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Behavior of the Amphiphile CHAPS Alone and in Combination with the Biopolymer Inulin in Water and Isopropanol−Water Media

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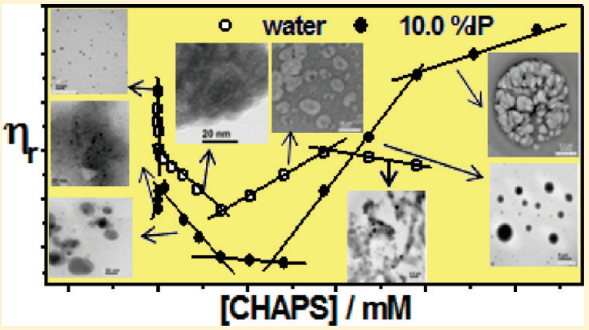
ABSTRACT: Self-aggregation of the zwitterionic surfactant 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS) in water and isopropanol−water media, and interaction of the amphiphile with the biopolymer inulin in these media were investigated. The micellar properties of the zwitterionic surfactant and its associated interfacial and bulk properties along with the related energetic, and aggregation number were determined. The different stages of interaction of the CHAPS−inulin combines were identified and assessed. The complexes were formed and aggregated in solution at different stages of their molecular compositions. The aggregated sizes were determined by dynamic light scattering study and the morphology in the solvent removed states were examined using scanning electron microscope and transmission electron microscope techniques. The results witnessed formation of ensembles of varied and striking patterns.



INTRODUCTION

The ternary interacting systems of polymer−surfactant−water are useful in processes such as detergency, cosmetics, paints, drug encapsulation, enhanced oil recovery, coatings, and so forth.[1−5] The involved research areas are of both academic and practical interests.[6−8] The field is being continuously cultivated using materials and their combinations; additives like alcohols are used (especially in cosmetics and pharmaceutics) for modification and controlling dispersity, solubility, and stability.[9,10] Such additives may behave like "cosurfactants"[11,12] to decrease critical micelle concentration (CMC), and "cosolvents" to enhance medium hydrophobicity and consequently increase CMC depending on their types and concentration.[13] They are thus used in the formation/preparation of disperse systems viz., micelles, emulsions, vesicles, gels, and so forth,[14−17] and also used in the reactivity of redox couple reactions.[18] These additives thus influence the fundamental properties of amphiphile, polymer, and their mutual interaction. For bio- and environmental friendly formulations along with nontoxic polymers and amphiphiles, isopropanol (IP) as solvent[19] and isopropyl myristate (IPM)[20] as nonpolar medium have potential uses. Although such combinations are in use, and are being continuously developed by the scientists, in terms of practical needs, the progress is still meager providing scope for further research. In this study, we have experimented with a less studied biopolymer (inulin) and a nontoxic (benign) amphiphile (3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS)) in both water and IP−water media to look into their interactions to produce results that would lead to their uses in pharmacochemical and biophysicochemical fields. By the use of IP, the ternary inulin−CHAPS−water combine becomes a quaternary system with interesting physicochemistry. Such quaternary systems have been only limitedly studied.[19a,41]

The biopolymer inulin is a β (2→1) fructosyl fructose unit containing polydisperse polysaccharide (Scheme 1A) having many uses and applications. It is a fat replacer, a favorable diabetic food ingradient, and an agent to promote growth of intestinal bacteria and increase absorption of both calcium and magnesium.[21−23] We have recently studied the solution behavior of inulin and observed that inulin forms aggregated globules in aqueous medium[24] and also exhibits distinct solution properties in aquo, aquo-dimethyl sulfoxide (DMSO) and aquo-IP media.[25] The biopolymers was found to form prolate type aggregates in water, bullet shaped assemblies in DMSO−water, and in IP−water the ensembles produced fingerprint type morphology.[25]

CHAPS is a zwitterionic derivative of cholic acid having combined properties of both sulfobetaine type detergents and bile salts.[26] It is frequently used in membrane protein isolation, surface modifier for specific protein adsorption, protein solubilization, purification, and denaturation.[26,27] It behaves as a neutral compound over a pH range (2−12), and does not exhibit conductivity or electrophoretic mobility.[26] Contrasting conventional surfactant with polar head and alkyl chain, it has a typical rigid steroid structure as that of cholic acid with three hydroxyl groups in α plane (Scheme 1B) whose orientation essentially

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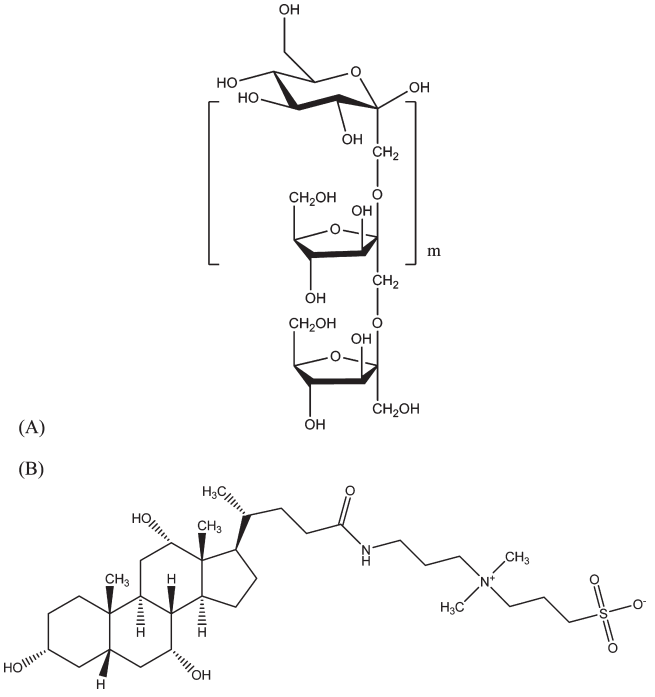
Scheme 1. Molecular Structure of (A) Inulin and (B) CHAPS



determines its properties.[28] The CMC of CHAPS has been reported to be in the range of 5.4 to 11 mM depending on solution condition.[29−31] The self-aggregation of CHAPS has been studied in various buffer solutions, but its surface properties and related thermodynamics are only scantly investigated. In recent years, Giacomelli et al.[32] and Sugihara et al.[33,34] have studied the surface and adsorption properties of CHAPS as well as its mixed micelle formation with bile salts and *N*-acyl(octa, nona and decanoyl)-*N*-methylglucamides (MEGA) surfactant series. In a recent study, Zhang et al.[35] reported two types of concentration-dependent aggregation and related morphologies of CHAPS in deuterium oxide solution. The study of the solution behavior of CHAPS is not extensive; its interaction with polymers in solution has been only limited.[36] CHAPS is a biocompatible amphiphile with prospects for using in pharmacy and medicine.

We have thus taken a detail experimental endeavor on the solution properties of CHAPS, i.e., its interfacial (Gibbs monolayer) and bulk behavior in aqueous and aquo-IP media by a number of techniques (tensiometry, fluorimetry, calorimetry and viscometry). The interaction of inulin with CHAPS in aqueous medium and IP−water medium was also investigated in detail. The hydrodynamic sizes of the polymer−surfactant interacted species in solution were determined by the dynamic light scattering (DLS) method. The morphologies of the pure inulin and its surfactant interacted complexes at different stages of interaction were investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM) methods. The physicochemistry of the behavior of CHAPS and CHAPS−inulin combines in their ternary and quarternary states was explored, and their pragmatic discussions are presented in what follows.

EXPERIMENTAL SECTION

(A). Materials. The inulin (from chicory) was a 99% pure product of Sigma (U.S.A.). Its weight average molar mass determined[17] by the static light scattering method was 4468 g mol^{-1}. Inulin isolated from natural sources ranges between (4000−6500) g·mol^{-1}. CHAPS was a product of Dojindo Laboratories, Kumamoto, Japan. Pyrene, cetylpyridinium chloride (CPC), and tryptophan were AR-grade products of Sigma, India. The IP was also AR-grade quality material from SRL (India). These materials were used as received. The concentration of the desiccated inulin used is expressed in weight percent throughout the text. Doubly distilled water (specific conductance, κ = 2−3 μs cm^{-1} at 303 K) was employed for preparation of all solutions.

(B). Methods. *(i). Tensiometry.* A calibrated Krüss (Germany) tensiometer, based on the du Noüy platinum ring detachment method, was used to measure the surface tension (γ) at the air/solution interface. Concentrated solution of CHAPS (150 mM) was stepwise added as required with the help of a Hamilton microsyringe in solvent or inulin solution (taken in a double-walled container) maintained at 303 ± 0.1 K. The surface tension was measured allowing ∼10 min for CMC determination and 20 min for the inulin−CHAPS interacting system equilibration following initial mixing for 5 min after each addition. The γ values were accurate within ±0.1 mN m^{-1}.

(ii). Viscometry. An Ubbelohde viscometer of 136.8 s average flow time for 13 mL water at 303 K was used in the study. It was placed in a thermostatted water bath of accuracy ±0.1 K. The solvent medium or inulin solution was taken in the viscometer, and concentrated surfactant solution was progressively added in stages with Hamilton microsyringe, and the flow times of the solutions were measured after thorough mixing and thermal equilibration. The standard deviations of the measured viscosities were within ±0.5%. Each set of measurements was duplicated, and their flow times were close. The mean values were recorded and used.

(iii). Fluorimetry. Fluorescence measurements were taken in a Perkin-Elmer LS 55 (U.S.A.) luminescence spectrometer. In the determination of the CMC of CHAPS and inulin−CHAPS interaction, pyrene (0.1 μM) was used as a probe. The excitation wavelength was 332 nm, and the emission spectra were recorded in the range of 350−500 nm. A concentrated surfactant solution either in solvent or in polymer solution was added to the same solvent/solution (also containing 0.1 μM pyrene) in multisteps and measuring the fluorescence intensity in each step after thorough mixing. The CMC of CHAPS, and the stages of interaction for the polymer−surfactant combinations were determined from the plot between the ratio of the intensities of the first (373 nm) and third (383 nm) vibronic peaks (I_1/I_3) versus [CHAPS] in the usual way.

The aggregation number (n_A) of the CHAPS micelle and inulin-induced CHAPS micelles above the critical aggregation concentration (CAC) were determined at 358 nm from the static fluorescence quenching (SFQ) of tryptophan (the probe at concentration 0.1 μM) by the quencher CPC. The excitation wavelength of tryptophan was 275 nm, and the emission spectra were recorded in the range of 290−480 nm. The fluorescence intensity was measured at each stage of addition of CPC in the surfactant solution. In the determination of n_A of CHAPS micelles, tryptophan was found to be a better option than pyrene. The latter produced nonconsistent high values, in disagreement with literature reports.[43,44] Hence, pyrene fluorescence measurements were taken to find out the polarity index (I_1/I_3) values and the CMC of CHAPS micelles; tryptophan was used for obtaining the n_A values.

In the SFQ method, the relation used for obtaining the aggregation number was

$$ln\left(\frac{F_0}{F}\right) = \frac{n_A[\mathrm{CPC}]}{[CHAPS]_t - \mathrm{CMC\ or\ CAC}} \quad (1)$$

where F_0 and F represent nonquenched and quenched fluorescence intensities, respectively, $[\mathrm{CHAPS}]_t$ is the total concentration of CHAPS in solution, and [CPC] is the concentration of the quencher added in the system. The linear plots between $\ln(F_0/F)$ versus [CPC] yielded n_A from the slope.

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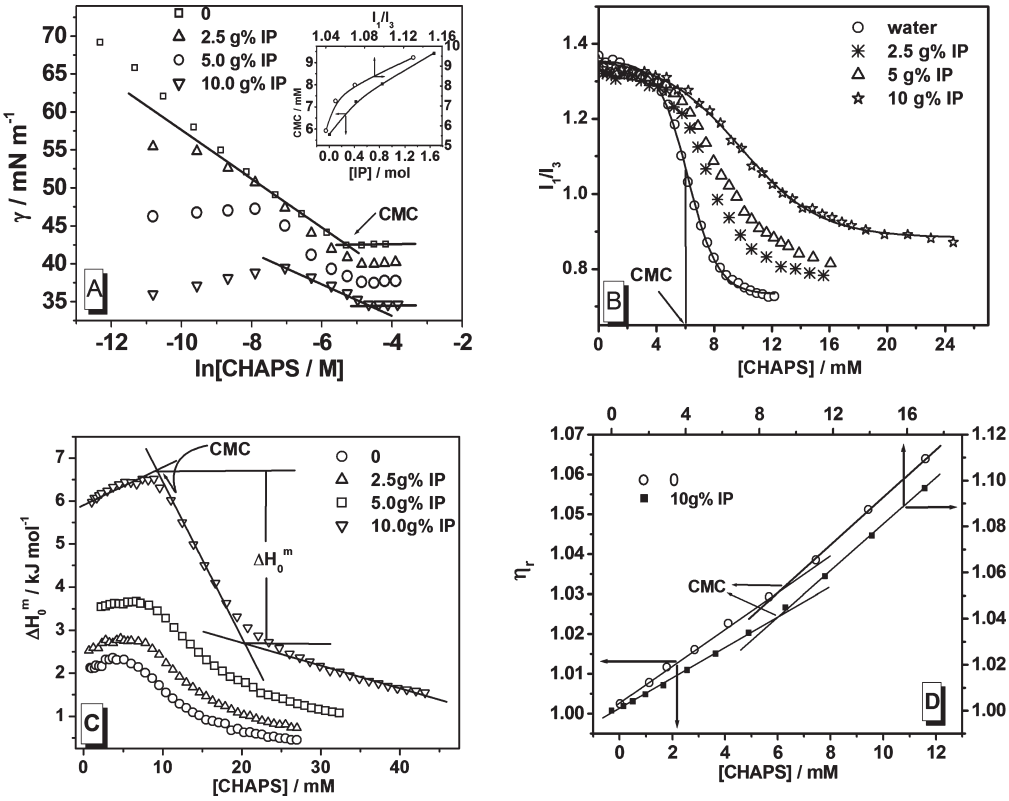

Figure 1. Determination of the CMC of CHAPS in water and IP−water media at 303 K by (A) tensiometric, (B) fluorimetric, (C) microcalorimetric, and (D) viscometric methods.

(iv). Microcalorimetry. An OMEGA isothermal titration calorimeter (ITC) of MicroCal (Northampton, MA, U.S.A.) was used for thermometric measurements. During measurements, temperature was kept constant by circulating water by a Neslab RTE100 (U.S.A.) water bath at 5 K below the temperature in the calorimetric cell (303 K) as per recommended procedural requirement. The temperature in the calorimetric cells was accurate within ±0.01 K. The heat released or absorbed at each step of dilution of surfactant solution in either water or in inulin solution was recorded, and the enthalpy change per mole of injectant was calculated with the ITC software. The reproducibility was checked from repeat experimentations. Further details of the method and data processing can be found in the literature.[37,38]

(v). Dynamic Light Scattering. DLS measurements were taken at 173° angle in a Malvern Zetasizers Nano-zs apparatus with a He−Ne laser (λ = 632 nm) at 298 K. The sample cells were placed in a temperature-controlled, refractive index-matched bath filled with cis−trans decahydronaphthalene (decalin). All experimented solutions were filtered 3−4 times through membrane filters (porosity 0.25 μ) to remove dust particles. The mean values of duplicated experiments are reported.

(vi). Transmission Electron Microscopy. The TEM measurements on samples were taken with a JEOL JEM 2010 (Tokyo, Japan) high-resolution transmission electron microscope (HRTEM) operating at 200 kV. For preparing the TEM sample, a drop of the desired solution was placed onto the carbon-coated copper grid giving some time for spreading. It was subjected to slow drying under vacuum. Under such conditions, morphological changes of the sample were considered minimal.

(vii). Scanning Electron Microscopy. SEM measurements were taken in an FEI, Quanta 200 (Netherlands). A drop of the inulin/inulin−CHAPS interacted sample solution was placed on a piece of glass slide giving time for spreading; after solvent removal it was spin coated on a stab followed by gold−palladium coating under a pressure of 10^{-1} mbar.

RESULTS AND DISCUSSION

Amphiphile Behavior of CHAPS in Water and IP−Water Media. The solution behavior of CHAPS in water and IP−water media was examined by tensiometry, fluorimetry, microcalorimetry, and viscometry methods. Typical experimental findings are illustrated in Figure 1A−D. Tensiometry plots have clearly indicated the self-association of the amphiphile in water and mixed (IP−water) solvent. Similar were the findings from calorimetry, fluorimetry, and viscometery as exemplified in the figure. In the plots, the locations of the CMC are identified. In fluorimetry, the first derivatives of the Sigmoidal courses between I_1/I_3 and [CHAPS] were considered as CMCs from the inflection points. A comprehensive exhibit of the results is presented in Table 1. The average values of the CMCs obtained from the different methods are also reported in the table. In the aqueous medium, it is 5.76 mM; in literature,[29,30] it ranges between 5.4 and 11.0 mM. A comparison of our results with the published reports may not be straightforward, since the self-aggregation of CHAPS depends on various factors, such as pH, ionic strength, solvent medium, temperature, and so forth. Being zwitterionic, CHAPS has been studied at various pH in the range 2−12; in the present study, we studied it under neutral conditions (pH, 6.8) in water, and in IP−water (pH, 6.72) at 303 K without adding any other agent to influence the process. We have observed the increase in CMC by the addition of IP in the medium. IP produced nonpolarity in the medium and acted as a cosolvent to hinder the aggregation process, and hence the CMC increased. The polarity increment (I_1/I_3) ratio of the first and third vibration peaks of the pyrene fluorescence at CMC are given in column 7 in Table 1. In terms of both polarity (I_1/I_3) and

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Table 1. CMC, Interfacial Properties, and Energetics of Micellization of CHAPS in Water and IP−Water Media at 303 K[a,b,c,d]

	CMC											
[IP]/g %	ST	Flr	Mcal	Vis	Avg.	I_1/I_3 at CMC	Γ_{max} x10^6	A_{min}	$-\Delta G^0_{ad}$	$-\Delta G^0_m$	$-\Delta H^0_m$	ΔS^0_m
0	5.10	6.18	5.64	6.10	5.76	1.04	1.53	1.08	50.8	23.1	1.54	71.0
2.5	7.08	7.58	6.90	7.46	7.25	1.05	1.36	1.22	51.9	22.5	1.71	68.7
5	7.91	8.24	7.91	8.15	8.05	1.07	1.13	1.47	55.5	22.3	2.04	66.7
10	9.46	9.81	9.25	9.20	9.43	1.13	0.89	1.86	60.7	21.8	4.03	58.7

[a] The $d\gamma/d \log C$ factor was obtained from the slope of their γ versus log C plots. π_{CMC} = surface pressure of amphiphile at the air/water interface at CMC ($\gamma_{water} - \gamma_{CMC}$); N = Avogadro's number. [b] CMC, Γ_{max}, A_{min}, ΔG^0_{ad}, ΔG^0_m, ΔH^0_m, and ΔS^0_m are expressed in mmol dL^{-1}, mol m^{-2}, nm^2 molecule^{-1}, kJ mol^{-1}, kJ mol^{-1}, kJ mol^{-1}, and J mol^{-1} K^{-1}, respectively. Errors in CMC_{ave}, I_1/I_3, Γ_{max}, A_{min}, ΔG^0_{ad}, ΔG^0_m, ΔH^0_m, and ΔS^0_m were ±6 (with out IP, ± 11%), ± 7, ± 8, ± 6, ± 3, ± 7, ± 6 and ±10%, respectively. [c] The CMC of CHAPS obtained at 1 and 2 g % IP−water were 6.84 and 7.41 mM, respectively, by fluorimetry at 303 K; in 1 and 2 g % EtOH−water, the CMC values were 8.04 and 8.92 mM, respectively. [d] The relation used for calculation of the parameters

$$\Gamma_{max} = -\frac{1}{2.303RT}\lim_{C \to CMC}\frac{d\gamma}{d\ log\ C}; \quad A_{min} = \frac{10^{18}}{N\Gamma_{max}}; \quad \Delta G^0_{ads} = \Delta G^0_m - \frac{\pi_{CMC}}{\Gamma_{max}}$$

molarity of IP, the CMC increment trends are presented in the inset of Figure 1A. As reported, above a certain concentration of alkanol, micelle formation becomes doubtful or nonexistent.[39,40] We have observed that above 10 g% IP, micelle formation of CHAPS was doubtful, and scattered data of a measured physical property without convincing breaks were observed. Although alkanols are often considered cosurfactants (at low concentration) and cosolvents (at higher concentration), here IP acted like a cosolvent (it increased the CMC at the studied concentrations). IP broke the water structure, decreasing the spontaneity of micelle formation. Dan et al.[41] reported that at IP g % less than 6.62, the alkanol acted like a cosurfactant, and decreased the CMC of sodium dodecylsulfate (SDS). Usually alkanols behave as cosurfactant at low concentration and cosolvent at higher concentration; consequently the CMC of a surfactant initially decreases, and increases at higher concentration, producing a minimum in the CMC−[alkanol] plot. Such results are reported in recent literature for SDS both in IP−water[41] and ethanol−water[42] media. Similar behavior was also observed by Desnoyers and his group[11] from the thermodynamic transfer functions of surfactants from water to mixed alkanol−water media (including IP). On the other hand, for CHAPS, decrease in CMC in lower amphiphile concentration was not observed in IP−water as well as in ethanol−water media (see footnote *c*, Table 1). Thus, CHAPS behaved differently from SDS because of the presence of OH groups in the molecule, which possibly interacted with the IP by way of conformation changes of the amphiphile. To resolve the issue, more studies on different types of surfactants are required in different alkanol−water media.

The solution behavior of CHAPS was further studied from the determination of the micelle aggregation number, n_A in the studied media. The n_A value was found to be 15 in water, and 6, 4, and 3 in 2.5, 5.0, and 10 g % aquo-IP media, respectively, by the SFQ method. In literature, n_A of CHAPS micelles in aqueous solution was reported to be 10 and 8 through apparent surface tension[43] and light scattering[44] measurements, respectively. Lowering of n_A by the presence of nonaqueous solvent in water was also reported earlier.[45−48] The decrease was found to be appreciable. By its structure breaking effect, IP replaced water from the solvation domain[49] of micelle, and affected the aggregation property of CHAPS. Further, CHAPS has a rigid steroid structure (Scheme 1B) like the bile acid, cholic acid,[50] with three hydroxyl groups in the α plane whose orientation should determine its properties. Like bile acids, it showed low aggregation number in water.[51] In the presence of IP, n_A became much reduced by way of conformational changes in the presence of interacting IP molecules in the medium.

From the calorimetric experiments, the standard enthalpy of micellization of CHAPS (ΔH^0_m) was evaluated (cf. Figure 1C for the estimation rationale); the values are listed in Table 1. It was observed that the standard free enthalpy values were low and became progressively more exothermic by the increased presence of IP in the medium. The standard Gibbs free energy change (ΔG^0_m) of micellization and the corresponding changes in the entropy (ΔS^0_m) were also evaluated following the standard procedure;[29] these values are also presented in Table 1. In the calculation of ΔG^0_m, the relation $\Delta G^0_m = RT \ln X_{CMC}$ (where X_{CMC} is the CMC of CHAPS expressed in mole fraction units) was used. The $\Delta G^0_m \gg \Delta H^0_m$, hence the process was essentially entropy controlled. Since CHAPS fall in the steroid class and are structurally close to cholic acid, also with three OH groups in the molecule, their ΔH^0_m values deserve a comparison. At 303 K, ΔH^0_m(CHAPS) and ΔH^0_m(sodium cholate, NaC)[52] in aqueous medium were found to be −1.54 and 0.53 kJ mol^{-1}, respectively. Usually, nonionic[52,53] and zwitterionic[54,55] surfactants produce endothermic ΔH^0_m, but ΔH^0_m(CHAPS) was exothermic. Neither the steroid skeleton nor the molecular neutrality spoke in favor of ΔH^0_m of CHAPS. Energetically, it behaves with a separate identity. In the presence of IP in the medium, that identity became more prominent with increasing magnitude of the exothermic ΔH^0_m.

In addition to the above, the Gibbs surface excess (Γ_{max}) of CHAPS at the air/water interface as well as the minimum area covered by the amphiphile headgroup (A_{min}) and the Gibbs free energy of adsorption (ΔG^0_{ad}) at the CMC were also estimated. The surface excess of CHAPS decreased with increase in the amount of IP, which may be explained as due to decrease in the solvophobicity of the medium on replacing water by IP. The relations used for the calculation are given in footnotes *a* and *d* of Table 1. The ΔG^0_{ad} values were all greater than the ΔG^0_m values; the adsorption process was more spontaneous than the process of micellization; their average ratio was 2−3, depending on solvent composition suggesting 2- to 3-fold efficacy of the former process than the latter. Interestingly, the initial part of the tensiometric profiles (Figure 1A) continuously changed with higher proportion of IP in the medium. The stepwise declining state with negative slope became almost parallel (nearly zero slope) at 5 g % IP followed by a distinct positive slope at 10 g % IP

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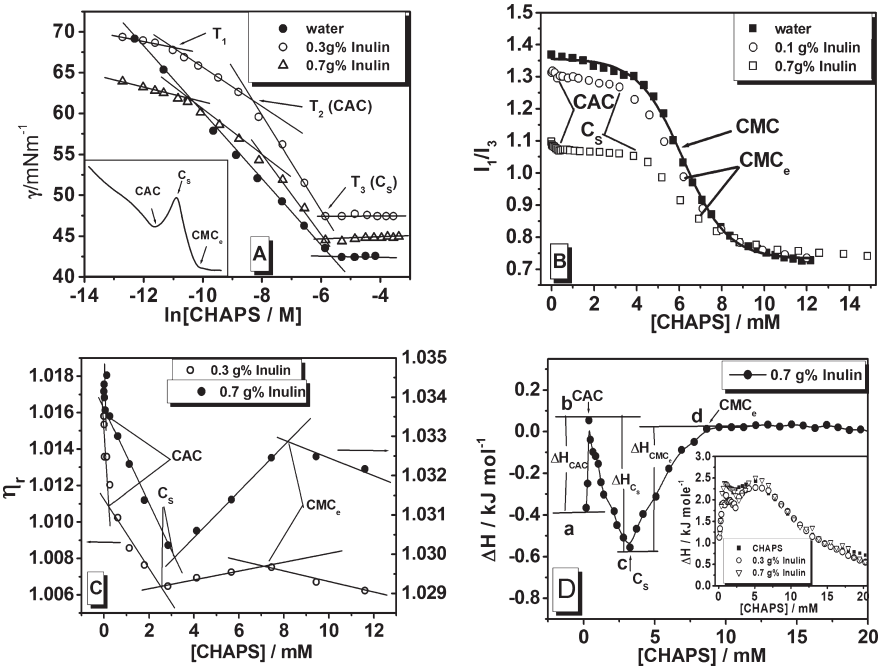

Figure 2. (A) Tensiometric profile for inulin−CHAPS interaction with dilution of CHAPS at 303 K. (B) Variation of I_1/I_3 versus [CHAPS] for the dilution of CHAPS and in the presence of polymer at 303 K. (C) Relative viscosity versus [CHAPS] for the interacting system of inulin−CHAPS; transition points are indicated in the diagram at 303 K. (D) Difference curve of titration of inulin solution (0.7 g%) and CHAPS in water at 303 K. Inset: Enthalpogram for the dilution of CHAPS in water and in the presence of polymer at 303 K.

in the medium, which attained a maximum γ and then declined. The surface active IP lowered the γ of the mixed solvent ~35 mN m^{-1} that increased to ~40 mN m^{-1} at [CHAPS] = 0.86 mM. In the IP−water medium, a partition equilibrium for IP between the interface and the bulk prevailed. The added CHAPS interacted with IP through their OH groups, forming a complex, consequently disturbing the partition equilibrium. Since IP molecules left the interface for the bulk to reestablish the distribution equilibrium causing the γ to increase, the process continued up to [CHAPS] = 0.86 mM. The CHAPS started to get adsorbed at the interface and caused decline in γ. Upon surface saturation, the tension remained constant at the point of micelle formation. This was the principle of decreased solvophobicity (mentioned above) that caused decrease in Γ_{max} of CHAPS with increasing proportion of IP in the medium. The increased presence of IP at the interface also reduced the concentration of CHAPS to decrease its excess there.

Interaction of CHAPS with Inulin in Aqueous Solution. The solution behavior of CHAPS changed by its interaction with inulin in aqueous solution. The cationic amphiphiles alkyltrimethylammonium bromides (ATABs) were found to fairly interact with inulin in aqueous solution.[56] The zwitterionic amphiphile CHAPS also interacted fairly by way of hydrogen bonding and hydrophobic interaction. The tensiometric, fluorimetric, viscometric, and calorimetric probing results (displayed in Figure 2A−D) clearly supported the phenomenon. The polymer inulin is moderately water-soluble (5 g%); it weakly reduces the surface tension of water by nearly 3 mN m^{-1} at 303 K. Normally, by the interaction of a polymer with an amphiphile, a state of CAC appears, wherefrom induced small micelles start to form in the system, and get bound to the polymer at specific sites, which completes at a concentration called the saturation concentration, C_s. From that state, amphiphile monomers populate the interface and start forming normal micelles in solution at the saturation point, CMC_e (called the extended CMC).[57−60] In many systems, the polymer−micelle complex with its changed molecular configuration forms viscous solution and/or become turbid due to the formation of coacervates (associated complex ensembles) that disintegrate in the excess presence of normal micelles making the solution less viscous and less turbid (kind of translucent and homogeneous).[61] These phenomena modify the results of the probing process of addition of amphiphile in a medium in the absence of a polymer. Such results for the CHAPS−inulin interacting system are illustrated in Figure 2A−D. Distinct points of CAC, C_s, and CMC_e are marked in the displayed profiles; the results are also presented in Table 2. Of the four different displays in the figure, that of tensiometry showed features different from interacting polymer−amphiphile systems normally reported in the literature.[56,62,63] A probable explanation of the fact is given in the following with reference to the results displayed in Figure 2A.

In the beginning of addition in solution, amphiphile monomers start binding to the polymer sites, and after a certain stage of addition (depending on the type of the combination), the CAC state appears. The decreasing γ versus ln[amphiphile] profile normally shows a break wherefrom the formed hydrophilic amphiphile−polymer complex at the interface is transferred into the bulk, making the interface free of both amphiphile and polymer; as a result γ increases until the polymer gets saturated with the induced small micelles at the point of saturation, i.e., C_s, in the bulk. On further addition, the amphiphile molecules start to crowd the interface, resulting in a decrease in γ that continues until the interface is saturated; hence normal free micelle formation in the bulk begins causing a distinct break in the plot at CMC_e (cf. inset Figure 2A for a nonscale to scale general profile). In the present study, of the three breaks in tensiometry

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Table 2. Interaction Characteristic of CHAPS with Inulin in Aqueous Medium at 303 K[a, b, c]

	tensiometry			fluorimetry			viscometry			microcalorimetry		
[inulin]/g % (w/v)	T_1	T_2	T_3	CAC	C_s	CMC_e	CAC	C_s	CMC_e	CAC	C_s	CMC_e
0.1	0.011	0.25	2.82	0.21	2.43	6.21	0.25	2.77	7.11	0.31	2.15	6.04
										(0.26)	(−0.39)	(0.37)
0.3	0.013	0.22	2.87	0.26	2.69	6.52	0.21	3.09	7.49	0.32	2.40	6.92
										(0.32)	(−0.41)	(0.44)
0.5	0.015	0.24	3.31	0.23	2.82	6.73	0.20	3.22	7.98	0.29	2.76	7.69
										(0.35)	(−0.61)	(0.50)
0.7	0.020	0.26	3.38	0.20	2.96	7.21	0.24	3.79	8.30	0.28	3.22	8.61
										(0.46)	(−0.74)	(0.68)
1.0	0.035	0.34	3.85	0.23	3.95	8.83	0.26	4.10	8.61			

[a] T_1, T_2, T_3, CAC, C_s, and CMC_e are given in mM. Their errors are within ±5−8%. [b] Enthalpy values in parentheses are expressed in kJ mol^{-1}. Their errors are within ±4%. [c] In the experiments, dilution of polymer by the addition of CHAPS solution was within 2−3%. It is neglected in the data presentation.

(T_1, T_2 and T_3), T_2 and T_3 on the whole corresponded to CAC and C_s, respectively, found from other methods (fluorimetry, viscometry and calorimetry); T_1 remained unassigned. It is considered that after CAC, the amphiphile-complexed inulin (being neutral) preferred the interface (instead of sinking in the bulk), causing γ to decrease after CAC until the C_s point was reached, wherefrom the free micelle solution injected in the system rearranged by dilution and started to stay in solution making $C_s \equiv CMC_e$. The interface remained covered by both CHAPS monomers, and the inulin−CHAPS complex, and hence the bulk process of CHAPS−inulin interaction after C_s, could not be registered by the interface sensitive method of tensiometry. Consequently, the $C_s \equiv CMC_e$ (by tensiometry) is less than CMC_e (by other methods). This equivalence of C_s with CMC_e is a unique example of polymer−amphiphile interaction, which is rarely found in the literature.[62−64] We may mention here that tensiometric profiles for the interaction of inulin with octadecyltrimethylammonium bromide (OTAB) showed almost nonchanged (flat) courses between CAC and C_s, and decline thereafter, which was also an uncommon finding.[56]

The η_r versus [CHAPS] courses without and with inulin showed large differences. In the presence of the polymer, a decrease of η_r was observed up to C_s with a prior break at CAC because of increased compactness in the configuration of the complex. After C_s, the complex expanded by way of interaction with CHAPS, causing increase in viscosity up to CMC_e. In the post CMC_e stage, in a free micellar environment, the assembled complexes disintegrated to smaller entities with decrease in the solution viscosity as reported earlier.[56,62]

The enthalpogram for the dilution of concentrated solution of CHAPS (25-fold CMC) in water and aqueous inulin solution of 0.3 and 0.7 g % are exemplified in the inset of Figure 2D. The resultant enthalpogram for 0.7 g % (heat of dilution subtracted display) is presented in the main diagram. The crest at b and the trough in the profile at c stood for CAC and C_s, respectively, followed by a rise meeting at the point of zero slope, i.e., d ≡ CMC_e . The height a → b represented ΔH_{CAC}, the length b → c represented ΔH_{Cs}, and the height c → d stood for ΔH_{CMCe}. This is a rational way of estimating the enthalpy values associated with the processes in support of the modulation profile of the resultant enthalpogram of interaction of CHAPS with inulin.

The resultant enthalpogram has distinctive features, which are lacking in the enthalpogram obtained without subtraction of the enthalpy of amphiphile dilution (inset plot). Upon addition of concentrated solution (≫CMC) of CHAPS in inulin solution, to start with (up to the CAC point and beyond), demicellization and dilution of the amphiphile takes place followed by interaction with the polymer (inulin). In the advanced stage of addition, heat of micellar dilution followed by interaction with the polymer (by way of micelle disruption/reformation and binding) contributes to the enthalpy of the process, which continues up to the CMC_e point, wherefrom the heats of dilution of CHAPS without and with inulin merge together. The different involved processes between CAC and CMC_e are better understood by the subtraction of heats of dilution of CHAPS in water from those observed in the presence of the polymer (the subtracted heats rationally become zero in the post CMC_e stage (Figure 2D)).

The parameters presented in Table 2 by different methods are on the whole matching; the observed small to moderate differences/anomalies are ascribed to the sensitivity differences of the methods and the measurement uncertainties. The CAC values were found to be independent of the methods and [inulin]. The calorimetric results were ∼12% greater. The C_s and CMC_e values were [inulin] dependent but, on the average, fairly matching the results found from other methods. Polymer concentration-independent CAC values of surfactants are found in the literature.[57,65] The enthalpies for both CAC and CMC_e formation were endothermic, whereas the micelle binding to inulin was exothermic. All these observed enthalpies represented the resultants of various related (specific and non specific) processes whose deciphering is a hard task. Such attempts are rarely found in the literature.[57,66,67] The endothermicity of CAC formation had a major component coming from the release of water molecules by the entry of amphiphiles to form smaller micelles, which was followed by the exothermic binding of the micelles to the vacant sites and their adjacents that continued up to C_s. In the post-C_s stage, the prime processes (micellar dilution followed by breakdown and reorganization by the action of the polymer in solution) proceeded with absorption of heat up to the critical stage of CMC_e to make the enthalpy of the process endothermic.

For more understanding of the interaction process, SFQ experiments were used to assess the aggregation number (n_A) of the bound micelles of CHAPS with the inulin at concentrations of 0.1−1.0 g % using eq 1. In the experiment, the [CHAPS]

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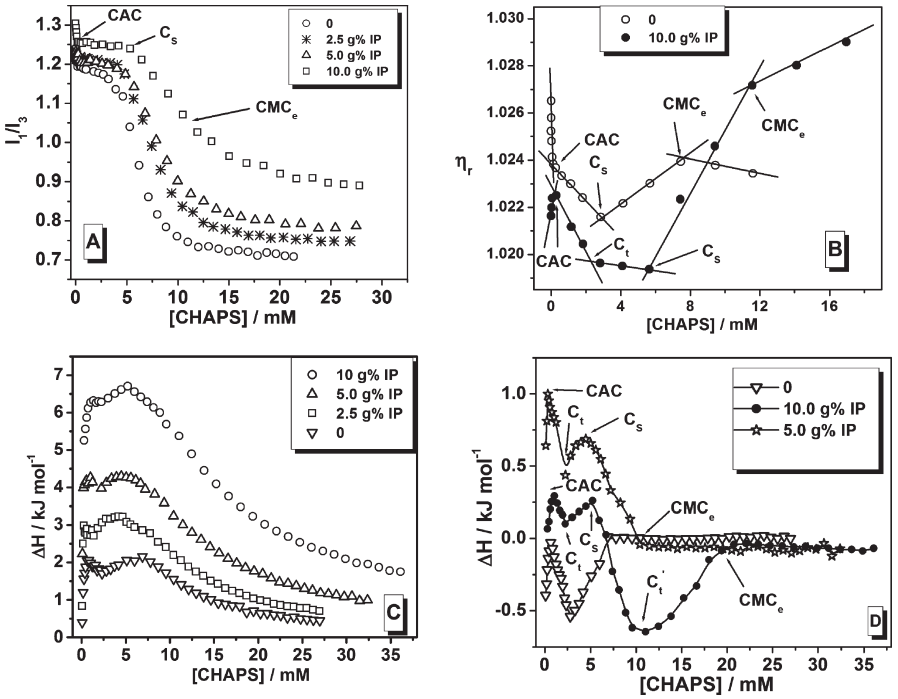

Figure 3. (A) I_1/I_3 versus [CHAPS] for inulin−CHAPS systems in aquo and aquo-IP media at 303 K. (B) Relative viscosity versus [CHAPS] for the interacting system of inulin−CHAPS in aquo and aquo-IP (10 g %) media at 303 K. (C) Enthalpogram for the dilution of CHAPS in water and water−IP at 303 K. (D) Difference curve of titration of inulin solution in water and water−IP media at 303 K.

Table 3. Interaction Characteristic of CHAPS with Inulin in IP−Water Medium at 303 K

	fluorimetry			viscometry				microcalorimetry[a, b]			
[IP]/g %	CAC	C_s	CMC_e	CAC	C_t	C_s	CMC_e	CAC	C_t	C_s	CMC_e
0	0.23	2.82	6.73	0.20		3.22	7.98	0.29		2.76	7.69
								(0.35)		(−0.61)	(0.50)
2.5	0.25	4.13	8.32	0.12	1.19	4.38	9.15	0.15	0.66	3.74	8.62
								(0.35)	(−0.70)	(0.33)	(−0.52)
5.0	0.43	4.58	9.10	0.20	2.33	4.88	10.6	0.31	2.24	4.45	10.4
								(0.36)	(−0.57)	(0.25)	(−0.72)
10.0	0.61	5.26	10.5	0.26	2.54	5.65	11.6	0.95	2.29	5.23	11.1
								(0.23)	(−0.19)	(0.16)	(−0.90)

[a] CAC, C_s, C_t and CMC_e are given in mM. Their errors are within ±5−8%. For 10 g % IP, $CMC_e \cong C_t'$ in Figure 3D. The expected CMC_e at $\Delta H = 0$ in the graph (Figure 3D) was 20.0 mM; see text for comment). Enthalpy values in parentheses are expressed in kJ mol^{-1}. Their errors are within ±4%. [b] In the experiments, dilution of polymer by the addition of CHAPS solution was within 2−3%. It is neglected in the data presentation.

was 1.85 mM (>CAC) and the average CAC found from the four methods (0.26 mM) was considered. The n_A values determined on the whole remained nearly constant (6, 8, 8, 8, and 6) with changed [inulin] of 0.1, 0.3, 0.5, 0.7, and 1.0 g %, respectively. The reports on the aggregation number of polymer-bound surfactant aggregates (CAC) can be found in the literature.[68−70] Turro et al.[71] reported the aggregation number of the polymer-bound micelles of poly(vinylpyrrolidone) (PVP)−SDS combination by the dynamic fluorescence quenching probe method that produced values 30−40% smaller (25−45) than those for SDS micelles in the absence of polymer (60−70). The n_A of CHAPS micelles in aqueous medium herein determined by the SFQ method (mentioned above) was 15. The inulin bound micelles of CHAPS were ∼50% smaller than that without inulin.

Interaction of CHAPS with Inulin in IP−Water Medium. Interaction of CHAPS with inulin in IP−water medium is discussed with reference to Figure 3. The results (shown in Table 3) on CAC were grossly independent of solvent composition. However, at 10 g % IP, both fluorimetry and calorimetry produced higher CAC values. This matched with the increased CMC of CHAPS in IP−water medium compared to that in water. The presence of IP enhanced the CAC values by their mutual interaction. It was found that both C_s and CMC_e also increased with increasing IP content in water. The C_s and CMC_e were more influenced by IP compared with CAC.

The nature of the I_1/I_3 versus [CHAPS] plots in water (Figure 2B) and IP−water (Figure 3A) media were comparable; for the viscosity and enthalpy plots they were different. In the

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Table 4. DLS Results of Inulin−CHAPS Interacted Species in Water and IP−Water Media at 298 K

	hydrodynamic diameter (D_h)[a]/nm (PDI)				
[inulin]/g %	0	CAC	C_s	CMC_e	$\gg CMC_e$
0.1	60.1, 210 (0.371)	34.5, 219 (0.408)	88.3, 245 (0.512)	41.7, 188 (0.448)	–
0.3	55.2, 204 (0.566)	44.3, 212 (0.591)	92.7, 353 (1.00)	56.2, 275 (0.818)	–
0.5	57.4, 192 (0.610)	56.1, 201 (0.672)	101, 390 (0.806)	67, 351 (0.541)	–, 151 (0.711)
0.7	55.6, 166 (0.682)	77.2, 194 (0.694)	110, 415 (1.0)	85, 396 (0.685)	–
	D_h for CHAPS interaction inulin (0.5 g%) at various [IP] at 298 K				
[IP]/g %	0	CAC	C_s	CMC_e	$\gg CMC_e$
2.5	45.6, 110 (0.628)	85.9, 321 (0.822)	131, 439 (0.766)	104, 571 (0.583)	84.7, 249 (0.352)
5.0	58.3, 127 (0.662)	68.2, 451 (1.0)	54.5, 682 (0.818)	90.0, 846 (0.865)	94.6, 930 (0.731)
10.0	63.9, 249 (0.719)	174, 580 (0.690)	178, 882 (0.585)	172, 775 (0.435)	196, 1007 (0.783)

[a] Smaller values for D_h^I and larger for D_h^{II} (as introduced in the text). Errors in D_h within ±12%.

viscosity plots in IP−water medium, and extra distinct break between CAC and C_s (marked as C_t) was observed. We consider that after CAC, the small micelles became bound to the polymer in two distinct stages. In the post CMC_e region, while the viscosity mildly declined in water, it moderately increased in 10 g % IP−water medium; by multiple interaction with CHAPS and IP, the polymer configuration expanded to produce viscosity increase. Similar breaks between CAC and C_s were also observed in the enthalpograms (Figure 3D) which is also denoted by C_t. What the fluorimetry failed to sense could be probed by the flow and thermal properties of the system.

In the enthalpograms of 10 g % IP−water medium, a second minimum at C_t' between C_s and CMC_e appeared. This C_t' was comparable with the CMC_e obtained by both fluorimetry and viscometry; the value at zero enthalpy condition (i.e., the expected CMC_e) was much larger (20 mM). Higher percentage of IP in water made distinct differences in the interaction between inulin and CHAPS in solution. The enthalpy values associated with the different involved processes are presented in the parentheses in the calorimetry results following the rationale indicated in Figure 2D. The values were all small, having an increasing trend with increasing IP content in the medium. Such results reported on carbohydrate polymer (modified cationic cellulose)−anionic surfactant (Na-decanoyl sarcosinate) systems were also fairly low.[67]

DLS Results of Inulin−CHAPS Interaction in Water and IP−Water Media. The results of DLS measurements on inulin-CHAPS interaction at different stages, viz., CAC, C_s, CMC_e, and $\gg CMC_e$ in water and IP−water media, are presented in Table 4. Both hydrodynamic diameter (D_h) and polydispersity index (PDI) were determined and presented. In the studied systems, two distinct types of dispersions were observed (Figure 4), producing two sets of results (D_h^I and D_h^{II}) except one (Figure 4B, Table 4 at [CHAPS] $\gg CMC_e$ for 0.5 g % inulin). In the absence of CHAPS, results were virtually independent of [inulin] except at 0.7 g %, where the D_h^{II} value was ∼15% lower than the rest. The hydrodynamic diameters at C_s were all greater than that at CAC, whereas they were all lower at CMC_e (by way of disintegration or fragmentation of the formed assemblies).[72−74] In the IP−water medium, the hydrodynamic diameters increased with increasing presence of IP at all situations with minor variations (2.5 g% at [CHAPS] $\gg CMC_e$). The presence of IP altered the solvent behavior to influence the configuration of the formed complex. Increased environment nonpolarity made the neutral complex expand/swell. The PDI values in water and in IP−water media were fairly high, and, consequently, the configurations of the formed species in the systems were fairly multidisperse.

SEM and TEM Studies of Inulin−CHAPS Complex. Inulin and its complexes with varied [CHAPS] and [IP] were of different types (shapes) and sizes as found from SEM and TEM measurements. In Figure 5, the SEM and TEM images of inulin and its complexes with CHAPS at different levels of compositions are displayed. The SEM and TEM results are identified without and with prime signs, respectively. The images represent dried (solvent removed) samples of the materials. Pure inulin produced two groups of ensembles (globular and bent) in SEM (A), which were two distinct globular forms in TEM (A′). The complex of composition between CAC and C_s evidenced isolated dispersed spheres of nearly homogeneous type by SEM (B), which in TEM (B′) produced smeared fingerprint like arrays. The complex formed in the range C_s and CMC_e evidenced swelled non-homogeneous tubular morphology in SEM (C), and mostly oval shaped rings in TEM (C′). At [CHAPS] > CMC_e, the SEM display (D) looked like disintegrated/deaggergated isolated bodies, which appeared with nearly similar configuration in the TEM image (D′). A′ and D′ revealed two types of particle size distributions with 22 and 135 nm in A′, 66 and 156 nm in B′, respectively. The average dimension of the oval shaped rings in C′ was 1.4 (major axis/minor axis). On the whole, there were two groups of such ensembles. The fingerprint-like portions in

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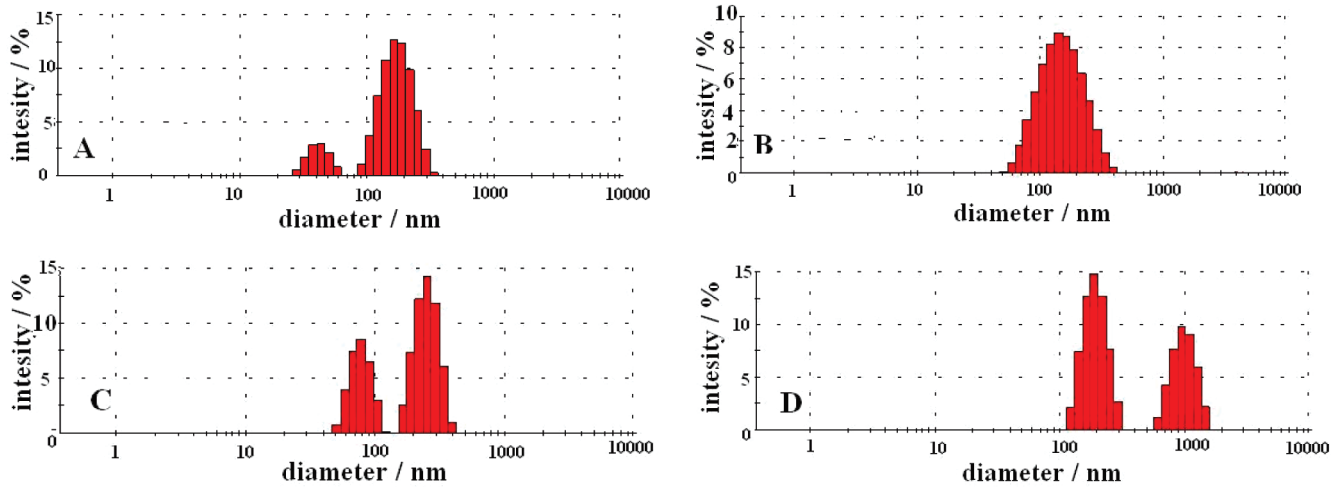

Figure 4. Particle size distribution profiles at 298 K for 0.5 g % inulin: (A) pure inulin; (B) with [CHAPS] ≫ CMC_e in aqueous medium; (C) pure inulin; (D) with [CHAPS] ≫ CMC_e in 10 g % IP-aquo medium.

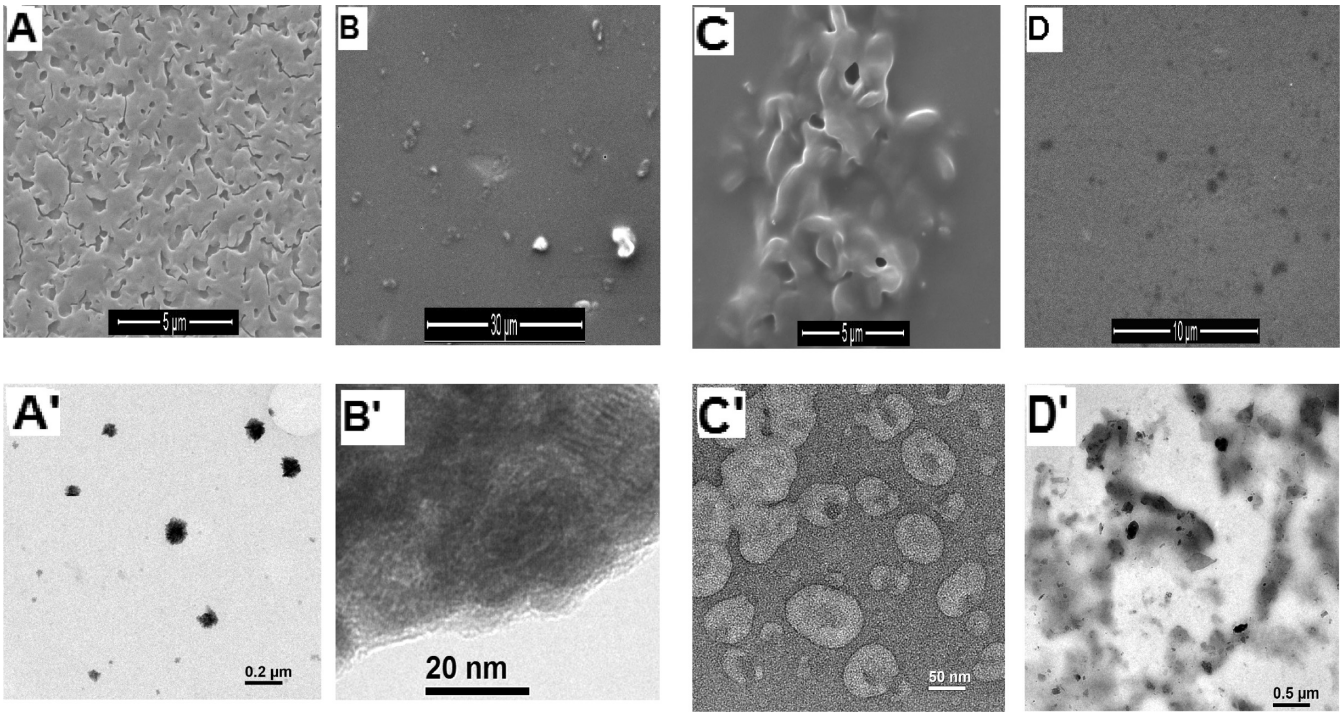

Figure 5. SEM and TEM images of pure inulin (0.5 g %) and inulin(0.5 g %)−CHAPS complex in aqueous medium. SEM: (A) pure inulin; (B) between CAC and C_S; (C) between C_S and CMC_e; (D) with [CHAPS] > CMC_e. TEM: A′, B′, C′ and D′ are respective TEM morphographs of A, B, C, and D of SEM images.

B′ had a spacing of 0.50 nm, and the lines consisted of dots of dimension 1.2 nm.

In 10 g% IP−water medium, both the SEM and TEM images were more varied and distinct (Figure 6). Here also the SEM and TEM displays are identified by letters without and with prime notations, respectively. The SEM picture (A) of pure inulin looked like dispersed cumin seed-like particles, which in TEM (A′) appeared as a fingerprint-like pattern with 2.8 nm spacing consisting of dots of average dimension of 6.2 nm. Between CAC and C_s, conglomerated rice grain-like particles forming an exotic pattern was found by SEM (B). In the corresponding TEM image (B′), globular and near globular type particles of varied sizes were observed. The complex formed in the range of C_s and CMC_e studied by SEM evidenced smaller particles arranged in different patterns (C), which produced perfectly spherical bodies of small, medium, and large sizes in the TEM illustration (C′). This was a striking observation. At [CHAPS] > CMC_e, broken rock-type materials of large size appeared in the SEM picture (D). In the corresponding TEM image (D′), loosely arranged ensembles of small to large globular and near globular particles forming spherical entities were observed. In increased concentration of IP in the medium, the formation of particles of varied geometries

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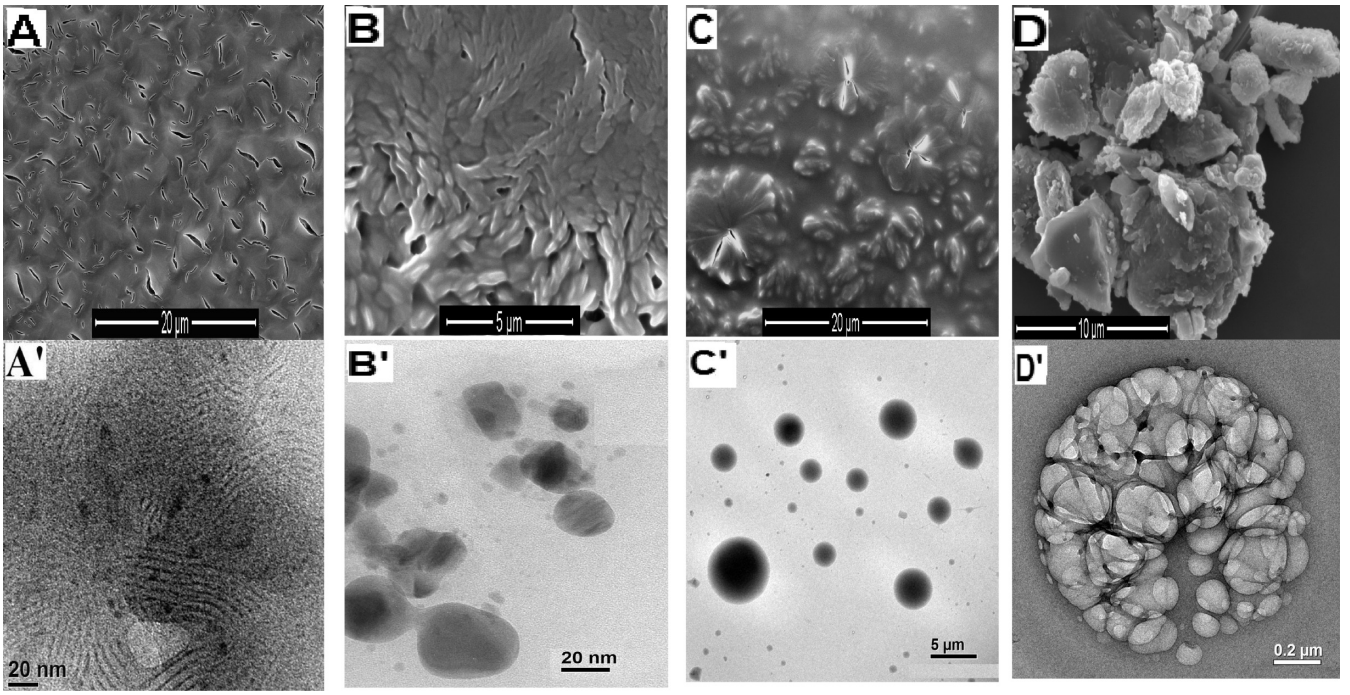

Figure 6. SEM and TEM images of pure inulin (0.5 g %) and inulin(0.5 g %)−CHAPS complex in 10 g % IP-aquo medium. SEM: (A) pure inulin; (B) between C_t and C_s; (C) between C_s and C_t'; (D) with [CHAPS] > CMC_e. TEM: A′, B′, C′ and D′ are respective TEM morphographs of A, B, C, and D of SEM images.

and patterns was observed. The possibilities of their uses as biological materials warrant exploration.

■ CONCLUSIONS

Polymer−surfactant interaction studies and the products formed thereby are important and useful investigations having application potentials in pharmaceutics, drug delivery, synthesis of nanoparticles, and so forth. The plan of studies in this area thus requires (i) detailing of existing and allied studies with explanation of the phenomena observed, and (ii) innovating and selecting newer systems and investigating their behaviors with multiple types of measurements for a clear understanding. The presently studied system falls in a new category in this field, where the biopolymer inulin having many potential uses remains mostly unexplored/unattained in terms of interaction with surfactants and lipids. Similarly, the environment and biofriendly surfactant CHAPS has been only limitedly studied for its surface chemical and interaction with polymers. We have endeavored to understand the solution behavior of CHAPS in water and IP−water media and also examine its interaction with inulin in the media, and understand the way they interact, the products that are formed in the process, and the dimensions and morphologies of the ensembles formed in solution for possible uses of the interacted products (materials).

The amphiphile (CHAPS) self-aggregates in water; in IP−water medium, the process occurs with increased concentration and ∼60% decrease in aggregation number in the studied concentration range of 2.5−10 g %. IP acts as a cosolvent with water in this range unlike other surfactants. The surface-active IP molecules compete with CHAPS for accommodation at the interface, affecting the Gibbs monolayer with (i) decreased surface excess (at the CMC points), and (ii) concomitant increased area per headgroup of CHAPS molecule with increasing concentration of IP in the medium. The study of ternary systems of water with a pair of surface-active materials (IP and CHAPS) and information on their interfacial adsorption from solution are rare, which makes the present study novel and worth pursuing. The presence of IP makes the micellization process less spontaneous with increased exothermicity and decreased process entropy.

The ternary system of water, inulin, and CHAPS produces CAC, C_s, and CMC_e, with CAC independent but both C_s and CMC_e dependent on [inulin]. In the quarternary system of water, inulin, IP, and CHAPS, all the parameters formed with differences. In addition to the above, an intermediate transition between CAC and C_s, called C_t, is registered in the viscosity and calorimetry profiles. The CHAPS aggregate-bound inulin produces structural changes of the formed complex in two stages prior to reaching the stage of C_s, which is nonresponsive to the system micropolarity, and thus produces no inflection in the I_1/I_3 versus [CHAPS] plots. However, the system enthalpy also shows an inflection between CAC and C_s. Additionally, an extra inflection is produced in the enthalpogram of 10 g % IP with a second change at C_t between C_s and CMC_e. Thus, interaction of CHAPS evidence different types of manifestations whose monitoring depends on the methodology adopted for exploration.

The CHAPS−inulin combination different types of products with varied consistencies (viscosities) and configurations by intermolecular interaction and self-assembly formation. The sizes of the overall dispersions (assuming spherical bodies) are found from DLS study to be on the higher side of nanodimensions. IP produces expanded and swelled sizes compared to those without it. SEM and TEM images show distinct morphologies and shapes of different types, some of which appear exotic. The varied proportions of CHAPS and IP interacting with inulin

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produce materials whose utility values in drug encapsulation and delivery as templates for nanomaterial synthesis and pharmaceutical formulations need to be explored. It may be added that the study of such a quaternary system is a complex issue. We have presented and discussed a number of features of the interaction phenomenon, and attempted their interpretation with some speculations. Further detailed study in this direction using varied experimental techniques would be worthwhile.

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Notes

§Deceased.

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