and with salt, NaCl. Strong interactions producing complexes stabilized by both electrostatic and hydrophobic interactions have been envisaged. A multitechnique approach, involving tensiometry, conductometry, viscometry, microcalorimetry, and turbidimetry have been used for the study. Characteristic features of the interaction at the interface and in the bulk owing to phenomenological differences have been assessed. Rationalization of the results with physicochemical correlation has been attempted.

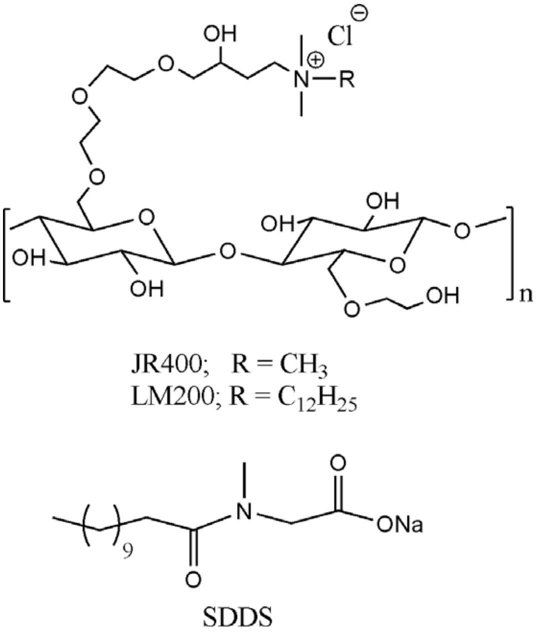
2. Materials and methods

2.1. Materials

The polycation, N,N-dimethyl-N-methyl derivative of hydroxyethylcellulose (JR400), and the hydrophobically modified polycation, N,N-dimethyl-N-dodecyl derivative of hydroxyethylcellulose (LM200) (shown in Scheme 1) were supplied by Amerchol, Union Carbide Chemicals and Plastics Co., USA, and were used as received. The average molar masses were approximately 500,000 and 100,000 Da (Dhoot, Goddard, Murphy, & Tirrell, 1992; Goddard & Leung, 1992), respectively. The degree of substitution was 2.0×10^{-4} mol of chains per gram of the polymer. This corresponds to approximately 3.4% by weight, or one substitution per 19 glucose units (Thalberg & Lindman, 1989). AR-grade Sodium N-Dodecanoyl Sarcosinate (SDDS, purity > 97%) was obtained from Fluka (Germany). NaCl was AR-grade product of Merck (Germany). The materials were used as received. All solutions were prepared in doubly distilled water of specific conductance, 2–4 μS cm^{-1} at 303 K. The concentration of polymer used has been expressed in % (w/v) throughout the text.

2.2. Tensiometry

Tensiometric measurements were taken with a calibrated du Noüy tensiometer (Krüss, Germany) by the platinum ring detachment technique. The solution was taken in a double-walled thermostated container and the additive was stepwise added as required using a Hamilton microsyringe. During measurements, 20 min time for equilibration was allowed after surfactant addition and through mixing. The accuracy of the measured γ was ±0.1 mN m^{-1}.



Scheme 1. Structures of cationic celluloses JR400 and LM200, and Sodium N-Dodecanoyl Sarcosinate (SDDS).

2.3. Conductometry

The conductivity measurements were performed with a Jenway (UK) conductometer in a conductivity cell of unit cell constant. The same procedure of addition of the surfactant solution as in tensiometry in 10 ml of polymer solution of a desired strength was followed. The accuracy of measurements was within ±1.0%.

2.4. Viscometry

The viscosity measurements were taken in a calibrated Ubbelohde viscometer (placed in a water bath) with a clearance time of 200.4 s for 13 ml of water in a temperature controlled water bath of accuracy ±0.1 °C. Polymer solution of the desired strength was taken in the viscometer, and concentrated surfactant solution was progressively added in stages with a Hamilton microsyringe, and the flow times of the solutions were measured after thorough mixing and thermal equilibration. The accuracy of viscosity measurements was within ±2.0%. Each measurement was duplicated, and the mean value was recorded and used.

2.5. Microcalorimetry

An OMEGA, ITC, microcalorimeter of Microcal, Northampton (USA), was used for thermometric measurements. 1.325 ml of JR400/LM200 solution of a desired strength was taken both in the reaction and the reference cells. The injection syringe (350 μl) was filled with concentrated SDDS solution, which was injected at equal time intervals of 300 s in multiple steps in the polymer solution under constant stirring (350 rpm) condition. The heat released at each step of addition was recorded and the enthalpy change per mole of SDDS was calculated using the ITC software. The experiment of surfactant dilution was also performed following the same injection protocol as that of interaction experiments, taking either water or salt solution in the reference cell. All measurements were taken at thermostated condition maintained by a Neslab RTE 100 circulating water bath at a lower temperature within 5° of the experimental temperature. The temperature in the cell compartment of the calorimeter was automatically scanned up to the desired level of 303 K with an accuracy of ±0.01 K. Each run was duplicated to check reproducibility. The measurement error was found to be ±0.5%. Further details of the method and data processing are found in earlier literature (Hait et al., 2003; Majhi & Moulik, 1998).

2.6. Turbidimetry

The turbidimetric experiments were performed in a Shimadzu, 1601 (Japan) spectrophotometer operating in dual beam mode using a matched pair of quartz cuvettes of path length 1 cm under thermostated condition (303 ± 0.1 K). The measurements were taken in the transmittance (%T) mode. In actual experiment, concentrated SDDS solution was progressively added with a microsyringe into the sample cell containing 3 ml of JR400 or LM200 solution of a desired strength, and the solution was mixed using a magnetic stirrer. It was allowed 5 min time before taking measurement. The turbidity index ($100 - \%T$ at $\lambda_{max} = 305$ nm) was plotted against [SDDS]. The measured values were corrected with a blank experiment corresponding to the dilution of the polymer solution.

3. Results and discussion

3.1. Interaction in aqueous environment

The self-association and related properties of SDDS in aqueous medium were reported earlier (Basu Ray et al., 2009). The interaction behaviors of the amphiphile with the polysaccharides, JR400 and LM200 both at the interface and in the bulk are presented below.

Tensiometry offers information on the aforesaid interaction at the air/solution interface. The γ-log C profiles for JR400–SDDS are illustrated in Fig. 1. The patterns at different [JR400] were similar. Initially, the DDS$^-$ ions adsorbed at the air/solution interface, interacted with the moderately surface active JR400, and lowered the surface tention (γ) of the solution. The DDS$^-$ primarily interacted by way of charge interaction; hydrophobic interaction between surfactant tail and the hydroxyethyl group was minor. Bai, Catita, Nichifor, and Bastos (2007) and Deo et al. (2003) have reported the importance of hydrophobic interaction between hydrophobically modified polyelectrolytes and surfactants of the same charge. There, the attractive hydrophobic interaction predominated over the columbic repulsion between the similarly charged polymer sites and the surfactant head groups. In the present system, the attractive electrostatic forces and the weak hydrophobic interaction operate in conjunction. With surfactant addition, the γ decreased up to a certain [SDDS] called the critical aggregation concentration (CAC), beyond which small amphiphile aggregates (like micelles) continued to associate with the polymer segments (Dan et al., 2007, 2009b). The CAC formation is a polymer induced amphiphile aggregation process. Interaction of negatively charged gelatin at pH = 9.0 (above its isoelectric pH of 4.84) with cationic surfactants ATABs (alkyltrimethylammonium bromides) has also demonstrated similar features (Mitra, Bhattacharya, & Moulik, 2008, 2009). The CAC of SDDS was found to decrease with increasing [JR400] (Table 1). Increased [polymer] co-operatively induced the amphiphile aggregation to decrease CAC. The ionic aggregate attached JR400 complex at the air/solution interface sank in the bulk making the interface free of the adsorbate. Thus, beyond CAC, γ increased and maximized at C_s. At C_s, the polymer chain in the bulk was considered saturated with the adhered small DDS$^-$ aggregates. The C_s values increased with increasing [JR400] as expected from the mass balance consideration (Table 1). Also the small micelle decorated polysaccharide complex self-associated in solution by interchain hydrophobic and nonspecific interaction to form a coacervate phase. A visibly turbid colloidal dispersion was formed on long standing (it was transparent initially). Beyond C_s, SDDS monomers progressively occupied the free interface reducing γ; the process was complete at CMC$_e$ (the extended CMC of SDDS) where free larger micelles started to form in solution making γ practically independent of [SDDS]. The γ_{cmc} for different [JR400] were more or less the same, meaning formation of similar

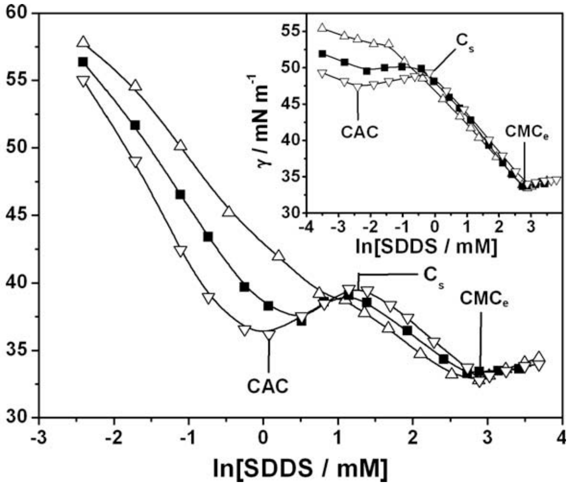


Fig. 1. Tensiometric profiles for the interaction of SDDS with JR400 (main plot) and LM200 (inset) at 303 K. Δ, 0.05% (w/v); ■, 0.1% (w/v); ∇, 0.2% (w/v).

Table 1
Interaction characteristics of SDDS with JR400 and LM200 in aqueous medium at 303 K.[a]

	JR400			LM200		
Tensiometry						
% (w/v)	CAC	C_s	CMC$_e$	CAC	C_s	CMC$_e$
0.05	2.11	2.90	16.8	0.16	0.24	14.5
0.1	1.67	3.15	17.4	0.12	0.56	15.1
0.2	0.95	3.58	17.9	0.09	0.84	15.6
Viscometry and conductometry[b]						
% (w/v)	CAC	C_s	CMC$_e$	C_s		CMC$_e$
0.05	2.05	2.82 [2.82]	13.3 [13.8]	0.25		12.1 [13.1]
0.1	1.56	3.26 [3.18]	13.6 [13.9]	0.61		12.6 [13.2]
0.2		[3.61]	[14.7]			[13.5]
Microcalorimetry[c]						
% (w/v)	C_s	C^*	CMC$_e$	C^*		CMC$_e$
0.05	1.82 (0.76)	3.40 (−1.05)	13.1 (1.76)	1.36 (−0.21)		11.9 (1.85)
0.1	2.49 (1.96)	4.46 (−2.02)	13.5 (1.72)	2.32 (−0.85)		12.1 (1.75)
0.2	3.38 (2.54)	5.62 (−2.59)	14.5 (1.77)	3.37 (−2.84)		12.2 (1.70)
Turbidimetry						
% (w/v)	T_1	T_2	T_3	T_2		T_3
0.05	1.66	5.40	16.7	5.40		15.1
0.1	2.16	5.12	18.9	3.46		16.5
0.2	2.57	4.53	21.3	1.98		17.1

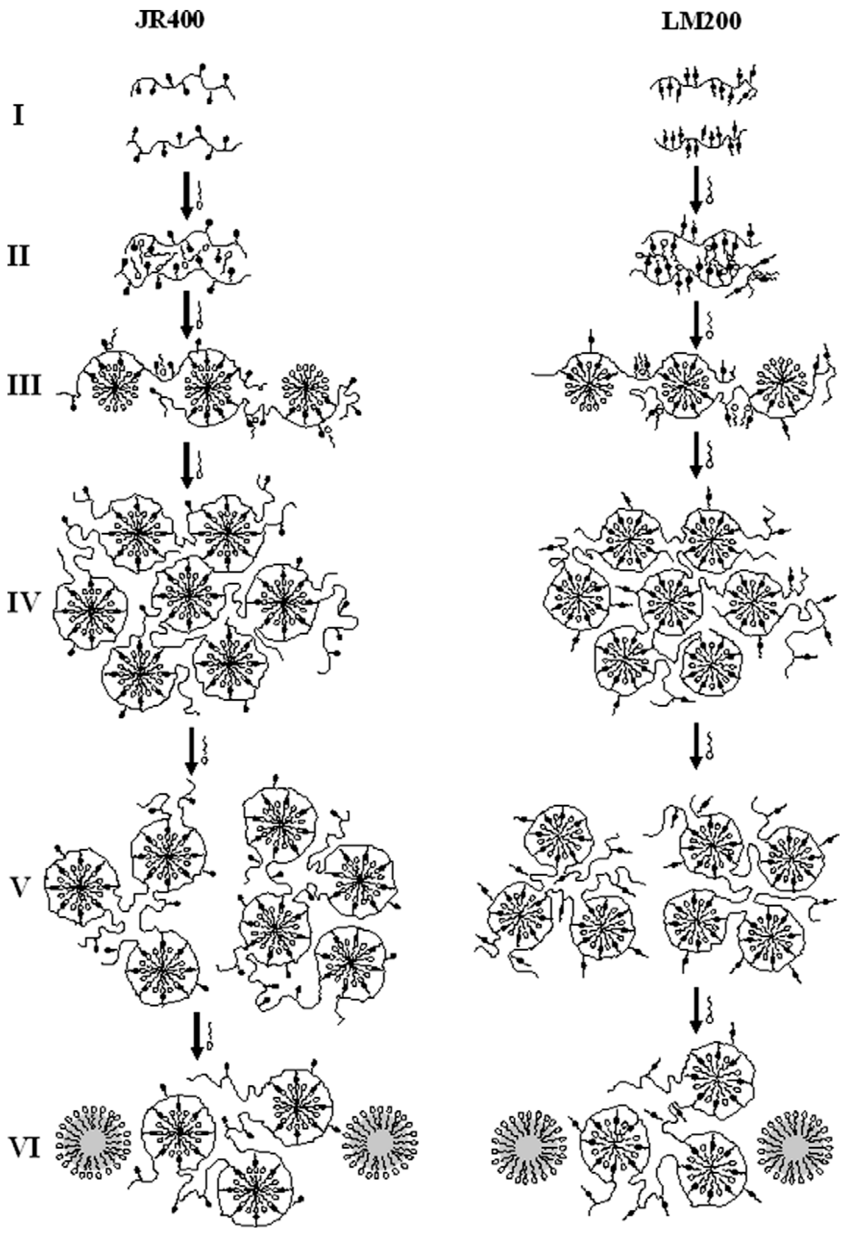
[a] CAC, C_s, C^*, CMC$_e$, T_1, T_2, and T_3 are given in mM. Their standard deviations are within ±5–8%.

[b] Results by conductometry are presented in third brackets.

[c] Enthalpy values expressed in kJ mol^{-1} of SDDS are presented in first brackets. Their standard deviations are within ±4%.

types of JR400–SDDS complexes in solution with comparable interfacial compositions. The CMC_e values evidenced a mild increase with increasing [JR400] (Table 1). The turbidity of the solution was affected by the increased presence of SDDS. Near CMC_e, the coacervate started to disintegrate into smaller entities that became totally soluble at [SDDS] >> CMC_e. We have recently demonstrated this phenomenon of disintegration of inulin (a carbohydrate polymer)-ATAB (alkyltrimethylammonium bromide) coacervate at higher [ATAB] by TEM study (Dan et al., 2009b). The formation, completion and solubilization of the coacervates occurred in the bulk. The corresponding interfacial behavior was manifested in the displayed tensiometric profile.

The interaction profiles of the LM200–SDDS system with reference to the inflection points are illustrated in the inset of Fig. 1. The magnitudes of the inflection points are presented in Table 1. The differences from JR400 were as follows: (i) LM200 being more hydrophobic lowered γ_{water} more compared to JR400 (addition of 0.05%, 0.1% and 0.2% (w/v) LM200 lowered γ_{water} (72 mN m^{-1}) to 57.8, 53.6 and 51.3 mN m^{-1}, respectively; the corresponding γ_{water} values for JR400 were 65.0, 63.8 and 63.1 mN m^{-1}), (ii) the CAC and C_s values were fairly lower than that of JR400, (iii) increased hydrophobicity of LM200 produced easier CAC formation and complexation; its lower molar mass than JR400 produced lower C_s values, and (iv) the CMC_e values of LM200 were consequently also lower. The hydrophobicity of the dodecyl chain attached to the cationic centers on the substituent helped easier formation of small micelles with lower CAC for LM200 than JR400. Another basic difference of LM200 from JR400 was that the former formed induced small mixed micelles whereas latter formed small normal micelles with SDDS (Regismond et al., 1996; Winnik & Regismond, 1996). The above described events in all sequential stages of interaction of SDDS with JR400 and LM200 in solution are depicted in Scheme 2.



Scheme 2. Different stages of interaction of JR400 and LM200 with SDDS in aqueous medium. (I) Individual polymer chains in dilute solution. (II) Appearance of a kind of polymer induced amphiphilic assemblies with addition of SDDS. (III) Formation of well defined normal small micelles (for JR400) and induced mixed micelles (for LM200) at CAC. (IV) Aggregated assemblies of the polymer–micelle complexes forming coacervates. (V) Disintegration of the coacervates at C_s < [SDDS] > CMC_e. (VI) Complete disintegration with formation of free necklace-bead type complex and free normal SDDS micelles in solution at [SDDS] >> CMC_e.

The conductometric profiles of SDDS addition in the polymer solution produced either one or two inflections. The results with 0.1% (w/v) JR400 and LM200 are illustrated in the inset of Fig. 2. For the first, the mild initial break fairly agreed with the C_s realized by tensiometry and other bulk property related methods (viscometry and microcalorimetry to be subsequently discussed). The conductance course appeared with a higher slope than the initial beyond the C_s point. In the post C_s stage, formation and binding of the small SDDS aggregates (like that between CAC and C_s) was absent; it was only SDDS monomers that prevailed in the environment to produce a linear course with a higher slope. The second break at CMC$_e$ in the plot corresponded to the formation of free micelles of SDDS in the solution. The condensation of the counter Na^- ions in the electrical double layer (Stern layer) of the free micelles caused a decline in conductance in the post CMC$_e$ region. The failure to detect the CAC by conductometry was not a new observation (Chakraborty, Chakraborty, Moulik, & Ghosh, 2007; Mitra et al., 2008). Interestingly, for LM200 the method could not locate the C_s point either. Although to some extent lower than tensiometry, the C_s values for JR400 by conductometry fairly agreed with viscometry and microcalorimetry. The probing of a process by different methods may or may not yield similar results; the information generated may become system specific also. Thus, tensiometry probed the interaction process on the basis of interfacial conditions, whereas conductometry, viscometry and microcalorimetry probed it by way of physicochemistry in the bulk. It was seen that CMC$_e$ values obtained from tensiometry were greater than that found by the other three methods, which were comparable with one another (Table 1).

The viscosity method probed the bulk complexation process in terms of the configurational changes of the polymer–surfactant combine. The relative viscosities of the JR400 and LM200 solutions were measured with progressive SDDS addition. Representative illustrations at 0.1% (w/v) for both JR400 and LM200 are depicted in Fig. 2 (main plot). The results are presented in Table 1. For JR400 four regions with three distinct inflections were observed in the profile. The viscosity of the polymer decreased by interaction with SDDS; the polymer configuration tended to become compact. The first mild break agreed with the CAC found by tensiometry. The viscosity manifested CAC point was absent for LM200. After CAC, η_{rel} decreased significantly for JR400, which for LM200 happened right from the beginning. This was the region where the small amphiphile aggregates associated with the polymer segments wherein rapid change in compact complex configuration was envisaged. The phenomenon continued up to C_s, beyond which η_{rel} remained practically unchanged. In this region, the complexed polymer–aggregates of overall globular geometry resulted. It is known that free species of spherical or globular geometry produce low and almost constant viscosity (Dan et al., 2009a). Beyond the CMC$_e$ point, associated complex (coacervate) disintegrated into smaller entities with change in configuration (elongation) by interaction with excess SDDS and the free micelles. As a consequence viscosity increased. But the system did not regain their original status; their fluidity remained fairly higher than initial. The complexed entities were reasonably compact. The phenomenon was more prominent for the more hydrophobic LM200 than JR400. The CAC, C_s and CMC$_e$ values from viscometry fairly agreed with the results obtained by other methods, and followed a similar trend as discussed above.

Isothermal titration calorimetry is a sensitive method for identification of different stages of interaction between polymer and surfactant and estimation of the related enthalpies per mole of surfactant (Bai et al., 2005, 2007; Dan et al., 2007; Mitra et al., 2008). The enthalpograms for the interaction of SDDS with JR400 and LM200 are depicted in Figs. 3 and 4, respectively. The transition points and the related enthalpies (ΔH) are identified in the main diagrams with illustrations of the polymer concentration variation profiles in the inset. The nature of the illustrations is unique in comparison with the results on many other polymer–surfactant systems (Bai et al., 2005, 2007; Dan et al., 2007; Mitra et al., 2008).

The enthalpograms of dilution of SDDS in water and in the presence of JR400 produced a striking initial difference. A sharp initial maximum followed by a minimum was observed; the maximum intensified with increasing [JR400] (Fig. 3, main plot and inset). In the post minimum stage, the enthalpogram structures were similar with a mild left shift. The initial crest corresponded to C_s and the trough to C^*; the rest part stood for free micelle formation of the amphiphile after completion of polymer–small SDDS aggregate association. The height between 'a' and 'b' was the enthalpy of the small aggregate binding with polymer and the self-association of the resulting complex (ΔH_s). The desolvation of the polymer sites and their vicinity to accommodate the micelles made the resultant enthalpy of the interaction process endothermic. The decline in enthalpy between 'b' and 'c' resulted from the interaction process

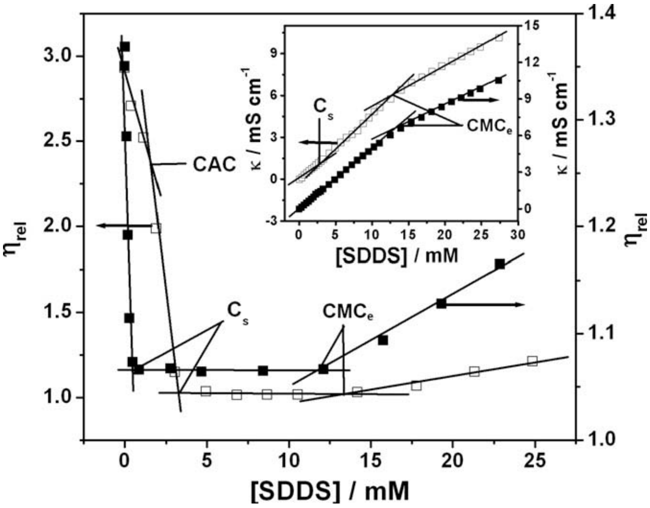


Fig. 2. Relative viscosity versus [SDDS] profiles for the interacting systems of 0.1% (w/v) JR400–SDDS (□) and 0.1% (w/v) LM200–SDDS (■) at 303 K. η_{rel} of the polymer solution is relative to the viscosity of the SDDS solution at their studied concentrations. *Inset:* Conductometric results for the same interacting systems.

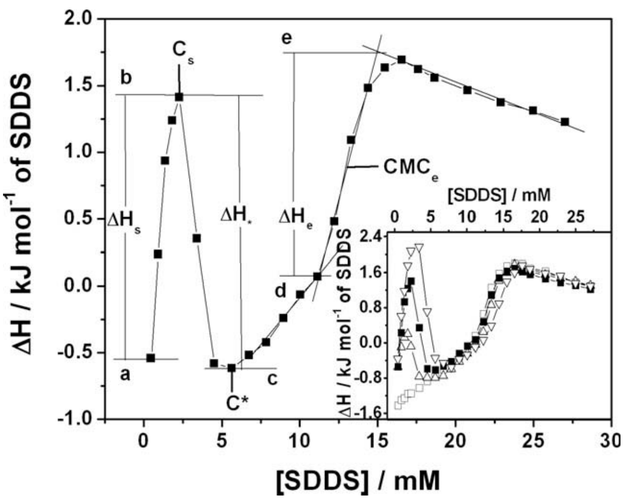


Fig. 3. Enthalpograms for the dilution of SDDS in 0.1% (w/v) JR400 solution at 303 K. Transition points are indicated on the diagram. *Inset:* The same events at varied polymer concentrations of 0 (□), 0.05 (Δ), 0.1 (■) and 0.2 (∇) % (w/v) at 303 K.

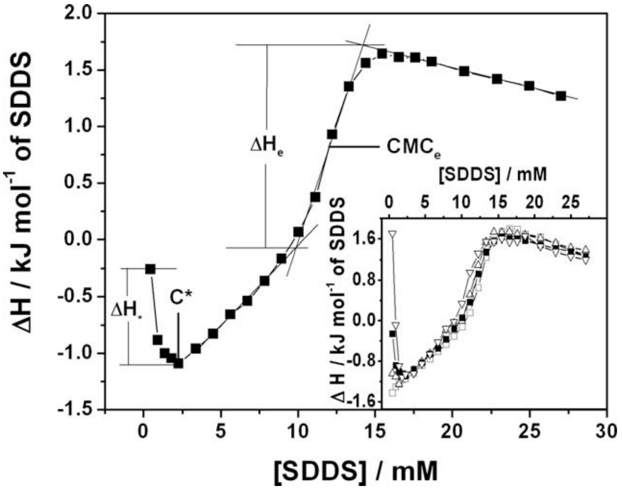


Fig. 4. Enthalpograms for the dilution of SDDS in 0.1% (w/v) LM200 solution at 303 K. Transition points are indicated on the diagram. *Inset:* The same events at varied polymer concentrations of 0 (□), 0.05 (Δ), 0.1 (■) and 0.2 (∇) % (w/v) at 303 K.

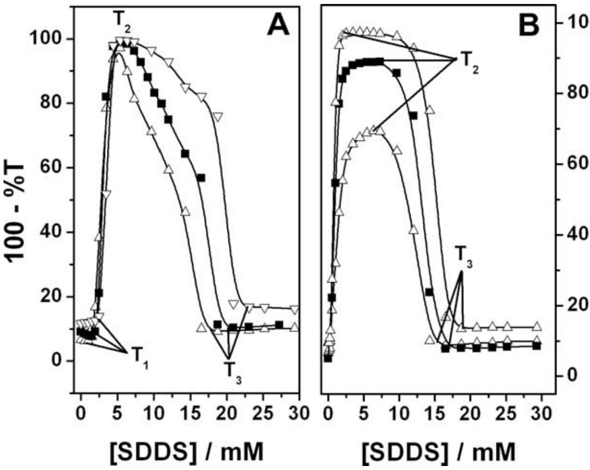


Fig. 5. Turbidity–[SDDS] dependence with JR400 (A) and LM200 (B) at different polymer concentrations at 303 K. Δ, 0.05% (w/v); ■, 0.1% (w/v); ∇, 0.2% (w/v). The transition points are defined in the text.

constituted of (i) reorganization of the adhered micelles in the polymer segment, (ii) conformational changes of the polymer chain, (iii) cross linking among the polymer chains to shelter the mixed micelles (only for LM200), (iv) local solvation/structure modification, and (v) other nonspecific interactions in the system. The enthalpy (ΔH_{*}) corresponding to the above involved processes in the overall respect was exothermic. The point C^{*} thus referred to the completion of the processes (i) to (v) in the system. The rise with a long inclined tail, thereafter, a sharp upward turn corresponded to $\mathrm{CMC_e}$ formation with an enthalpy change between the points 'd' and 'e' (cf. SDDS micellization studied by Basu Ray et al. (2009)). The initial inclined tail resulted from non-ideality (ionic interaction) of the amphiphile species during the dilution process of the micellar solution (Chakraborty & Moulik, 2007; Thongngam & McClements, 2005). The results ΔH_s, ΔH_{*}, and ΔH_e are recorded in Table 1. In the LM200–SDDS system, the initial rise to C_s was absent, instead a sharp decline ([LM200] dependent) was observed (Fig. 4). The rest portion of the enthalpogram was similar to that of JR400. These results are also presented in Table 1. Like conductometry, microcalorimetry also failed to detect C_s for LM200, and CAC for both the polymers.

In the studied interacting systems as well as in other similar processes, turbidity is a consequence of interaction of the formed complex to yield coacervates in the bulk (Bai et al., 2005; Chakraborty, Chakraborty, & Ghosh, 2006; Mitra et al., 2008; Wang et al., 1999). The turbidimetric profiles are presented in Fig. 5. For JR400–SDDS system the solutions remained clear up to [SDDS] = T_1; the turbidity (depicted as 100 – %T) steeply rose, thereafter. The initial break point corresponded to the onset of coacervation. T_1 increased with increasing [JR400]. The increase continued up to T_2 (maximum turbidity), and then started to decline in a nonsymmetric manner. Thus, the coacervates maximized and started to disintegrate and disperse at higher [SDDS] to reach the minimum turbidity point T_3 where the complex was in the environment of free micelles formed in solution, and remained in the highest state of dispersion akin to micellar solubilization. Similar observations on depletion of the turbidity by the action of excess surfactant associated with free micelles in solution have been reported in the literature (Bai et al., 2005; Chakraborty et al., 2006; Lundin, Macakova, Dedinaite, & Claesson, 2008; Mitra et al., 2008; Wang et al., 1999). For LM200–SDDS system the coacervates started to from at a very low [SDDS] making its point of start undetectable; thus, the T_1 state was missing. The turbidity in SDDS–LM400 also declined steeply after reaching a maximum but the profile was more symmetrical (bell shaped) than that of SDDS–JR400. Thus, the disintegration of the coacervates in excess SDDS environment was in stages for JR400, which for LM200 was a smooth and continued phenomenon. In both cases T_2 and T_3 followed similar trends i.e., T_2 decreased and T_3 increased with increasing [polymer] (Table 1).

3.2. Effect of added NaCl

Addition of salt decreases the CMC of ionic surfactants by way of formation of a denser electrical double layer that screens the electrostatic interaction between the surfactant head groups. On increasing [NaCl], both the CMC of SDDS and its endothermic enthalpy of micellization (ΔH_{CMC}) decreased (Table 2, footnote 'c'). The CMC values herein found from microcalorimetry for SDDS with varied [NaCl] fairly agreed with our earlier report (Basu Ray et al., 2009).

The tensiometric profiles for the interaction of SDDS with 0.1% (w/v) of both JR400 and LM200 in the NaCl environment are documented in Fig. 6. The general patterns with and without NaCl were comparable. The interaction parameters declined for both the polymers with NaCl addition. Electrostatic screening caused the effect. At [NaCl] > 10 mM, CAC values in LM200 system were very low and undetectable. The results are presented in Table 2. The parameters CAC, C_s, and $\mathrm{CMC_e}$ determined by tensiometry for both JR400 and LM200 were more affected compare to other methods. Method dependent interaction parameters are not uncommon in surface chemical studies (Dan et al., 2007). And such observations are system specific.

The enthalpograms for SDDS interaction with JR400 and LM200 produced similar patterns with and without NaCl addition. Illustrations are presented in Fig. 7 for 0.1% (w/v) polymer solution along with the dilution profile of SDDS in 10 mM NaCl solution. Radical differences in the interaction profiles at [SDDS] < C^{*} were observed. In the post C^{*} region, there were only parallel shifts of the enthalpograms. Both C_s and $\mathrm{CMC_e}$ decreased in the NaCl environment. In the salt medium, the polymer configurations were relatively compact and lesser amount of SDDS aggregates were required to saturate the available sites. Thus, $\mathrm{CMC_e}$ (without salt) was greater than $\mathrm{CMC_e}$ (with salt). The enthalpies of the amphiphile self-association corresponding to both CAC and $\mathrm{CMC_e}$ decreased in the presence of NaCl.

Table 2
Interaction characteristics of SDDS with 0.1% (w/v) of both JR400 and LM200 at different [NaCl] at 303 K.[a]

	JR400			LM200		
Tensiometry						
[NaCl]/mM	CAC	C_s	CMC$_e$	CAC	C_s	CMC$_e$
10	1.52	3.11	12.4	0.06	0.51	11.0
50	0.93	2.98	9.61	–	0.36	8.23
100	0.63	2.12	6.77	–	0.21	6.80
Microcalorimetry[b,c]						
[NaCl]/mM	C_s	C^*	CMC$_e$	C^*	CMC$_e$	
10	2.78 (1.50)	7.86 (−1.05)	11.7 (1.26)	1.85 (−1.48)	10.2 (1.65)	
50	2.29 (1.67)	6.75 (−0.80)	7.59 (0.46)	1.36 (−0.52)	6.12 (1.13)	
100	2.12 (1.89)	5.84 (−0.72)	6.18 (0.22)	0.92 (−0.18)	4.02 (0.85)	
Turbidimetry						
[NaCl]/mM	T_1	T_2	T_3	T_2	T_3	
10	2.38	5.42	16.5	3.46	14.3	
50	2.43	5.38	15.4	3.38	10.8	
100	2.48	5.08	14.3	3.06	8.05	

[a] CAC, C_s, C^*, CMC$_e$, T_1, T_2, and T_3 are given in mM. Their standard deviations are within ±5–8%.

[b] Enthalpy values expressed in kJ mol^{-1} of SDDS are presented in first brackets. Their standard deviations are within ±4%.

[c] In presence of 10, 50 and 100 mM NaCl, microcalorimetrically obtained CMCs of SDDS are 10.8, 5.87 and 4.17 mM, respectively, and the corresponding endothermic enthalpies of micellization (ΔH_{CMC}) are 1.69, 1.9 and 0.86 kJ mol^{-1}.

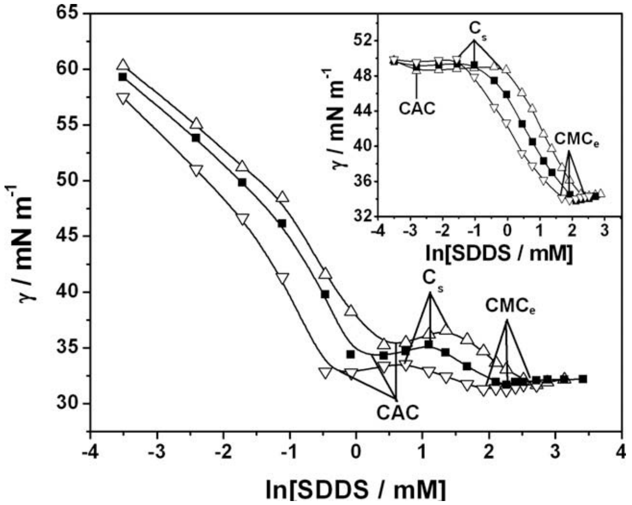


Fig. 6. Tensiometry profiles for 0.1% (w/v) JR400–SDDS (main plot) and 0.1% (w/v) LM200–SDDS (inset) systems at 303 K in NaCl environments of strength 10 mM (Δ), 50 mM (■) and 100 mM (∇).

The appearance of coacervate formation and its degradation in NaCl environment are depicted in the inset of Fig. 7. The profiles were more symmetric in the presence of salt (cf. Fig. 5). The electrostatic screening effect on the phenomenon was mild to moderate. The onset of turbidity (T_1) and its maximum (T_2) were only mildly affected by the NaCl addition. The threshold value (T_3) for coacervate solubilization considerably decreased with increasing [NaCl].

3.3. Interaction of mixed polymers with SDDS

Polymer composites often perform better than individuals, and are thus fairly useful. Herein we have studied the interaction of SDDS with mixtures of JR400 and LM200 in three different mole ratios viz., 2:1, 1:1 and 1:2 for an overall 0.2% (w/v) of the mixtures. The interaction profiles realized by different methods are exemplified in Fig. 8, and the salient features are presented in Table 3. They are concisely described and discussed below.

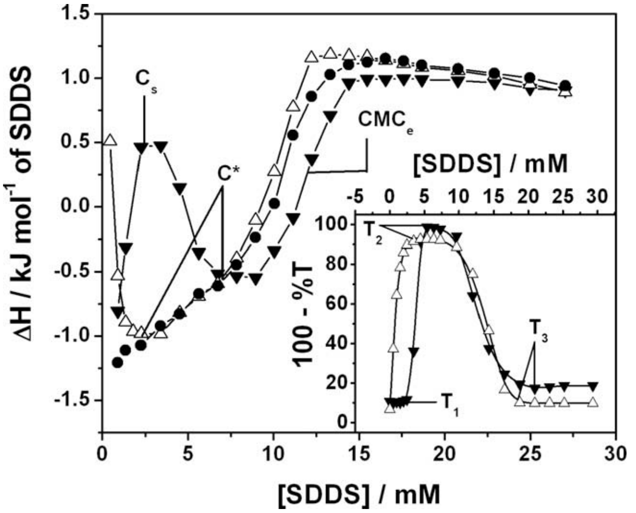


Fig. 7. SDDS dilution enthalpograms in 10 mM NaCl (●), 0.1% (w/v) JR400 in 10 mM NaCl (▼) and 0.1% (w/v) LM200 in 10 mM NaCl (Δ) at 303 K. *Inset:* Turbidity–[SDDS] plots for 0.1% (w/v) JR400 in 10 mM NaCl (▼) and 0.1% (w/v) LM200 in 10 mM NaCl (Δ) at 303 K.

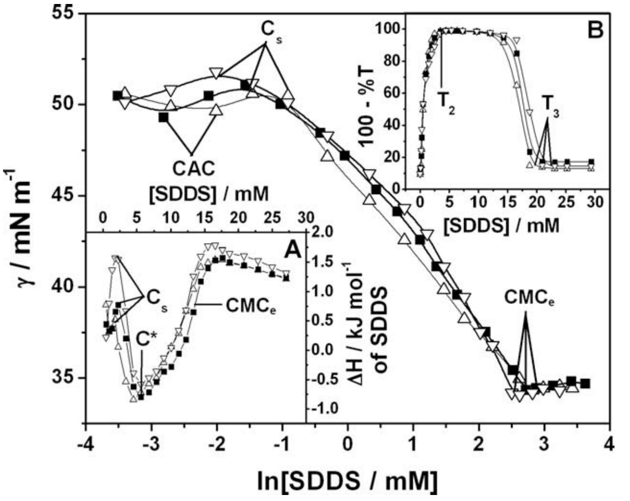


Fig. 8. Tensiometric profiles for JR400 and LM200 mixtures at different ratios at 303 K (main plot). *Inset A:* Enthalpy of dilution of SDDS in mixed 0.2% (w/v) JR400–LM200 solution at 303 K. *Inset B:* Turbidity–[SDDS] profiles for the JR400 and LM200 mixtures at 0.2% (w/v) at 303 K. Δ, 1:2 JR400:LM200; ■, 1:1 JR400:LM200; ∇, 2:1 JR400:LM200.

The tensiometric features (Fig. 8, main plot) at all the studied ratios were comparable with that of LM200–SDDS interaction (cf. Fig. 1, inset). A competitive interfacial complexation of more hydrophobic LM200 over JR400 was reflected on the tensiometric isotherm. The CAC by tensiometry became fairly affected in the polymer combines with increasing proportion of JR400; no CAC point was detected for the 2:1 mixture. The C_s values by tensiometry also decreased with increasing proportion of JR400 in the mixture whereas they evidenced a mild increase as found from microcalorimetry. The microcalorimetry profiles (Fig. 8, inset A) resembled the JR400–SDDS interaction (cf. Fig. 3). The magnitudes

Table 3
Interaction characteristics of SDDS with the mixture of JR400–LM200 at overall 0.2% (w/v) in aqueous medium at 303 K.[a]

JR400:LM200	Tensiometry			Microcalorimetry[b]			Turbidimetry	
	CAC	C_s	CMC_e	C_s	C^*	CMC_e	T_2	T_3
1:2	0.13	0.38	13.7	1.82 (0.22)	4.54 (−1.37)	12.5 (1.80)	3.49	19.1
1:1	0.06	0.21	13.1	2.21 (0.46)	5.61 (−1.57)	13.6 (1.70)	3.42	19.8
2:1	–	0.13	12.2	2.29 (1.05)	5.61 (−2.13)	13.0 (1.73)	3.62	20.9

[a] CAC, C_s, C^*, CMC_e, T_1, T_2, and T_3 are given in mM. Their standard deviations are within ±5–8%.

[b] Enthalpy values expressed in kJ mol^{-1} of SDDS are presented in first brackets. Their standard deviations are within ±4%.

of C_s of course were fairly greater by microcalorimetry than tensiometry. The CMC_e values by both the methods of tensiometry and calorimetry were nearly comparable. The C^* values were fairly higher and close to that produced by JR400. The endothermicity for CAC formation increased whereas that for free micelle formation remained practically unchanged (Table 3).

The coacervation related turbidity patterns of the three studied composites hardly witnessed any difference (Fig. 8, inset B). Almost symmetrical flat-top bell-shaped profiles were observed with increasing [SDDS] in the mixture. The first inflection, T_1 in turbidimetry observed for JR400 was absent; all the three compositions yielded more or less the same T_2 (maximum turbidity) values. The final point, T_3 (solubilization of the coacervates into the free micellar solution) only showed a mild increase with the increased proportion of JR400 in the mixtures. Both T_2 and T_3 for the mixtures in overall respect were reasonably higher than their individuals. The mixed polymers were favorably coacervated consuming greater [SDDS] and showed greater stability than their individuals. In the overall perspectives, the interfacial behaviors of the mixed systems were guided by the more hydrophobic LM200 whereas the bulk behaviors were fairly controlled by the JR400 component.

4. Conclusion

The carbohydrate polymer, JR400 has cationic centers in the molecule while the other member, LM200 has distinct $-C_{12}H_{25}$ hydrophobic residue along with cationic quaternary ammonium centers in it. Their modes of interaction with the anionic amphiphile Sodium N-Dodecanoyl Sarcosinate, SDDS, are although primarily of electrostatic in origin, hydrophobicity plays a fair role for LM200. Thus, at and beyond CAC normal small micellar entities are formed and anchor in the polymer segments and contours of JR400 whereas mixed micelles are formed by the combinations of the hydrophobic cationic substituents and the DDS^- ions of SDDS associating with segmental regions and folds for LM200. The CAC formation is thus more favorable with LM200 than JR400. Since the molar mass of the former is lower than the latter, the other parameters C_s, C^*, T_2, T_3 and CMC_e are all also lower for LM200 than JR400. The coacervation starts much earlier for LM200 making the initial turbidity point, T_1 indistinct for the polymer, which for JR400 is distinct. In presence of salt (NaCl) both CAC and CMC_e of SDDS decrease by electrostatic screening effect; likewise several other interaction parameters also decrease. The mixed polymer combinations evidence an overall synergism in their interaction behavior with SDDS. In presence of excess SDDS than C_s, the coacervates acquire overall negative charge and disintegrate into smaller entities, which ultimately opens up by way of electrostatic repulsion. The solution becomes clear consisting of micelle decorated polymer complexes embedded in the surrounding of free micelles. At the end, we may add that the amphiphilic salt SDDS (of a moderately week acid, HDDS) may influence the pH of the aqueous solution through acid–base equilibria and hence affect the interaction parameters. The measure change in pH of the studied systems was only 0.5 unit, which was enough low to affect the aggregation behaviors of SDDS.

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References

Antunes, F. E., Thuresson, K., Lindman, B., & Miguel, M. G. (2003). A rheological investigation of the association between a non-ionic microemulsion and hydrophobically modified PEG: Influence of polymer architecture. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 215*, 87–100.

Bai, G., Catita, J. A. M., Nichifor, M., & Bastos, M. (2007). Microcalorimetric evidence of hydrophobic interactions between hydrophobically modified cationic polysaccharides and surfactants of the same charge. *Journal of Physical Chemistry B, 111*, 11453–11462.

Bai, G., Nichifor, M., Lopes, A., & Bastos, M. (2005). Thermodynamic characterization of the interaction behavior of a hydrophobically modified polyelectrolyte and oppositely charged surfactants in aqueous solution: Effect of surfactant alkyl chain length. *Journal of Physical Chemistry B, 109*, 518–525.

Basu Ray, G., Ghosh, S., & Moulik, S. P. (2009). Physicochemical studies on the interfacial and bulk behaviors of sodium *n*-dodecanoyl sarcosinate (SDDS). *Journal of Surfactants and Detergents, 12*, 131–143.

Burke, S. E., & Palepu, R. (2001). Interactions of a hydrophobically modified cationic cellulose ether derivative with amphiphiles of like charge in an aqueous environment. *Carbohydrate Polymers, 45*, 233–244.

Burke, S. E., Palepu, R., Hait, S. K., & Moulik, S. P. (2003). Physicochemical investigations on the interaction of cationic cellulose ether derivatives with cationic amphiphiles in an aqueous environment. *Progress in Colloid and Polymer Science, 122*, 47–55.

Chakraborty, I., & Moulik, S. P. (2007). Self-aggregation of ionic C10 surfactants having different headgroups with special reference to the behavior of decyltrimethylammonium bromide in different salt environments: A calorimetric study with energetic analysis. *Journal of Physical Chemistry B, 111*, 3658–3664.

Chakraborty, T., Chakraborty, I., & Ghosh, S. (2006). Sodium carboxymethylcellulose–CTAB interaction: A detailed thermodynamic study of polymer–surfactant interaction with opposite charges. *Langmuir, 22*, 9905–9913.

Chakraborty, T., Chakraborty, I., Moulik, S. P., & Ghosh, S. (2007). Physicochemical studies on pepsin–CTAB interaction: Energetics and structural changes. *Journal of Physical Chemistry B, 111*, 2736–2746.

Chatterjee, A., Moulik, S. P., Majhi, P. R., & Sanyal, S. K. (2002). Studies on surfactant–biopolymer interaction. I. Microcalorimetric investigation on the interaction of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) with gelatin (Gn), lysozyme (Lz) and deoxyribonucleic acid (DNA). *Biophysical Chemistry, 98*, 313–327.

Dai, S., & Tam, K. C. (2001). Isothermal titration calorimetry studies of binding interactions between polyethylene glycol and ionic surfactants. *Journal of Physical Chemistry B, 105*, 10759–10763.

Dan, A., Chakraborty, I., Ghosh, S., & Moulik, S. P. (2007). Interfacial and bulk behavior of sodium dodecyl sulfate in isopropanol−water and in isopropanol−poly(vinylpyrrolidone)−water media. *Langmuir, 23*, 7531–7538.

Dan, A., Ghosh, S., & Moulik, S. P. (2009a). Physicochemical studies on the biopolymer inulin: A critical evaluation of its self-aggregation, aggregate-morphology, interaction with water, and thermal stability. *Biopolymers, 91*, 687–699.

Dan, A., Ghosh, S., & Moulik, S. P. (2009b). Physicochemistry of the interaction between inulin and alkyltrimethylammonium bromides in aqueous medium and the formed coacervates. *Journal of Physical Chemistry B, 113*, 8505–8513.

Deo, P., Jockusch, S., Ottaviani, M. F., Moscatelli, A., Turro, N. J., & Somasundaran, P. (2003). Interactions of hydrophobically modified polyelectrolytes with surfactants of the same charge. *Langmuir, 19*, 10747–10752.

Dhoot, S., Goddard, E. D., Murphy, D. S., & Tirrell, M. (1992). Surface force measurements on cationic polymer/hyaluronic acid mixtures on mica. *Colloids and Surfaces, 66*, 91–96.

Exerowa, D., Kashchiev, D., & Platikanov, D. (1992). Stability and permeability of amphiphile bilayers. *Advances in Colloid and Interface Science, 40*, 201–256.

Feitosa, E., Wyn Brown, W., & Hansson, P. (1996). Interactions between the nonionic surfactant $C_{12}E_5$ and poly(ethylene oxide) studied using dynamic light scattering and fluorescence quenching. *Macromolecules, 29*, 2168–2178.

Fosdick, L. S. (1956). Clinical experiment on the use of sodium n-lauroyl sarcosinate in the control of dental caries science. *Science, 123*, 988–989.

Goddard, E. D., & Leung, P. S. (1992). Capillary pressure behavior in pores with curved triangular cross-section: Effect of wettability and pore size distribution. *Colloids and Surfaces, 65*, 221–230.

Goddard, E. D. (1986a). Polymer–surfactant interaction part I: Uncharged water-soluble polymers and charged surfactants. *Colloids and Surfaces, 19*, 255–300.

Goddard, E. D. (1986b). Polymer–surfactant interaction part II: Polymer and surfactant of opposite charge. *Colloids and Surfaces, 19*, 301–329.

Goldraich, M., Schwartz, J. R., Burns, J. I., & Talmon, Y. (1997). Microstructures formed in a mixed system of a cationic polymer and an anionic surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 125*, 231–244.

Griffiths, P. C., Hirst, N., Paul, A., King, S. M., Heenan, R. K., & Farley, R. (2004). Effect of ethanol on the interaction between poly(vinylpyrrolidone) and sodium dodecyl sulfate. *Langmuir, 20*, 6904–6913.

Guillemet, F., & Piculell, L. (1995). Interactions in aqueous mixtures of hydrophobically modified polyelectrolyte and oppositely charged surfactant: Mixed micelle formation and associative phase separation. *Journal of Physical Chemistry, 99*, 9201–9209.

Hait, S. K., Majhi, P. R., Blume, A., & Moulik, S. P. (2003). A critical assessment of micellization of sodium dodecyl benzene sulfonate (SDBS) and its interaction with poly(vinyl pyrrolidone) and hydrophobically modified polymers, JR 400 and LM 200. *Journal of Physical Chemistry B, 107*, 3650–3658.

Lanigan, R. S. (2001). Final report on the safety assessment of cocoyl sarcosine, lauroyl sarcosine, myristoyl sarcosine, oleoyl sarcosine, stearoyl sarcosine, sodium cocoyl sarcosinate, sodium lauroyl sarcosinate, sodium myristoyl sarcosinate, ammonium cocoyl sarcosinate and ammonium lauroyl sarcosinate. *International Journal of Toxicology, 20*, 1–14.

Li, Y., & Dubin, P. L. (1994). Structure and flow in surfactant solution. In C. A. Herb & R. H. Prud'homme (Eds.), *ACS symposium series 253* (pp. 587). Washington, DC: American Chemical Society.

Lundin, M., Macakova, L., Dedinaite, A., & Claesson, P. (2008). Interactions between chitosan and SDS at a low-charged silica substrate compared to interactions in the bulk: The effect of ionic strength. *Langmuir, 24*, 3814–3827.

Majhi, P. R., & Moulik, S. P. (1998). Energetics of micellization: Reassessment by a high-sensitivity titration microcalorimeter. *Langmuir, 14*, 3986–3990.

Margolin, A., Sherstyuk, S. F., Izumrudov, V. A., Zezin, A. B., & Kabanov, V. A. (1985). Enzymes in polyelectrolyte complexes: The effect of phase transition on thermal stability. *European Journal of Biochemistry, 146*, 625–632.

Maulik, S., Dutta, P., Chattoraj, D. K., & Moulik, S. P. (1998). Biopolymer–surfactant interactions. 5: Equilibrium studies on the binding of cetyltrimethyl ammonium bromide and sodium dodecyl sulfate with bovine serum albumin, β-lactoglobulin, hemoglobin, gelatin, lysozyme and deoxyribonucleic acid. *Colloids and Surfaces B: Biointerfaces, 11*, 1–8.

Meier, W., Hotz, J., & Gunther-Ausborn, S. (1996). Vesicle and cell networks: Interconnecting cells by synthetic polymers. *Langmuir, 12*, 5028–5032.

Mitra, D., Bhattacharya, S. C., & Moulik, S. P. (2008). Physicochemical studies on the interaction of gelatin with cationic surfactants alkyltrimethylammonium bromides (ATABs) with special focus on the behavior of the hexadecyl homologue. *Journal of Physical Chemistry B, 112*, 6609–6619.

Mitra, D., Bhattacharya, S. C., & Moulik, S. P. (2009). A LB film morphological study with reference to biopolymer–surfactant interaction taking gelatin–CTAB system as a model. *Biophysical Chemistry, 139*, 123–136.

Mun, S., Rho, S.-J., & Kim, Y.-R. (2009). Study of inclusion complexes of cycloamylose with surfactants by isothermal titration calorimetry. *Carbohydrate Polymers, 77*, 223–230.

Rajstein, J., Fuks, M., Markitziu, A., & Gedalia, I. (2007). Solubility of enamel powder following treatment with s sodium-n-lauroyl sarcosinate containing toothpaste in the presence and absence of fluoride. *Journal of Oral Rehabilitation, 10*, 469–471.

Regismond, S. T. A., Winnik, F. M., & Goddard, E. D. (1996). Surface viscoelasticity in mixed polycation anionic surfactant systems studied by a simple test. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 119*, 221–228.

Sen, S., Sukul, D., Dutta, P., & Bhattacharyya, K. (2002). Solvation dynamics in aqueous polymer solution and in polymer–surfactant aggregate. *Journal of Physical Chemistry B, 106*, 3763–3769.

Sokolov, E., Yeh, F., Kohkhlov, A., Grinberg, V., & Chu, B. (1998). Nanostructure formation in polyelectrolyte–surfactant complexes. *Journal of Physical Chemistry B, 102*, 7091–7098.

Thalberg, K., & Lindman, B. (1989). Surface force measurements on cationic polymer/hyaluronic acid mixtures on mica. *Journal of Physical Chemistry, 93*, 1478–1483.

Thongngam, M., & McClements, D. J. (2005). Influence of pH, ionic strength, and temperature on self-association and interactions of sodium dodecyl sulfate in the absence and presence of chitosan. *Langmuir, 21*, 79–86.

Tsekov, R., & Ruckenstein, E. (1993). Effect of thermal fluctuations on the stability of draining thin films. *Langmuir, 9*, 3264–3269.

Wang, Y., Kimura, K., Huang, Q., & Dubin, P. L. (1999). Effects of salt on polyelectrolyte–micelle coacervation. *Macromolecules, 32*, 7128–7134.

Winnik, F. M., & Regismond, S. T. A. (1996). Fluorescence methods in the study of the interactions of surfactants with polymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 118*, 1–39.