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Rheological and Fluorescence Investigation of Interaction between Hexadecyltrimethylammonium Bromide and Methylcellulose in the Presence of Hydrophobic Salts

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The interaction of hexadecyltrimethylammonium bromide (HTAB) and methylcellulose (MC) has been investigated in aqueous medium employing rheological and fluorescence probing experiments. The associated physicochemical properties of the polymer−surfactant mixed system such as critical aggregation concentration (cac), critical micelle concentration (cmc), micellar aggregation number (N), micellar micropolarity index (pyrene I_1/I_3 values), and viscosity curve are studied as a function of HTAB concentration. The effects of sodium benzoate (NaBz), sodium hexanoate (NaHx) and sodium chloride (NaCl) on the behavior of the polymer−surfactant solution have been followed systematically. The obtained experimental findings unfold significant information with respect to the effects of the salts on the solution behavior of the mixed system in addition to gelation characteristics.

Introduction

Interactions involving ionic surfactants and nonionic polymers in aqueous solutions have been the focus of intense research activity in recent decades in view of their intrinsic fundamental interest and extensive practical applications in a number of industrial and technological fields.[1−3] Hydrophobically modified water-soluble polymers constitute a special class of macromolecules and are highly interesting and important due to their unusual rheological characteristics and widespread use as viscosity modifiers in various commercial formulations such as enhanced oil recovery, pharmaceuticals, foods, paints, cosmetics, personal care products, and so forth.[1−10] Methylcellulose (MC), the hydrophobically modified derivative of cellulose, exhibits interesting thermoreversible gelation in aqueous solution, and the phenomenon has been fairly well studied.[11−22] The gelation of MC is considered to be the result of hydrophobic association of methyl groups at higher temperatures when water becomes a poorer solvent for the polymer. The solubility of MC in water at low temperatures is reported to be due to the formation of cage-like water structures enclosing hydrophobic groups of MC. A number of factors, e.g., the type and concentration of surfactants and salts, temperature, pH, and so forth, alter the degree of hydrophobic association and affect the viscosity and gelation temperature of MC.[19−22] It is established that the interaction of surfactant with the polymer starts at a critical concentration, the critical aggregation concentration (cac), which is much lower than the critical micelle concentration (cmc) of pure surfactant. The surfactant may adsorb on the polymer chain in the form of monomeric units and/or form mixed micelles with the hydrophobic segments of the polymer depending on the concentration and the polymer−surfactant system. With the progress of the process and formation of polymer−surfactant complex, the properties of the mixed system undergoes char-

acteristic changes that can be monitored employing appropriate methodologies.[23−26]

The interactions of cationic surfactants with polymers compared with that of the anionic ones have been found to be considerably weak.[27−29] A few studies involving tetra- and hexadecyltrimethylammonium chloride and bromide (TTAC, TTAB, HTAC and HTAB) surfactants and cellulose ethers such as MC, carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC) and ethylhydroxyethyl cellulose (EHEC) have been reported.[17,30−33] Investigations describing the influence of surfactants on the solution properties of MC in detail are conspicuously limited.[22,34] Li et al.[34] studied the effect of varied concentrations of HTAB on the gelation temperature of MC using micro-differential scanning calorimetry (DSC) and rheometry. Partly, this work presents the effect of HTAB concentrations on the rheological behavior of MC with focus on viscosity versus shear rate curves. In addition, the aggregation number of HTAB at various concentrations in the presence of MC were determined using the steady state fluorescence method to develop a correlation between rheological and aggregation behaviors.

Salts are known to affect the properties of polymer−surfactant solutions due to screening of electrostatic interactions. For example, Lindman et al.[35−37] demonstrated the effect of surfactant concentration and salinity on dynamic and rheological features of EHEC−ionic surfactant systems. Dubin et al.[38] showed that surfactant counterions play a direct role in the stabilization of polyethylene oxide (PEO)/sodium dodecyl sulfate (SDS) complexes. Benraou[39] reported that interaction between cesium and tetraalkylammonium dodecylsulfates and PEO or polyvinyl pyrollidone becomes weaker as the hydrophobicity of the surfactant counterion is increased. The effect of salts on the gelation behavior of MC has been documented, with anions being found to be more effective than cations in modulating the properties of MC solutions.[19−21] However, the influence of salts on cac, rheology, and aggregation number (N) of the surfactants in the case of neutral polymer−ionic surfactant

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systems remains unexplored. It is reported that the carboxylates with hydrophobic groups affect the adsorption, micellization, and clouding behavior of single and mixed surfactant combinations in a significantly different way compared with inorganic salts.[40,41] Except for our preliminary studies on the interaction of HPC with hexadecylbenzyldimethyl ammonium chloride in the presence of hydrophobic salts,[42] we are not aware of any investigation on the effect of hydrophobic salts, as additives, on the polymer−surfactant complexation phenomenon and their rheological behavior, although these salts are considered potential candidates for tuning the properties of such polymer−surfactant formulations.

The present investigation deals with the effect of varied concentrations of sodium benzoate (NaBz), sodium hexanoate (NaHx), and NaCl on cac, N, gelation temperature, and viscosity versus shear rate curves of an MC−HTAB system employing rheological and steady state fluorescence probing techniques.

Experimental Section

Materials. MC, with the trade name of Methocel A4C, was purchased from Dow Chemical Company. The original MC was in a form of white fine powder. The manufacture's specifications indicate that the product has an average degree of methoxyl substitution of 1.8 and a number average molecular weight of 41 000. The viscosity range was reported by the manufacturer to be 400 cP at 20 °C for a 2 wt % aqueous solution. The material was used as received without further purification. Prior to use, the MC was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature.

HTAB, NaCl, and NaBz were Sigma-Aldrich products. NaHx was synthesized by neutralizing hexanoic acid (Merck, India) with concentrated sodium hydroxide solution. The salt was precipitated by adding acetone and purified by recrystallization from water with acetone followed by drying under vacuum. Pyrene (99%, Sigma-Aldrich) was purified by sublimation, followed by recrystallization from ethanol prior to use.

Methods. *Preparation of Solutions.* Aqueous solutions of MC (1 wt %) at various concentrations of the surfactant and salt (NaCl, NaBz and NaHx) were prepared by dispersing the weighed MC powder, HTAB, and the salt in deionized and doubly distilled water at 70 °C and then kept at about 10 °C overnight to make the solutions homogeneous and transparent. In the case of the MC (1%)−HTAB mixture, the concentration of HTAB ranged from 0 to 20 mM, while in MC (1%)−HTAB−salt systems, it was fixed (6 mM) and salt concentrations varied from 0 to 50 mM. The obtained solutions were clear and transparent (∼25 °C) and used for determination of aggregation number, viscosity versus shear rate curve and gelation temperature. A concentrated HTAB solution (50 mM) in water or 1% MC solution maintained at desired salt concentrations was prepared separately and, with the help of a Hamilton microsyringe, was gradually added to water or 1% MC solution containing the desired salt concentration for cmc/cac determination.

Fluorimetry. Steady-state fluorescence quenching measurements in pyrene−cetylpyridinium chloride probe−quencher combinations were taken for obtaining the aggregation number of pure HTAB or HTAB/MC systems. The fluorescence emission spectra of pyrene were recorded with a FluoroMax-3 JY Horiba fluorimeter with an excitation wavelength of 335 nm and an emission wavelength of 385 nm. The band-passes for excitation and emission were set at 1 and 0.5 nm, respectively. About 3 mL of surfactant/polymer solution was placed in a 4-mL quartz cell thermostatted at 25 ± 0.1 °C. The pyrene spectrum was scanned in the range of 350 to 400 nm at
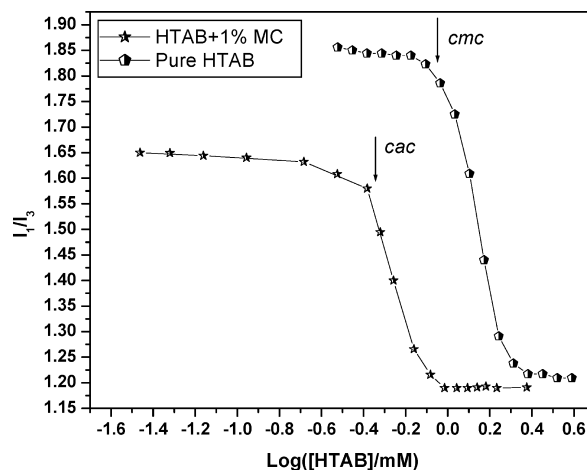
Figure 1. Representative illustration of the variation of I_1/I_3 as a function of the logarithm of surfactant concentration (mM) for HTAB and HTAB+1%MC systems at 25 °C.

a rate of 0.5 nm/s. The I_1 and I_3 intensities were measured corresponding to the emission intensities at 373 and 384 nm respectively. The aggregation numbers were determined from the spectral measurements obtained upon progressive addition of quencher−cetylpyridinium chloride (0−0.2 mM) to the solution of HTAB or HTAB−MC(1%) containing pyrene.

For the determination of cmc/cac, an aqueous solution of MC (1%) at a given salt concentration containing pyrene (2 μM) was taken in a quartz cell, and a stock solution of HTAB/HTAB+MC (1%) having the same concentration of the given salt and pyrene was added progressively by a Hamilton microsyringe, and the spectra were recorded. The plots of the ratio of I_1/I_3 versus [HTAB] yielded cmc/cac values.

Rheological Measurements. A Rheometer AR 2000 (TA Instruments, USA) was used for rheological experiments. Cone and plate geometries were used (cone diameter = 40 mm, cone angle = 1° 59′ 50″ and truncation = 56 μm) for the viscosity measurement and parallel plate geometry was used (diameter = 60 mm and gap = 500 μm) in the peltier plate for the measurement of gelation temperature. A thin layer of low-viscosity silicone oil was used to cover the free surface of the solution to prevent evaporation of solvent. The measurement temperatures were from 20° to 75 °C. The measurements were taken by (i) changing shear rate and (ii) temperature ramp methods. All the dynamic viscoelastic measurements (i.e., temperature sweep) were carried out at frequency of 1 Hz and low shear strains to ensure the linearity of viscoelasticity.

Results and Discussion

Interaction of HTAB with MC in the Absence of Salts. Pyrene I_1/I_3 values measured in aqueous HTAB solution at 25 °C in the absence and presence of 1% MC are shown in Figure 1 as a function of the logarithm of HTAB concentration. The I_1/I_3 ratio of pyrene emission spectra, called micropolarity index, is sensitive to the polarity of the medium sensed by pyrene molecules. The magnitude of the ratio varies directly with the polarity of the medium.[43] It is evident from the figure that, for compositions below the cmc of pure surfactant system, I_1/I_3 values are larger compared to the same in the presence of 1% MC. This effect is ascribed to the presence of hydrophobic domains in the polymer coil available to pyrene molecules even in the absence of HTAB. After the upper plateau region, there is a sharp decrease in the I_1/I_3 ratio, which is due to the progressive solubilization of pyrene into aggregates formed by

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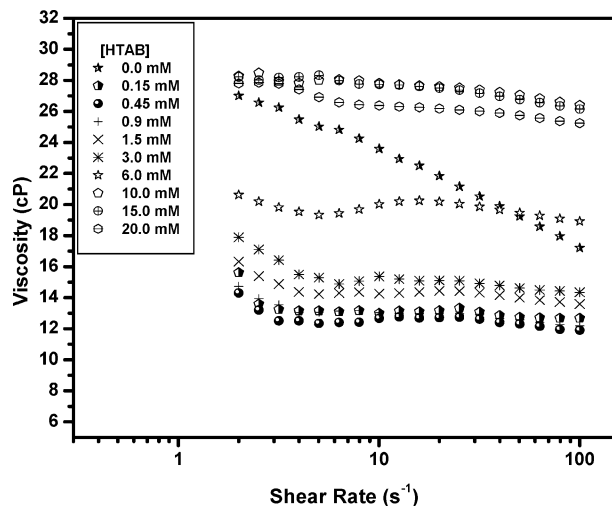
Figure 2. Viscosity curves of 1% MC as a function of shear rate without and with addition of various HTAB concentrations. Legend shows the different concentrations of HTAB used.

Figure 3. Viscosity of 1% MC as a function of HTAB concentration at various shear rates.

hydrophobic residues of polymer together with the hydrocarbon chains of surfactant molecules. This onset of decrease in I_1/I_3 values marks the cmc or cac of surfactant. Therefore the values for cmc or cac were taken as inflection point of such curves. The value of cmc, 0.9 mM, thus obtained for HTAB at 25 °C is in agreement with the literature.[34] The cac value of HTAB (∼0.42 mM) in the presence of MC (1%) is considerably less than its cmc indicating polymer−surfactant interaction. In the presence of MC, the HTA$^+$ ions of HTAB molecules are expected to form complexes with the hydrophobic zones of the MC chains by virtue of hydrophobic interactions, thereby resulting in cac < cmc.[34,44] The lower plateau region in Figure 1 may be attributed to total pyrene solubilization into the micelles for pure HTAB and polymer−surfactant complexes for the HTAB/MC system. Similar values of I_1/I_3 values at the bottom plateau region for HTAB and HTAB/MC systems indicate that MC hardly alters the pyrene-occupied hydrophobic pockets in the aggregates.

The steady-shear viscosity as a function of the shear rate for the pure aqueous 1% MC and HTAB+ MC (1%) systems corresponding to various HTAB concentrations is depicted in Figure 2. The results clearly demonstrate the shear thinning behavior in pure polymer solution. The addition of HTAB (0.15 mM) by contrast significantly reduces the viscosity, which is found to be almost independent of shear rates covered in this study except below 10 s^{-1} where slight shear-thinning is observed. Thus, the addition of HTAB transforms the solution from a non-Newtonian fluid to near Newtonian one. On increasing surfactant concentration, the viscosity decreases slightly up to the cac and shows an increasing trend beyond this point. At higher surfactant concentrations, the viscosity value exceeds that of pure polymer solution crossing over the viscosity−shear rate curve at 6 mM surfactant solution. At each shear rate, the viscosity of the polymer solution increases abruptly above the cac and reaches its maximum value at around 10 mM of HTAB and then shows a slight decrease. This is depicted by Figure 3 at various shear rates. A slight shear thinning is observed at low shear rates up to 6 mM HTAB followed by weak shear rate dependence. However, almost Newtonian behavior is found above this concentration level over the whole range of shear rate investigated.

A recent theoretical study[45] dealing with adsorption of surfactants on a semiflexible polymer proposes that the bound
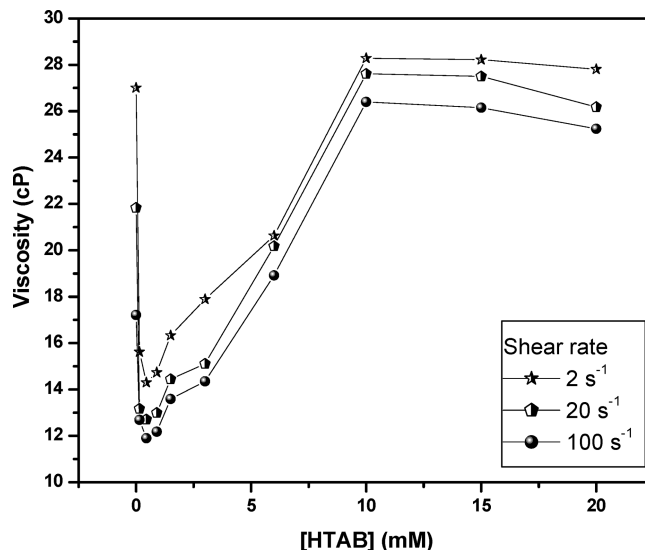
molecules may modify local characteristics of polymer conformation, thereby altering its stiffness and thus driving a coil-to-globule collapse. The abrupt viscosity drop in the EHEC−SDS system[46] having an SDS concentration close to its cmc is considered as an experimental support in favor of this preposition and is explained in terms of intense intramolecular hydrophobic association. In a like manner, the viscosity decrease down to the cac may be ascribed to hydrophobic association leading to intramolecular contraction. The viscosity increase of the mixed system corresponding to the surfactant concentration above the cac may probably be due to the enhanced electrostatic repulsion among the micelles bound on the polymer backbone yielding conformational expansion of polymer chains. The process of chain expansion goes on until the polymer backbone is saturated with micelles. In the present case of the HTAB−MC system, viscosity attains maximum value at 10 mM HTAB (∼10 times cmc of HTAB in water). A small viscosity reduction is observed above this concentration at each shear rate. The phenomenon may be ascribed to the electrostatic screening of the polyme- bound micelle charges or the formation of free micelles leading to the contraction of polymer−surfactant complexes and a consequent viscosity drop.

The aggregation number, N, of micelles in polymer−surfactant systems was determined from steady-state fluorescence data[47−49] using the equation
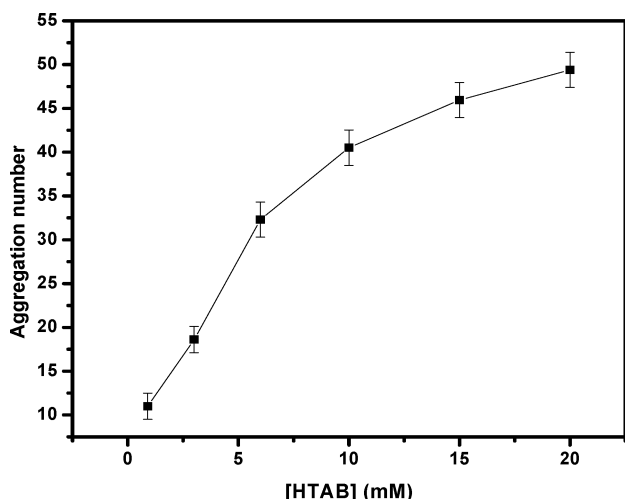
$$\ln\left(\frac{I_0}{I}\right) = N\frac{[Q]}{(C_t - cac)} \qquad (1)$$

where $[Q]$, C_t, and cac are, respectively, the quencher concentration, total surfactant concentration, and critical aggregation concentration of surfactant in the presence of polymer. I_0 and I are the fluorescence intensities in the absence and presence of quencher for the first vibronic peak of pyrene emission spectra. The variation of $\ln(I_0/I)$ as a function of $[Q]$ at various surfactant concentrations in the presence of 1% MC solution is given in Figure 4. The values of N determined from the slopes of the linear fits, at various surfactant concentrations, are plotted in Figure 5 showing that the aggregation number of HTAB micelles at all concentrations is lower in the presence of polymer than in its absence, measured at 6 mM concentration of HTAB

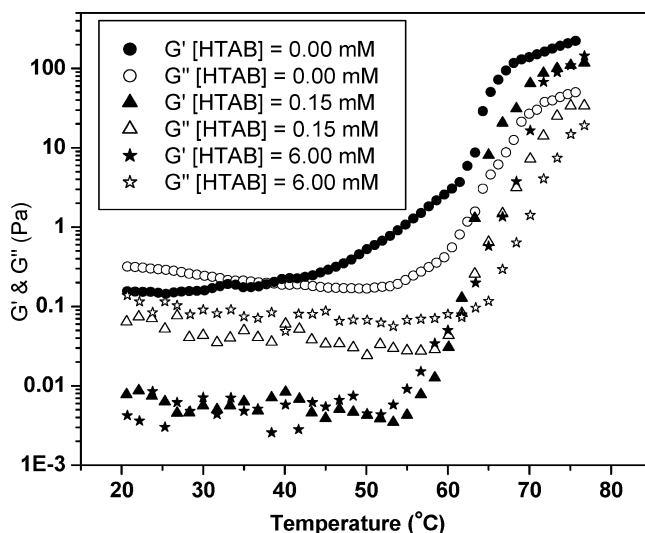**5086** *J. Phys. Chem. A, Vol. 114, No. 15, 2010*

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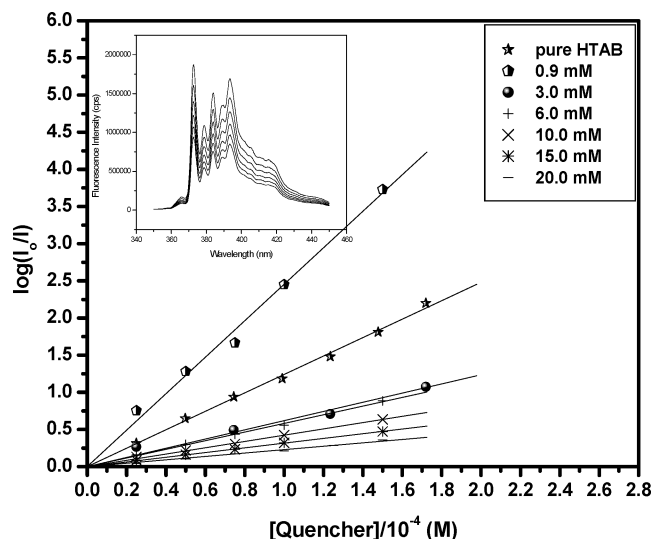
Figure 4. Linear $\ln(I_0/I)$ versus $[Q]$ plot for the determination of the aggregation number of HTAB at various surfactant concentrations at 25 °C. Inset: The basic pyrene fluorescence spectra with increasing concentration of cetylpyridinium chloride quencher.
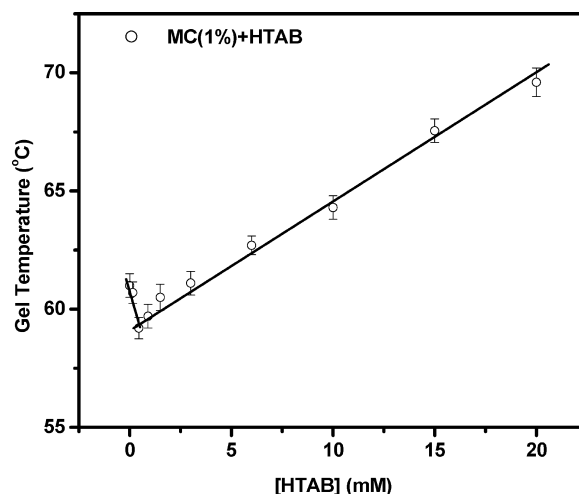

Figure 6. Storage modulus G′ (filled symbols) and loss modulus G″ (open symbols) as a function of temperature in a heating process at about 1 °C/min for 1% MC solution in the absence and presence of various HTAB concentrations.

Figure 5. Variation of aggregation number of HTAB in the presence of 1% MC as a function of [HTAB].

Figure 7. Gelation temperature of 1% MC solution as a function of HTAB concentration.

(59). This weakening of aggregation could be attributed to an indirect effect of the polymer on the solvent properties and/or pyrene solubilization.[25] The N values increase from 11 to 50 with the increase in surfactant concentration, rapid increase being observed up to 10 mM HTAB, and, beyond this, micellar growth slows down at higher concentrations. It may be pointed out that the number of polymer-bound micelles as well as their aggregation numbers increase up to 10 mM HTAB, leading to a large increase in viscosity (Figure 3). However, above this concentration a small increase in N values along with the decrease in viscosity (Figure 3) indicates the generation of free micelles in solution as a result of polymer chain saturation.

In order to investigate the effect of HTAB on the gelation of MC, dynamic viscoelastic measurements were performed at different temperatures for the aqueous 1% MC solution and in the presence of different surfactant concentrations. Figure 6 exhibits three distinct regions for pure polymer solution. The first region is before crossover of the storage modulus (G′) and loss modulus (G″); G′ is lower than G″ indicating viscoelastic behavior of a simple liquid. The two crossover at approximately 38.4 °C and, while continued small decrease of G″ is observed up to 52 °C, G′ gradually increases with the temperature up to

61.5 °C. The high G′ value compared to that of G″ indicates the formation of a weak but elastic structural entity of MC. However, an abrupt increase of G′ above 61.5 °C is found up to the third plateau region at about 68 °C. The crossover of G′ and G″ is usually considered as an indication of polymer gel temperature (GT).[50] However, Li et al.[18,34] on the basis of micro-DSC and rheological studies suggested that abrupt increase in G′ should be taken as GT. The GT of 1% MC thus obtained is plotted as a function of HTAB concentration in Figure 7. It is evident that GT depicts a small decrease initially up to the cac value of HTAB (0.42 mM) followed by linear increase up to the highest concentration (20 mM) used in this study. Similar to the results of Li et al.,[34] we observed a salt-out effect prior to attaining the cac value. However, after the cac, HTAB mainly contributes to GT increase due to salt-in phenomena. Initial salt-out effect may be attributed to the strong interaction of the water molecules with Br⁻ ions furnished by HTAB and consequent competition between the MC chains and Br⁻ for water molecules leading to poor solubility of MC in water. Thus, on heating, aggregation of the hydrophobic groups of MC will be facilitated, resulting in gel formation at a lower temperature in the presence of HTAB. However, the salt-in effect of HTAB may be

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TABLE 1: Critical Micellar Concentration (cmc) and Critical Aggregation Concentration (cac) of Aqueous HTAB and HTAB/MC Systems, Respectively at 298.15 K[a]

	Pure HTAB System		
	cmc/10^{-1} (mM)		
[salt] (mM)	NaCl	NaBz	NaHx
0	9.20	9.20	9.20
5	8.54	1.01	3.09
20	6.56	1.36	1.69
35	4.58	1.82	2.72
50	2.61	2.29	3.55

	HTAB+1%MC System		
	cac/10^{-1} (mM)		
[salt] (mM)	NaCl	NaBz	NaHx
0	4.21	4.21	4.20
5	4.16	0.29	0.23
20	3.77	0.40	0.19
35	3.31	0.79	0.30
50	2.53	1.39	0.48

[a] The average error in cmc and cac is ±3%.
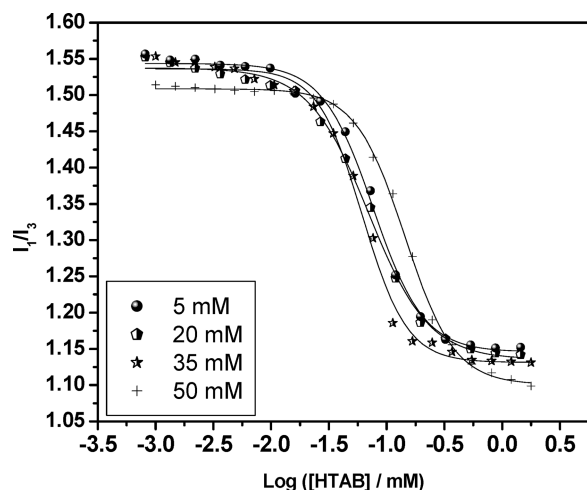
Figure 8. Representative plots of the variation of I_1/I_3 as a function of the logarithm of HTAB concentration for the HTAB+1%MC system in the presence of various concentrations of NaHx at 25 °C.

interpreted on the basis of the formation of micelles on MC chains.[34] Since MC undergoes gelation as a result of hydrophobic association, the surfactant micelles should be removed, facilitating the exposure of the hydrophobic groups to water and eventually helping MC to form gel networks. The proportion of micelles increases with increase in HTAB concentration, and thus high temperature is required to defunct the micelles for the occurrence of gelation.

Interaction of HTAB with MC in the Presence of Salts. *Effect of Salts on cmc and cac Values.* The values of cmc and cac of HTAB in pure aqueous and 1% MC solutions in the presence of different concentrations of NaHx, NaBz, and NaCl obtained from the plots of pyrene I_1/I_3 ratios against HTAB concentration at 25 °C are presented in Table 1. Figure 8 shows a prototype plot of I_1/I_3 versus log[HTAB] at different NaHx concentrations. It is evident from Table 1 that the cmc of HTAB decreases continuously with the increase of [NaCl], while, in case of NaBz or NaHx, a minimum is observed. In the presence of NaBz, a drastic decrease followed by a slow increase is observed. Salts are known to reduce the repulsions between surfactant head groups in the micelles due to their electrostatic

screening effect and hence reduce cmc. However, salts with a hydrophobic moiety are expected to reflect an additional ability to reduce the polarity of water—a factor that contributes to the increase of cmc. In this context, it is expected that the most pronounced decrease in cmc would be observed in the presence of NaCl. However, the results show that the initial decrease in the cmc of HTAB is maximized in NaBz followed by NaHx, and is the least in NaCl. It is well-known[50−52] that the ions with hydrophobic moiety form a mixed micellar entity with surfactants. Thus, in the presence of NaHx, the $C_5H_{11}COO^-$ ions may penetrate into HTAB micelles through their hydrocarbon end with the ionic groups lying in the outer hydrophilic shell of the micelle, eventually leading to charge neutralization in the headgroup region of the micelle along with a simultaneous increase in hydrophobic interactions between the surfactant tails and alkyl chains of the additive. Such effects due to penetration favors micellization and hence decreases cmc values.[41,43,52,53] An NMR study[52,54] has revealed that benzoate ions get solubilized into the micelle even at low concentrations (<1 mM), favoring early micellization. In addition, the Bz^- ions are also likely to get adsorbed on the micellar surface as a result of interaction between the negative electrons of the benzene ring and the positively charged surfactant head groups.[54] This adsorption and penetration of Bz^- ions would be more effective in reducing the cmc compared with Hx^- ions that have hardly any adsorption propensity. In the low concentration range, NaBz as well as NaHx are expected to be more effective than NaCl in reducing cmc due to the combination of significant solubilization and salt effects compared to their solvent polarity lowering effect evidenced by the data in Table 1. The effects of NaBz and NaHx would also depend on the salt concentration, as most of the additives above a certain value will remain in the solution outside the micelles due to their limiting solubilizing power with consequent decrease in solvent polarity ultimately leading to increase in cmc. The reversal of the effects of NaBz and NaHx above a certain concentration indicates balance between the solubilization and salt effects (the factors favoring micellization) and the decreasing solvent polarity effect (the factor disfavoring micellization). In the presence of NaCl, exhibiting only the salt effect, a continuous decrease in cmc is observed.

The cac variation of HTAB with the salt concentration in the presence of 1% MC is similar to that found in the absence of polymer. This can be explained by taking into account the different roles of the salts. NaBz and NaHx furnish hydrophobic Bz^- and Hx^- ions in solution, which tend to get adsorbed on the hydrophobic regions of the polymer due to hydrophobic interactions, thereby imparting on it the polyelectrolyte character with negative charge on the polymer backbone. The resultant effect would enhance early micellization of HTAB favored by hydrophobic interactions with hydrophobic moieties of polymer as well as the electrostatic attraction with adsorbed hydrophobic counterions on the polymer backbone. This reduction in cac values in the presence of NaBz and NaHx by more than 1 order of magnitude supports this explanation (Table 1). With increasing salt concentration, a consequent increase in the concentration of hydrophobic counterions in aqueous phase will result in reduced solvent polarity, thereby disfavoring micellization. It is clearly seen that the cac of HTAB begins to increase above 5 mM and 20 mM concentrations of NaBz and NaHx, respectively, indicating a larger contribution of the latter factor. Therefore, the minimum in cac may be the outcome of the balance between these two factors. The binding of Bz^- ions on the polymer chain may be weaker than that of Hx^- due to

TABLE 2: Aggregation Number (N)^a and I_1/I_3 Values in Pre-, $(I_1/I_3)_{pre}$, and Post-, $(I_1/I_3)_{post}$, Micellar Regions of Aqueous HTAB and HTAB/1%MC Systems in the Absence and Presence of Different Concentrations of NaCl, NaHx, and NaBz at 25°C

[salt] (mM)	NaCl			NaBz			NaHx		
	$(I_1/I_3)_{pre}$	$(I_1/I_3)_{post}$	N	$(I_1/I_3)_{pre}$	$(I_1/I_3)_{post}$	N	$(I_1/I_3)_{pre}$	$(I_1/I_3)_{post}$	N
Pure HTAB System									
0	1.84	1.26	59	1.84	1.26	59	1.84	1.26	59
5	1.82	1.27	63	1.61	1.21	62	1.61	1.19	64
20	1.82	1.26	69	1.62	1.18	79	1.61	1.17	63
35	1.81	1.26	73	1.62	1.17	77	1.60	1.14	65
50	1.82	1.25	77	1.61	1.16	70	1.60	1.13	66
HTAB+1%MC System									
0	1.64	1.19	32	1.64	1.19	32	1.64	1.19	32
5	1.54	1.23	35	1.47	1.17	35	1.53	1.15	43
20	1.55	1.22	44	1.48	1.15	50	1.53	1.14	48
35	1.55	1.23	48	1.49	1.15	47	1.54	1.13	53
50	1.55	1.22	52	1.47	1.13	44	1.51	1.11	67

^{a} All aggregation numbers reported were determined at 6 mM surfactant concentration. Average error in I_1/I_3 values and aggregation numbers are ±0.02 and ±2, respectively.

presence of a negative electron cloud in the benzene ring, which makes it comparatively less hydrophobic than a Hx$^-$ ion and hence more prone to go into the aqueous phase and thus increase the cac. The Hx$^-$ ions, being more favorable entities to get adsorbed on the hydrophobic moieties of polymer chain, are therefore more effective in reducing the cac initially. In the presence of NaBz, the significantly large cac increase may also be considered as an indication of its greater tendency to influence the polarity of the solvent. Thus, inspite of the similar behavior of salts toward modulating the cmc and cac values, the involved mechanisms are quite different. The cac observed in the HTAB/MC system in the presence of NaCl undergoes continuous reduction because of the strong hydration characteristics of the furnished ions. This leads to dehydration of hydrophobic moieties of MC and hence facilitates the early micellization of HTAB as a result of enhanced hydrophobic interactions involving the dehydrated MC hydrophobes and surfactant tail groups.

Effect of Salts on Micropolarity. The $(I_1/I_3)_{pre}$ and $(I_1/I_3)_{post}$ values obtained from the plots of I_1/I_3 against log[HTAB] for different salts in the absence and presence of MC are given in Table 2, where $(I_1/I_3)_{pre}$ and $(I_1/I_3)_{post}$ denote I_1/I_3 values at the top and bottom plateau, respectively, and represent the micropolarity sensed by pyrene in the preaggregation (below the cmc or cac) and postaggregation (above the cmc or cac) regions of HTAB, respectively. The values were obtained by fitting a Boltzmann type function to the sigmoidal data using Microcal Origin 6.0 software. It is evident from the table that, at a given salt concentration, both $(I_1/I_3)_{pre}$ and $(I_1/I_3)_{post}$ values are lower in the HTAB+1% MC system than in the HTAB system alone. This might be related to the hydrophobicity of the polymer. The presence of NaHx and NaBz in HTAB or HTAB/MC systems decreases $(I_1/I_3)_{pre}$ values. However, there is no significant change in these values with NaCl addition in the HTAB system, but a detectable change in the HTAB/MC system relative to that without NaCl is observed. The additive induces salting-out effect and reduces the water content on the hydrophobic moieties of the polymer, resulting in reduced polarity sensed by pyrene molecules residing on the hydrophobic sites of the macromolecule.[25] The gelation phenomenon of MC in the presence of NaCl is evidence that NaCl is responsible for breakdown of the hydrogen bonded network formed by water molecules at the hydrophobic sites.[19] The nearly constant

$(I_1/I_3)_{pre}$ values in pure HTAB with added NaCl may result due to the absence of such an effect. The decreasing $(I_1/I_3)_{pre}$ values in the presence of NaBz and NaHx for both HTAB and HTAB/MC systems may be attributed to their salt effect and the decreasing solvent polarity. However, $(I_1/I_3)_{post}$ values in HTAB as well as HTAB/MC systems are found to be a function of NaBz and NaHx concentrations. It has been pointed out that the solubilization tendency of Bz$^-$ and Hx$^-$ ions into the free or polymer-bound micelles effectively reduces the interhead group repulsion leading to decreased micellar charge and hence lesser penetration into the palisade layer of the micelle, the probable residing sites of the probe molecules.[55] Such an effect would be more significant for NaHx than NaBz owing to its linear chain hydrophobic groups. At a given concentration, $(I_1/I_3)_{post}$ values in both HTAB and HTAB/MC systems are thus lower for NaHx compared to that of NaBz.
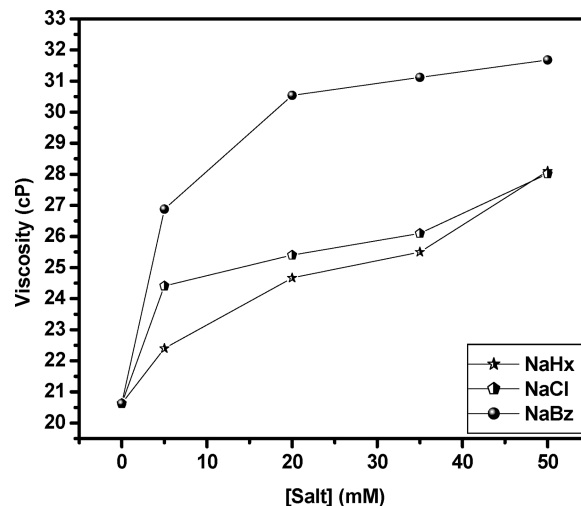
Effect of Salts on Aggregation Number of HTAB. Aggregation number (N) of 6 mM HTAB in the presence and absence of 1% MC has been evaluated at various salt concentrations replacing cac by cmc in eq 1. The obtained N values (Table 2) in both HTAB and HTAB/MC systems are found to increase in the presence of NaBz up to 20 mM but decreases above this concentration. However, N increases steadily in the presence of NaHx and NaCl in both the surfactant and surfactant−polymer systems. The initial increase of N in aqueous HTAB solution may result from solubilization and specific adsorption effects, but reduction in its value at higher NaBz concentration may be due to decrease of solvent polarity. The adsorption of Bz$^-$ ions on the hydrophobic sites of the polymer enhances micellization as a result of modified hydrophobic interaction between the surfactant and hydrophobes of MC as well as electrostatic attraction between positively charged surfactant moiety and negatively charged benzoate ion adsorbed on the polymer. As a result, micellar stabilization and hence increased N values are expected. However, the propensity of benzoate ions to go into the aqueous phase above a certain concentration results in overall reduction of solvent polarity allowing micelles to redissolve and thus yielding a decreased value of N. However, due to pronounced hydrophobicity, Hx$^-$ ions are preferentially solubilized in the micelles compared to the aqueous phase, thereby facilitating micellar stabilization on the polymer backbone and hence a synergistic aggregation behavior. It may be mentioned that the relative propensity of Bz$^-$ and Hx$^-$ ions to go into the micellar phase would be roughly related to the partition coefficient of their corresponding acids between octanol and water. The values 75.8 for hexanoic acid and 64.6 for benzoic acid[56] indicate the more hydrophobic nature of the former.

It is known that micelles bound to polymer hydrophobes have a low aggregation number and a high degree of ionization compared to free micelles.[30] Accordingly, the surfactant along the polymer chain would be distributed rather loosely around the hydrophobic region. The micelles generated from pure HTAB at 6 mM are nearly spherical and compact, and so incorporation of Hx$^-$ into HTAB micelles would have two opposing effects: (a) decreasing headgroup repulsions, and (b) chain length incompatibility between Hx$^-$ and hexadecyl chains of HTAB leading to loosening of micelle structure.[57] The initial increase of N followed by constant values indicates a balance between the two opposing effects. Because of the dehydration of hydrophobes of MC and screening of surfactant headgroup repulsion, NaCl tends to increase the aggregation number. The latter effect is well known to affect the micellar aggregation number of ionic surfactants, as observed in the case of pure HTAB solution.

HTAB and MC Interaction in Hydrophobic Salts

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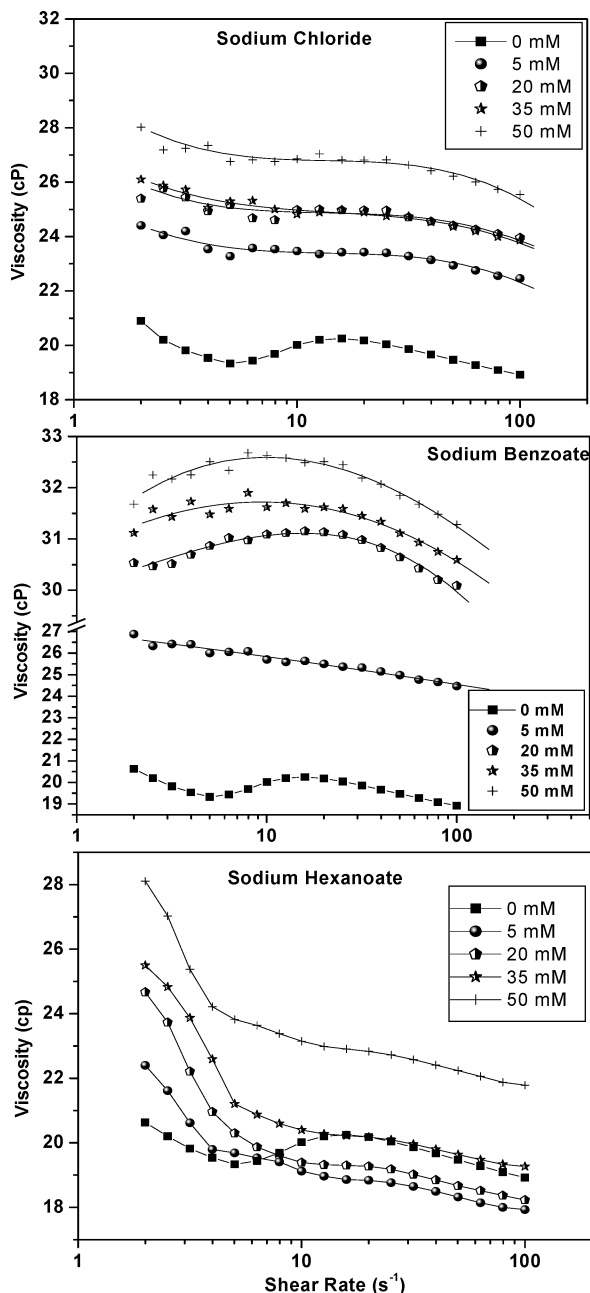
Figure 9. Viscosity curves of 1% MC + 6 mM HTAB system without and with various salt concentrations as a function of shear rate. Legends show different concentrations of salts used.

Figure 10. Viscosity of a 1% MC + 6 mM HTAB system as a function of salt concentration at a shear rate of 2 s^{-1}.

Effect of Salts on the Viscosity and Gelation of the HTAB/MC System. In order to study the effect of hydrophobic salts on viscosity and the gelation behavior of polymer−surfactant complexes in the solution, we investigated the viscosity variation of an HTAB (6 mM) + 1% MC system in the presence of different salt concentrations as a function of shear rate (Figure 9). It is observed that, at higher concentrations, NaBz induces a minor shear thickening at low shear rates followed by gradual shear thinning at higher shear rates. On the other hand, the addition of NaHx to the same system develops strong shear thinning at lower shear rates followed by almost Newtonian behavior at higher shear rates. It has been suggested[58] that surfactant solutions in the presence of sodium salicylate exhibit nonlinear characteristics as a result of the shear-induced structural transition of the entangled structure at equilibrium. At low shear rates, such systems depict shear rate independent viscosity and develop random and isotropic microstructures.

However, with increasing shear rates, dilute solutions undergo shear-induced transition when long, worm-like micelles are aligned completely collinearly in the flow direction leading to shear thinning, as observed in the case of linear polymer solutions.[58] At still higher shear rates, the interlayer coagulation of the aligned micelles occurs in dilute solution, leading to shear thickening. On increasing the shear rates further, such coagulated structures collapse because of the predominance of hydrodynamic forces, leading to shear thinning again. The behavior of the viscosity curve in the case of polymer systems has been interpreted in terms of balance between the destruction of interpolymer and intrapolymer association.[59] The disruption of interpolymer association with increasing shear rate results in decreased viscosity due to cross-linked network breakdown, while intrapolymer association disruption leads to viscosity increase because of the stretching out of the coiled polymer chains and consequent exposure of more hydrophobes for possible interpolymer association. The pure 1% MC solution in present study exhibits shear thinning because of the orientation of polymers in the shearing direction (Figure 2). The shear thinning of HTAB (6 mM) + 1% MC solution develops due to the formation of micelles on the polymer backbone, leading to stretching and aligning of the polymer coils due to repulsive interactions, thereby limiting the interpolymer association. However, the small shear thickening observed at a slightly higher shear rate is probably due to forced interpolymer aggregation. Similar behavior has been reported for surfactant solutions known to form long worm like micelles in the presence of hydrophobic additives.[54,60] The slow shear thinning observed at still higher shear rates may possibly be attributed to the collapse of the coagulated complexes.

The exceptional behavior of the polymer−surfactant system at high NaBz concentration may be interpreted in terms of negative aromatic π electron−positive charge interaction at the interface resulting in projecting out of COO$^-$ groups on the surface of polymer-bound micelles, thereby interacting with the micelles on the neighboring polymer chains, ultimately leading to substantial interpolymer interaction and consequent increase in viscosity (Figure 10; shear rate 2 s^{-1}). The collapses of interpolymer association at higher shear rates due to predominance of hydrodynamic forces lead to shear thinning. The solubilization of the Hx$^-$ moiety into the polymer-bound micelles effectively reduces the micellar charge, resulting in increased viscosity (Figure 10) due to reduced interpolymer
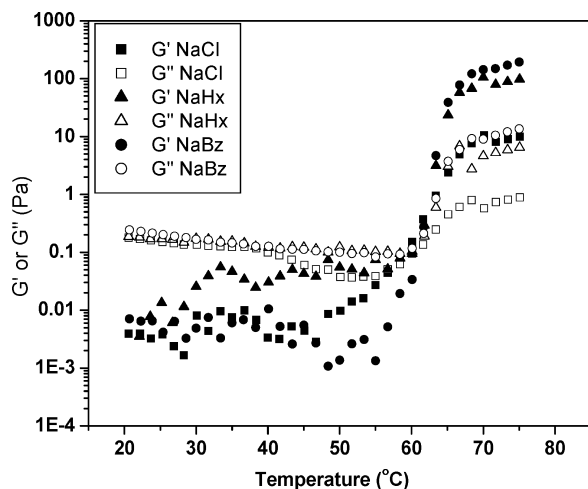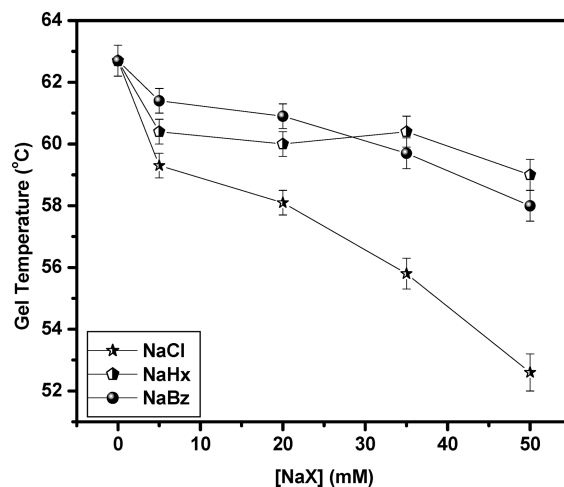
Figure 11. Storage modulus G′ (filled symbols) and loss modulus G″ (empty symbols) of a 1% MC + 6 mM HTAB solution as functions of temperature in a heating process at about 1 °C/min in the presence of 5 mM of various salts used.

Figure 12. Variation of gelation temperature of 1% MC + 6 mM HTAB system as a function of salt concentration.

repulsive interactions. However, lack of Hx⁻ ion adsorption at the micelle−water interface hardly makes any contribution to interpolymer association as observed in the case of NaBz. The shear rate would, therefore, induce alignment of polymer chains in the direction of flow, resulting in shear thinning (Figure 9). The reduction of interpolymer repulsions by NaCl due to screening of charge of the surfactant aggregates on the polymers causes viscosity increase (Figure 10). It is evident from Figure 10 that the effectiveness of NaBz for increasing viscosity at low shear rate is better than that of NaCl, which in turn is more effective compared with NaHx. The increase in aggregation number in a polymer−surfactant system in the presence of NaHx serves as evidence of polymer chain coiling. Similar behavior is not observed when NaCl is present in the system. The steep rise in viscosity produced by NaCl in comparison with that of NaHx may be the result of different types of forces operating in two cases. The NaCl/HTAB/MC solutions show almost near Newtonian behavior followed by shear thinning tendency at higher shear rates.

Gelation temperature of a 6 mM HTAB + 1% MC system was determined as the crossover point between G′ and G″ at different concentrations of NaCl, NaHx, and NaBz. A prototype graph at 5 mM additive concentration and the variation of GT as a function of additive concentration is shown in Figures 11 and 12, respectively. Li et al.[34] proposed that gelation of MC in the presence of HTAB occurs by destruction of surfactant cages formed above the cmc on the hydrophobic groups of the polymer. Thus, any additive that will enhance the hydrophobic interaction between surfactant and polymer would contribute to an increase in GT. On the other hand, factors such as salt-out effect[20] and solvent polarity reduction responsible for destruction of surfactant cage structure would decrease the gelation temperature of surfactant−polymer systems. A few salts undergoing feeble interaction with water molecules may help to disperse the MC molecules due to salt-in effect, thereby preventing MC chain association and hence gel formation. The behavior of GT in the present system may be rationalized by taking into consideration all the factors involved. As a result of salt-in effect, NaCl decreases water content adjacent to the hydrophobes of MC, and thus a lower temperature is needed to destroy the surfactant cage structure of hydrophobes. The hydrophobic salts NaBz and NaHx, due to their specific solubilization characteristics, enhance the hydrophobic associa-

tion involving the polymer and surfactant and thus lead to increased gelation temperature. However, simultaneous tendency to reduce solvent polarity, and some salt-in effect leads to decrease in gelation temperature. The overall effect, however, results in a small decrease in the gelation temperature in contrast to NaCl. Because of the higher solubility of NaBz in water compared to NaHx, it is found to be more effective in decreasing the GT at higher concentrations (Figure 12).

Conclusion

The interaction of HTAB and MC has been investigated in the absence and presence of NaBz, NaHx, and NaCl employing rheological and fluorescence measurements. The variation of steady-shear viscosity of MC as a function of the shear rate indicated non-Newtonian behavior which effectively transforms into Newtonian one by the addition of HTAB. The decreasing trend of viscosity values up to the cac of HTAB followed by increase until 10 mM HTAB and a small decrease ultimately has been attributed to intermolecular hydrophobic association, increase in aggregation number of micelles and their number on the polymer chain, along with the shrinkage of polymer−surfactant complex chains due to electrostatic screening of charges by free micelles.

The lowering of gelation temperature of MC down to the cac of HTAB followed by a large increase is considered to be due to the change in the salting-out effect of HTAB below the cac to its salting-in effect above the cac.

The behavior of NaBz and NaHx compared to that of NaCl is found to be distinctly different with respect to their effect on the viscosity versus shear rate curve, cac, gelation temperature, aggregation number, and pyrene I_1/I_3 values of polymer−surfactant system. The differences have been explained on the basis of their characteristic combined effects of solubilization, binding to the polymer backbone, electrolyte effect, and their solvent modifying tendencies in contrast to the only salt effect of NaCl. However, NaHx was slightly different from NaBz in its influence owing to its better propensity to get solubilized into the micelles.

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