Phase Behavior of Nonionic Polymer Hydroxypropylmethyl Cellulose: Effect of Gemini and Single-Chain Surfactants on the Energetics at the Cloud Point

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Nonionic cellulose ether−water systems have a characteristic feature of phase separation at certain temperatures, also termed the cloud point. The effect of various surfactants as additives on the phase behavior of nonionic cellulose ether, hydroxypropylmethyl cellulose (HPMC), has been studied. It was found that in the presence of ionic surfactants the cloud point (T_{CP}) of HPMC decreased when small amounts of surfactant were added, and at higher concentration it increased. In the case of alkyltrimethylammonium bromides, surfactants with a longer alkyl chain (cetyltrimethylammonium bromide, CTAB, and tetradecyltrimethylammonium bromide, TTAB) influenced the T_{CP} much more than that with a shorter alkyl chain (dodecyltrimethylammonium bromide, DTAB). Cetylpyridinium chloride (CPC) and cetylpyridinium bromide (CPB) were utilized to see the counterion effect on the T_{CP} of polymer. Anionic surfactant sodium dodecyl sulfate (SDS) was found to be more effective as compared to its cationic counterpart with the same alkyl chain (DTAB), whereas nonionic surfactants showed no influence. From these observations it was concluded that the driving force was the interaction between the charged head groups of the surfactants and polar sites present in the nonionic HPMC. Gemini surfactants (α,ω-bis(hexa/tetradecyldimethylammonium)alkane dibromides) showed more influence on the T_{CP} as compared to their conventional counterparts. The energetic parameters of clouding in HPMC in the presence of all surfactants used in the study were also calculated. Conventional surfactants had shown the contrast behavior of enthalpy and entropy changes at lower and higher concentration regions; i.e., ΔH_c^0 and $T\Delta S_c^0$ were positive at low concentration of surfactants but negative at higher surfactant concentrations. In the presence of gemini surfactants, both the enthalpy and entropy changes were always negative.

Introduction

Cellulose derivatives and other water-soluble polymers partake significant roles in various industrial applications and particularly in pharmaceuticals, petrochemicals, and personal care formulations.[1,2] In pharmaceuticals, they may serve as either drug-delivery agents or as an excipient for enhancing the stability of drugs, while in petrochemicals, they are useful in enhanced oil recovery.[3,4] In personal care formulations, they can be used as a viscosity modifier or as gelling agents.[5] In all these industries, surfactants also play an important role either alone or with the assistance of polymers. When these two entities are present in systems, they generally provide better properties as compared to a single entity.[6,7] Thus, surfactants and polymers in aqueous solutions attract attention in a wide field of practical applications as well as from a fundamentally academic point of view. Phenomena such as aggregation, swelling/deswelling, adsorption, solubilization, and phase separation can be controlled, influenced, and employed in specific applications.[8,9]

Water-soluble polymers having polar groups, for instance, hydroxyl, carboxylic acid, or ether groups, are capable of taking part in the hydrogen bonding structure of water. As the temperature rises, the hydrogen bonding is diminished, and the polymer solubility becomes less. Eventually, phase separation may occur.[10] A characteristic feature of nonionic cellulose ether/water systems is the existence of reversible phase separation including a lower critical solubility temperature, LCST, also denoted as cloud point, T_{CP}, above which the solution becomes "cloudy".[11] At the T_{CP}, the polymer precipitates out of the solution as a result of the same chemical potentials between the two phases.[12] Therefore, T_{CP} gives an easy and powerful tool for qualitative depiction of the polymer thermodynamics in systems with LCST behavior and their interactions with amphiphilic molecules.

Water-soluble nonionic derivatives of cellulose are physiologically harmless and are preferred for the use in foodstuffs and the pharmaceutical industry.[13−16] The phase behavior of these cellulose ethers can easily be tuned with the help of adding suitable additives. Several cellulose derivatives, like hydroxypropylmethyl cellulose (HPMC), considered in the present study, are distinguished by mixed hydrophobic and hydrophilic structural units. Additionally, these structural elements are, in general, erratically distributed along the polymer chain, and the substituents may consist of shorter or longer chains, giving rise to a varying degree of hydrophobicity.[17] The interactions of such complex structures with ionic surfactants can give the system extraordinary properties.[18−24] Effects of various surfactants, viz., cationic, anionic, and nonionic, on the cloud point of cellulose ethers have been studied.[18,25−38] Whereas studies with anionic surfactant sodium dodecyl sulfate are extensive, those including cationic as well as nonionic surfactant systems are relatively fewer. Drummond et al., in a comparative study of the interaction of surfactants (anionic, cationic, and nonionic) with

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hydroxypropyl cellulose (HPC),[27] had shown that anionic surfactants displayed much stronger affinity for HPC as compared to the cationic surfactants, while nonionic surfactants did not influence T_{CP} of the polymer. Furthermore, in this respect gemini surfactants have not been studied, and new unprecedented properties continue to be reported in the literature. Since gemini surfactants are the new generation surfactants, therefore the present work was carried out to study the effect of various surfactants including gemini surfactants on HPMC. This paper reports how a series of different classes of surfactants viz., cationic gemini, cationic conventional, anionic, and nonionic surfactants, affect the cloud point of HPMC. In these studies, the effect of various factors, such as chain length, charge on the head group, counterion, etc., was seen on the T_{CP} of the HPMC, and we hypothesized based on our results the main driving force responsible for the interaction between surfactant and polymers.

Experimental Section

Hydroxypropylmethyl cellulose, HPMC (mol wt $\approx$ 10 000, hydroxypropoxyl content $\sim$9 %, Fluka, Switzerland), cetyltrimethylammonium bromide, CTAB ($\geq$ 99.0 %, Merck, Germany), tetradecyltrimethylammonium bromide, TTAB (> 99 %, Merck, USA), dodecyltrimethylammonium bromide, DTAB (99 %, Tokyo Kasei, Japan), sodium dodecyl sulfate, SDS (99 %, Sigma, USA), Brij-56 (99 %, hydroxyl value 75 to 90, Merck, Germany), Brij-58 (99 %, hydroxyl value 45 to 60, Merck Germany), *N*-cetylpyridinium bromide monohydrate, CPB (98 %, E. Merck, Germany), and *N*-cetylpyridinium chloride monohydrate, CPC, (98 %, E. Merck, Germany) were used as received. Gemini surfactants α,ω-bis(hexa/tetradecylammonium)alkane dibromides (16-*s*-16, 14-*s*-14, $s = 4, 5, 6$) were prepared and purified as described elsewhere,[39] which gave H NMR spectra and C, H, and N analyses data consistent with their assigned structures.[40] For synthesis, the following materials were used without further purification: 1,6-dibromobutane ($\geq$ 98 %, Fluka, Switzerland), *N*,*N*-dimethylhexadecylamine ($\geq$ 95 %, Fluka, Switzerland), and *N*,*N*-dimethyltetradecylamine ($\geq$ 95 %, Fluka, Switzerland).

Freshly prepared stock solutions (dimineralized double-distilled water of specific conductivity (1 to 2)$\cdot 10^{-6}$ $S\cdot cm^{-1}$ was used throughout) of the polymers were used to obtain samples for T_{CP} measurements (containing HPMC with or without different surfactants). T_{CP} data were obtained by placing Pyrex glass tubes (containing the sample solutions) into a temperature-controlled bath, the temperature of which was ramped at the rate of 0.1 $K\cdot min^{-1}$ near the T_{CP}, and onset clouding was noted by visual inspection. The uncertainties in the observed values of T_{CP} were found to be $\pm$ 0.1 K.[41,42] (T_{CP} values are given in Table S1 and Table S2 in Supporting Information).

Results and Discussions

1. Effect of Surfactant on Cloud Point of HPMC. A number of surfactants, viz., 16-*s*-16, 14-*s*-14 ($s = 4, 5, 6$), CTAB, TTAB, DTAB, CPC, CPB, SDS, SDBS, TX-100, and Brij-56, were used in the present investigation. The aim behind this was to understand the effect of chain length, head group, and counterions on the clouding phenomena of cellulose ether, HPMC. Moreover, as the gemini surfactants are considered as a novel class of surfactants and possess better properties as compared to their conventional counterparts, a complete insight into the effect of 16-*s*-16 and 14-*s*-14 will provide the effect of the spacer length and hydrophobicity on the phase behavior of HPMC−surfactant systems.

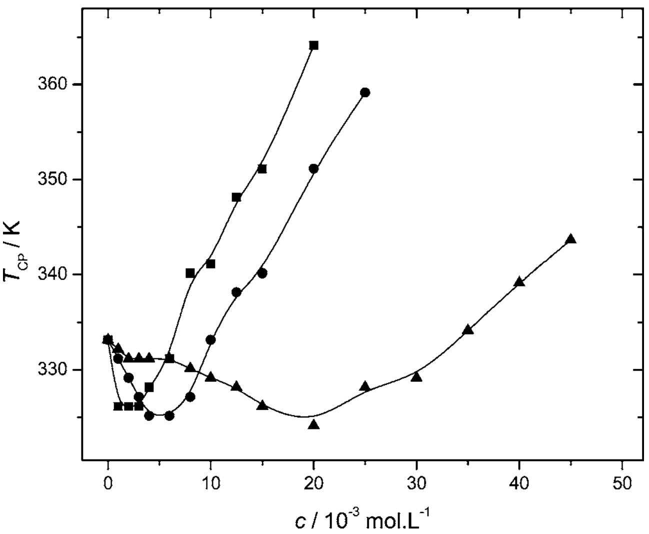

Figure 1. Effect of cationic surfactants of varying hydrophobicity: ■, CTAB; ●, TTAB; and ▲, DTAB on the T_{CP} of HPMC.

When the solution of pure HPMC (0.01 $g\cdot mL^{-1}$) is heated, phase separation occurs at about 333.15 K; this means that below this temperature HPMC molecules are surrounded by a network of water molecules. At higher temperature, entropy destroys the network, and phase separation occurs due to the weak van der Waals' attraction between the polymer chains.[10]

Figure 1 describes the effect of single chain alkyltrimethylammonium bromides on the cloud point of HPMC (0.01 $g\cdot mL^{-1}$). Any change in T_{CP} of a polymer/water system on the addition of the additive such as surfactant or salt can be ascribed to the variation of the hydrophobic/hydrophilic balance in the system and, as a result, modification of the interaction.[25] The interaction of polymers with ionic surfactants starts with the binding of surfactant and polymers, and the resulting complex could be considered as a polyelectrolyte. Ionic head groups of the surfactant and the polar residues present in the polymer domains are responsible for the interaction[8,9] between the surfactants and HPMC, and the interaction was further supported by the hydrophobic forces due to the nonpolar parts of both entities. It is evident from Figure 1 that addition of a small amount of surfactant causes the T_{CP} to decrease due to the beginning of the increased interaction between HPMC and surfactant. It is supposed that the decrease in T_{CP} on addition of an ionic surfactant is obtained only in the presence of an electrolyte, or the cmc of the surfactant is high so that the free monomers and counterions may act as a medium electrolyte.[43] A decrease in the T_{CP} in the presence of electrolyte is due to the salting out of the polymer.[25,26] The T_{CP} change of the polymer on addition of surfactant is governed by a delicate balance between electrostatic effects and hydrophobic interactions.[44] At higher surfactant concentration, there is a strong monotonic increase in T_{CP} indicating increased solubility of the polymer. This effect can be attributed to the binding of surfactants to the HPMC thereby imposing repulsive interaction between different polymer chains.[26,43,44] When a larger amount of surfactant is added, the increase in the effective charge density (due to the surfactant−polymer binding) may lead to increase in the repulsive electrostatic forces. Surfactants play an important role in polymer chemistry due to their amphiphilic nature.[8,9] For example, the hydrophobic portion of surfactants interacts with hydrophobic polymers or rather with hydrophobic groups of water-soluble polymers, and the formed complex has somewhat new properties due to the presence of the hydrophilic portion of the surfactant. The distinct increase of T_{CP} with higher

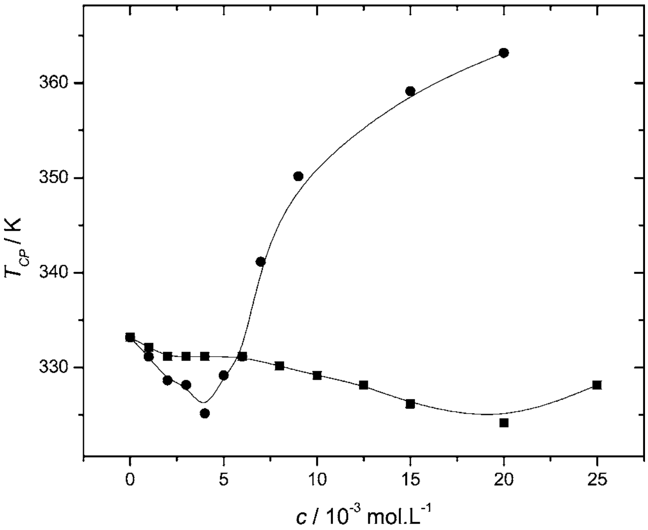

Figure 2. Effect of charge on the head group of surfactant on the T_{CP} of HPMC (■, DTAB and ●, SDS).

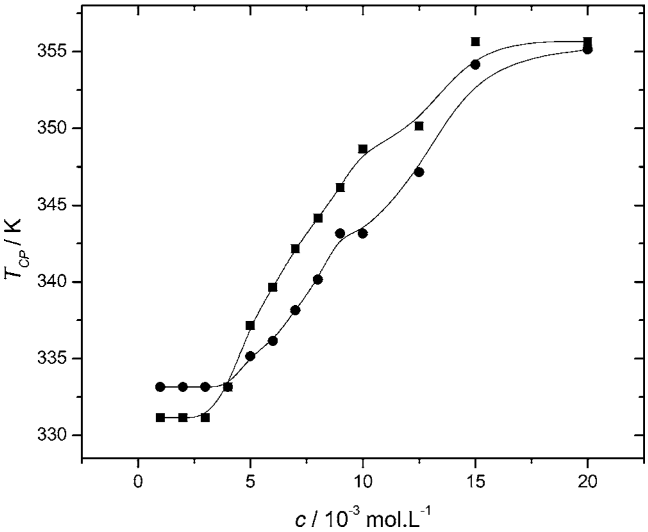

Figure 3. Effect of counterion of surfactant (■, CPC and ●, CPB) on the T_{CP} of HPMC.

concentration of surfactants is a usual sign of polymer's strong binding with surfactants. As it is well reported that hydrophobicity has a remarkable effect on the clouding phenomenon of polymers,[12] therefore, to see the effect of hydrophobicity we have taken three alkyltrimethylammonium bromides (CTAB, TTAB, DTAB) of different hydrophobicity. It is clear from Figure 1 that on increasing the concentration of DTAB there is a gradual decrease in the T_{CP} up to $20 \cdot 10^{-3}$ mol·L^{-1} of DTAB, and a further increase in the concentration increases the T_{CP} up to the entire concentration range used. TTAB and CTAB also behave in a similar fashion, but the decrease and further increase in T_{CP} was much steeper in the case of TTAB and largest in the presence of CTAB. This behavior is a clear indication of the active participation of hydrophobic interaction between the surfactants and polymer.

It is very well reported that anionic surfactants interact strongly with polymers as compared to the cationic surfactants.[43,45] While comparing the effect of charge on the head group we have taken DTAB and SDS (both with dodecyl chain) as model surfactant systems (Figure 2). The minimum in the T_{CP} curve of HPMC appeared at $4 \cdot 10^{-3}$ mol·L^{-1} SDS concentration which is consistent with earlier reported values.[18] SDS shows a remarkable effect as compared to the DTAB. The influence of SDS on T_{CP} of HPMC is clearly an indication of the stronger interaction of anionic surfactant with the polymers as compared to cationic surfactants.

Counterions do not have very much influence, as can be seen from the effects of CPC and CPB (Figure 3). However, unlike CTAB, addition of CPC and CPB does not show any minimum in the T_{CP} profiles of HPMC. Probably at low concentration of CPC or CPB, no interaction takes place due to the weaker interaction of these cationic surfactants (which was not found in the case of alkyltrimethylammonium bromides). However, at higher concentrations of CPC/CPB, an increase in cloud point is the indication of increased interaction between these two entities, which favors the fact that, at low surfactant concentration, initially interaction starts due to the electrostatic forces, while at higher concentration, hydrophobic forces dominate. It can be concluded that the hydrophobicity as well as the nature of the charge of the head group of the surfactant are important factors to alter the T_{CP} of HPMC.

Interestingly, nonionic surfactants (TX-100, Brij 56 and Brij 58) did not influence T_{CP} of the polymer up to the addition of about $25 \cdot 10^{-3}$ mol·L^{-1}. Here we speculate that the interaction between the surfactants and polymer starts either due to the electrostatic or ion−diople attraction, and in our systems, the latter case seems to be responsible for initiating the interaction between ionic surfactants and HPMC, followed by the assistance of hydrophobic interactions at higher concentration. For the case of nonionic surfactants, the dipole−dipole interactions are either too weak or insignificant to commence the interaction, resulting in the constancy of T_{CP} of the system. Furthermore, hydrophobicity independently does not have any significant impact on phase separation (though it plays an important role when the components are ionic in nature).

The presence of two hydrophobic and two hydrophilic groups makes the gemini surfactants special agents for performing various tasks.[46,47] Therefore, in this study, we have taken two series of gemini surfactants viz., 16-*s*-16 and 14-*s*-14 ($s = 4$, 5, 6), and compared their properties with the respective conventional counterparts, i.e., CTAB and TTAB. All the gemini surfactants show no minima in the T_{CP} curve of HPMC (unlike conventional ones), and that may be due to the stronger interaction of geminis with HPMC (as a result of which the minima disappeared). On increasing the [gemini], T_{CP} increases smoothly up to the solubility limits of the surfactants. The effect of hydrophobicity follows the trend faithfully in the case of gemini surfactants too; i.e., 16-*s*-16 shows (Figure 4) a larger influence on T_{CP} as compared to 14-*s*-14 (Figure 5). The studies above certain concentrations ($10 \cdot 10^{-3}$ mol·L^{-1} for 16-*s*-16 and $18 \cdot 10^{-3}$ mol·L^{-1} for 14-*s*-14) were not performed due to the solubility limits of these systems.

2. Thermodynamics of the Cloud Point. As is evident, the formation of the separate phases of the components present in the solution is recognized as the cloud point. Attempts have been made to explain the clouding in terms of energetics based on the solubility of the clouding species (in terms of mole fraction) in the presence of various additives.[48,49] The clouding components liberate their solvated water and set it aside from the solution. The T_{CP} is, therefore, deliberated as the solubility constraints of the clouding constituents at that temperature. The free energy of phase separation or clouding (ΔG_c^0)

$$\Delta G_c^{\ 0} = RT_{CP} \ln x \qquad (1)$$

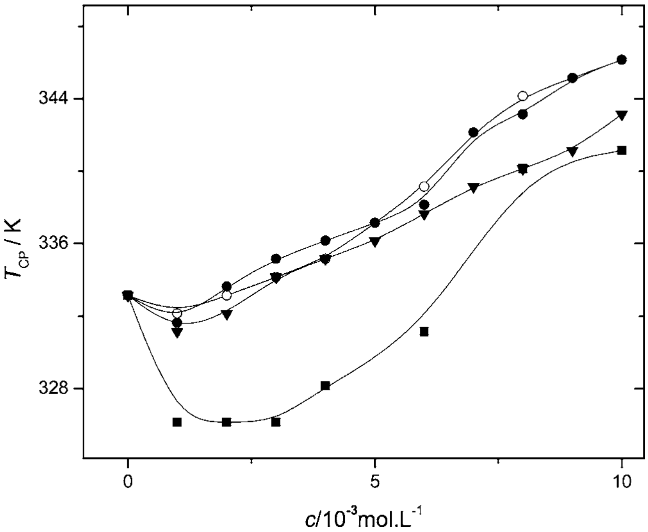

Figure 4. Effect of Gemini surfactants (○, 16-6-16; ●, 16-5-16; ▼, 16-5-16) in comparison to their monomeric counterpart (■, CTAB) on the T_{CP} of HPMC.

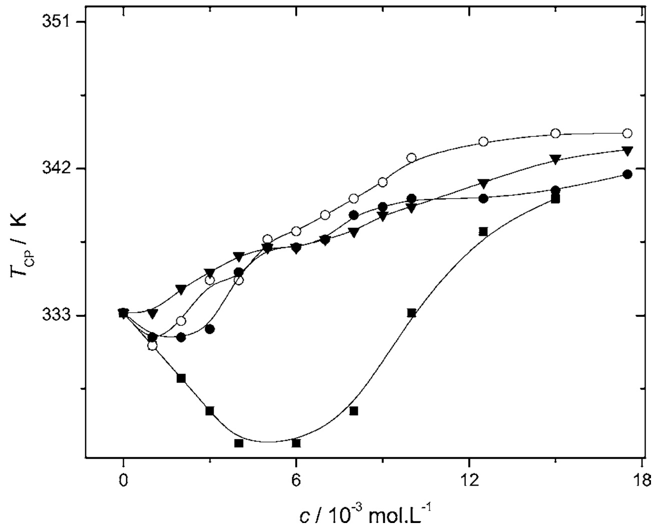

Figure 5. Effect of Gemini surfactant (○, 14-6-14; ●, 14-5-14; ▼, 14-4-14) in comparison to their monomeric counterpart (■, TTAB) on the T_{CP} of HPMC.

where x and R are the mole fraction solubility at T_{CP} and the gas constant (8.314 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), respectively.

ΔH_c^0 can then be obtained from the slope of the linear (least-squares) plot between ($\Delta G_c^0/T$) (Figure S1, Supporting Information) and ΔS_c^0 using the Gibbs−Helmholtz equation.

The values of the thermodynamic parameters at the cloud point with respect to HPMC concentrations are given in Table S1 (Supporting Information). The T_{CP} of HPMC decreases on increasing its concentration at fixed surfactant concentration ($6\cdot10^{-3}$ $\text{mol}\cdot\text{L}^{-1}$), and ΔG_c^0 becomes less negative (indicating that the clouding is becoming energetically less favorable on increasing the concentration of the polymer). The system becomes slightly more ordered on increasing the polymer as indicated by a decrease in the entropy of all the systems used in the study.

While seeing the effect of polymer concentration on the energetics of clouding, it was found that ΔH_c^0 was almost of comparable magnitudes for all the surfactants used except for the DTAB and SDS for which the T_{CP} phenomena is more endothermic and may be attributed to the shorter chain length of these surfactants.

The values of energetic parameters for all the surfactants at varying [surfactant] and 0.01 $\text{g}\cdot\text{mL}^{-1}$ HPMC are given in Table S2 (Supporting Information). In general, the ΔG_c^0 becomes less negative on increasing the surfactant concentration. For conventional surfactants (CTAB, TTAB, DTAB, CPC, CPB, and SDS), $\Delta G_c^0/T$ versus $1/T$ curves have two stages (a representative curve for DTAB has been given in Figure S1, Supporting Information). The first stage belongs to the lower concentrations of surfactants (usually below cmc) and is entropy controlled with a positive entropy and enthalpy, while the second stage is mainly controlled by enthalpy; i.e., the process is exothermic, and the system becomes more ordered in this stage.

Stage I: It is apparent from Table S2 (Supporting Information) that entropy of the system with conventional surfactants is positive for the endothermic process. The T_{CP} occurs due to the increased entropy of the system, therefore surfactant monomers, when added to the system, further increase the overall entropy due to their interaction with the polymer making the system more disordered by affecting the water structure. Therefore, the system becomes more disordered with the absorption of heat.

Stage II: The second stage is enthalpy controlled with negative entropy. This occurs probably due to the formation of ordered complexes which are generally formed at higher concentrations of surfactants (usually more than the cmc of surfactants in aqueous medium). The formation of complexes at higher concentration ends up with the release of heat with overall ordering of the system.

Gemini surfactants, on the other hand, show only one stage (Figure S2, Supporting Information) which is mainly controlled by enthalpy with a significant ordering of the system as compared to the conventional surfactants. A large amount of heat is liberated during the complex formation between the HPMC and the gemini surfactants. The disappearance of the first stage, which basically occurs before the complex formation between the surfactant and polymer, takes place probably due to the stronger interaction of gemini surfactants[29] (due to which the formation of the complex starts at very low surfactant concentration) as well as due to the very low cmc of the geminis.

Conclusions

Effect of surfactants (cationic, anionic, nonionic, and gemini) was seen on the cloud point (T_{CP}) of the nonionic polymer hydroxypropylmethyl cellulose (HPMC). With ionic surfactants, the T_{CP} first decreased and then started increasing after reaching a minimum, while nonionic surfactants did not show any impact. On increasing the hydrophobicity of cationic surfactants, the T_{CP} changes occurred more steeply. Anionic surfactant exhibited more influence on the T_{CP} as compared to the cationic with the same alkyl chain. Counterions did not show any substantial effect on T_{CP} change. One of the main findings of this work was that gemini surfactants had more influence on the T_{CP} and increase it smoothly without showing any minima, and this might be due to the stronger interactions of gemini surfactants as compared to their single-chain counterparts. From the individual effect of all types of surfactants, it is hypothesized that, although hydrophobicity has a remarkable impact on the polymer−surfactant interactions, the main driving force of the interaction between the surfactants and polymer was the ionic−dipole interaction between the head group and dipole of the surfactant and polymer.

Supporting Information Available:

Cloud point data and Figures S1 and S2 and Tables S1 and S2 associated with this article. This material is available free of charge via the Internet at http://pubs.acs.org.

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