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Interactions of a hydrophobically modified cationic cellulose ether derivative with amphiphiles of like charge in an aqueous environment

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Abstract

The interactions of a hydroxyethylcellulose ether derivative (Quatrisoft® LM200), substituted with cationic, hydrophobic side chains, with cationic surfactants, differing in the composition of the head group, were examined by conductivity, fluorescence, and dye solubilization techniques. The surfactants investigated included alkyl pyridinium chloride salts, alkyl trimethylammonium bromide salts, the alkyl dimethylammonium bromide salts, and alkyl ammonium bromide salts. All surfactants investigated interacted with the LM200 molecules to form micelle-like aggregates prior to the critical micellar concentrations of the surfactants. Hydrophobic interactions and the ability to form hydrogen bonds play a role in the polymer–surfactant association. This associative behavior was shown to depend significantly on both the polymer and surfactant concentrations. In addition, the polymer molecules also interact with each other in solution. The resulting hydrophobic polymer microdomains were detected using fluorescence probe studies. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Critical micelle concentration; Polymer–surfactant interactions; Fluorescence spectroscopy; Conductivity; Dye solubility; Surfactants aggregation numbers and quenching

1. Introduction

The phenomenon of polymer–surfactant interactions has become a major topic in colloidal research over the past few decades. Much of the interest in this area has stemmed from the numerous possible industrial applications such as pharmaceutical products, thickening agents, coatings, and cosmetic formulations. (Evani & Ros, 1987; Jönsson, Lindman, Holmberg & Kronberg, 1998; Lindman & Thalberg, 1993; Prud'homme & Uhl, 1984; Thalberg & Lindman, 1989). In the latter application, polymers that can induce micellization at surfactant concentrations below the critical micellar concentration (cmc) lead to products that cause less skin irritation due to the decrease in the surfactant monomer concentration, and hence the surfactant activity (Jönsson et al., 1998).

The most extensively studied systems involve both uncharged polymers with ionic surfactants and polyelectrolytes with oppositely charged surfactants (Evertsson & Nilsson, 1997, 1998; Holmberg, Nilsson, Singh & Sundelöf, 1992; Nilsson, Holmberg & Sundelöf, 1995; Persson, Nilsson & Sundelöf, 1996). They report strong interactions between SDS and these polymers. This contrasts with the very weak interactions that have been found in the case of uncharged polymers with cationic surfactants (García-Matéos, Pérez & Velázquez, 1997; Goddard, 1986a,b).

In the majority of these systems, the polymer and the surfactant molecules begin to interact at a particular concentration known as the critical association concentration (cac). It usually occurs at a surfactant concentration lower than the cmc. The interaction typically involves the formation of surfactant aggregates that bind to the polymer molecules. At higher surfactant concentrations (above the cmc), polymer-bound aggregates coexist with free micelles (Jönsson et al., 1998).

Extensive studies involving polyelectrolytes with oppositely charged amphiphiles have been reported in literature (Abuin & Scaiano, 1984; Goddard, 1986a,b; Goldraich, Schwartz, Burns & Talmon, 1997; Li & Dubin, 1994; Regismond, Winnik & Goddard, 1996; Wei & Hudson, 1995). It has been concluded that complex formation occurs in these systems. This interaction also begins at a concentration lower than the cmc. In the case of hydrophobically modified polyelectrolytes with oppositely charged surfactants, the hydrophobic interaction between the surfactant tails and the nonpolar sections of the polymer enhances the stability of the aggregates in the aqueous environment (Goddard, 1986a,b).

Hydrophobically modified polymers (HMP's) are

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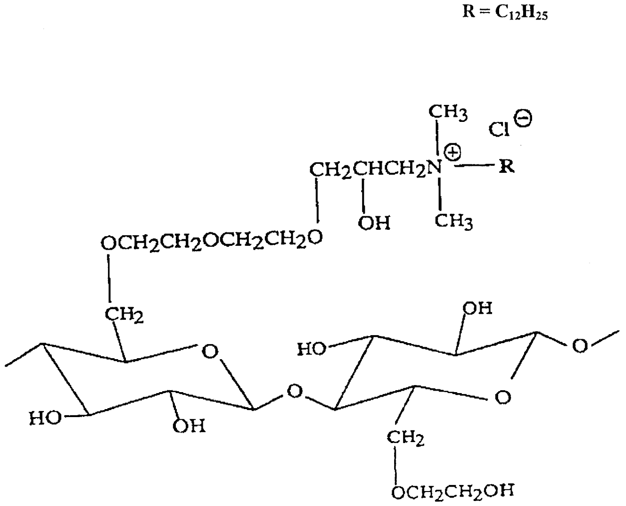

Fig. 1. Structure of a portion of Quatrisoft® LM200 polymer.

water-soluble polymers that have been modified with the addition of a nonpolar species. The presence of the hydrophobic segments may result in a tendency of the polymer to form hydrophobic aggregates (Regismond et al., 1996). In fact, many of the solution properties of these polymers are derived from their ability to form inter- and intramolecular associations (Lindman & Thalberg, 1993). The hydrophobic nature of these polymers provides them with the unique ability to form associations with surfactants of the same charge (Bakeev, Ponomarenko, Shishkavanova, Tirrell, Zezin & Kabanov, 1995). This phenomenon is lacking in traditional polyion–surfactant systems of like charge (Iliopoulos, Wang & Audebert, 1991; McGlade, Randall & Tcheurekdjian, 1987).

There have been reports about the existence of hydrophobic associations between the hydrophobically modified cellulose ether Quatrisoft® LM200 and four trimethylammonium-based surfactants (Goddard & Leung, 1992; Winnik, Regismond & Goddard, 1996). The I_1/I_3 ratio of the fluorescence spectrum of pyrene was used by Winnik et al. (1996) as an indication of the micropolarity of the environment of these aggregates. The anomaly observed in the I_1/I_3 plots for each surfactant in 1.0 g/L of LM200 was suggested to be an indication that the polymer and surfactant interact via a weakly cooperative mechanism Winnik et al. (1996). Goddard and Leung (1992) deduced the presence of polymer–surfactant interaction in the same systems from their studies of surface tension and phase behavior.

In the present study, we investigate the mechanism of association between LM200 and four different types of cationic surfactants. The surfactants chosen for this study include alkyl pyridinium chloride salts (C_nPC), alkyl trimethyl, dimethyl and ammonium bromide salts (C_nTAB,C_nDAB, and C_nAB). Systematic studies involving variations of both the surfactants head group and the alkyl chain length facilitated the characterization of the multifaceted interaction process. An analysis of the results obtained through conductivity, steady-state fluorescence, and dye solubilization experiments, suggests the presence of micelle-like polymer–surfactant aggregate formation prior to the surfactant cmc. This type of association is fueled mainly by hydrophobic attractions. Hydrogen bonding is an additional interaction occurring in the polymer–surfactant systems containing surfactant with head groups that have the ability to form hydrogen bonds with the polymer backbone. The polymer–surfactant associations present in these systems were found to be quite dependent on the nature of the surfactant present in these systems.

2. Experimental section

2.1. Materials

Quatrisoft® LM200 is the chloride salt of an *N*,*N*-dimethyl-*N*-dodecyl derivative of hydroxyethylcellulose, having a molecular mass of approximately 100 000 Daltons (Fig. 1). The degree of substitution was determined to be 2.0×10^{-4} mol of $C_{12}H_{25}$ per gram of polymer; this corresponds to a substitution of approximately 3.4% by weight or one substitution every 19 glucose units (Thalberg & Lindman, 1989). The polymer was from Amerchol Inc., and was used without further purification.

The dodecyl, tetradecyl, and hexadecyltrimethylammonium bromide salts were purchased from Aldrich. The decyltrimethylammonium bromide salt was obtained from TCI America. The dodecyl and hexadecylpyridinium chloride salts were also received from Aldrich. All of the commercially available surfactants were purified by repeated recrystallization. The decyl and tetradecylpyridinium chloride salts were prepared by refluxing the appropriate alkyl chloride with pyridine for 48 h. The dodecyldimethylammonium bromide salt and the decyl and dodecylammonium bromide surfactants were synthesized by combining the corresponding amine with hydrogen bromide (48%). The amines were purchased from Aldrich, while the hydrogen bromide was received from Fisher Scientific. The surfactants were purified by repeated recrystallization from acetone and diethylether. The purity of these surfactants was tested by chloride or bromide analysis using the conductometric method. Silver nitrate solution was used as the standard. All surfactants were found to be better than 99% pure.

The two probes used in the fluorescence study were both received from Aldrich. The pyrene (99% optical grade) was purified by repeated recrystallization followed by sublimation. *N*,*N*,*N*′,*N*′-Tetramethyldiaminodiphenylketoimine hydrochloride (Auramine-O) was used as received.

The dye solubilization studies were conducted with the oil soluble dye Sudan III. It was purchased from Sigma, and had a purity of greater than 95%. It was also used as received.

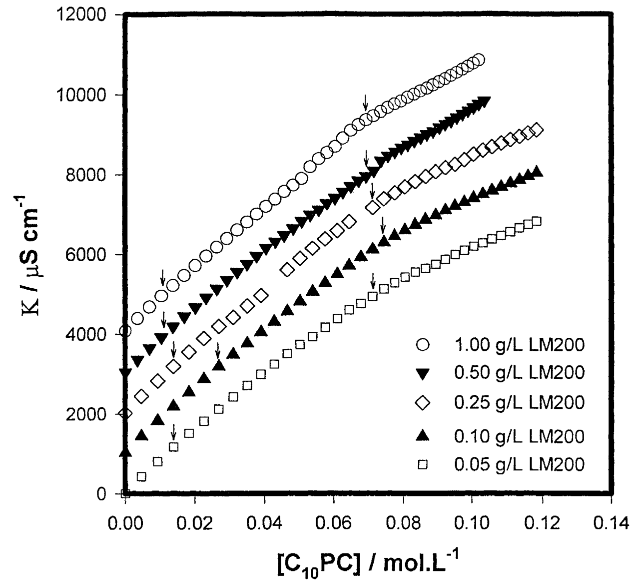

Fig. 2. Specific conductivity of C_{10}PC–LM200 systems as a function of a polymer concentration (arrows at lower conc. indicate CAC values and at higher concs. cmc values).

2.2. Solution preparation

All solutions were prepared with triply distilled grade deionized water. Deionization was carried out using a millipore purification system. The polymer stock solutions were made 24 h prior to use. All polymer–surfactant solutions were prepared using stock polymer solutions, and sonicated to ensure homogeneity.

The pyrene fluorescence experiments involved fixing the concentration of pyrene at 1.0×10^{-6} M in all solutions. All surfactant solutions were prepared with solvents containing pyrene.

The aggregation numbers of the surfactants were determined using static quenching. Pyrene was used as the probe and cetyl pyridinium chloride was used as the quencher. The solution preparation involved preparing a surfactant solution at a concentration well above the cmc. The pyrene concentration was fixed at 1.0×10^{-6} M. The solution was covered to eliminate light and allowed to stir for 24 h. The solution was then divided into two equal portions. The quencher was added to one of the portions to make a stock quencher solution of 1.0×10^{-3} M. This solution along with the nonquencher solution were used to create solutions of varying quencher concentrations.

The auramine-O studies were performed using solutions prepared from a probe stock solution. A solution of 5.0×10^{-3} M auramine-O in the solvent of choice was prepared in each case. A 500 µl volume of the stock was added to a series of 10 ml volumetric flasks that were used to prepare the surfactant solutions. The auramine-O concentration was kept constant at 2.5×10^{-4} M for each sample.

The dye solubilization studies involved saturation of each surfactant solution with Sudan III. The excess solid was filtered off after 24 h of equilibration in a temperature controlled water bath at 298 K.

2.3. Conductivity

The conductivity studies were performed using a conductometric titration method. The solvent (water or polymer solution) was contained in a thermostated-jacketed beaker. The conductivity measurements were carried with an automatic conductivity CDM 83 bridge operating at 1000 Hz and a platinum cell. The cell constant was 0.978 cm^{-1}. Conductivity titrations containing at least thirty different concentrations of surfactant were carried out at 298 K.

2.4. Fluorescence

Pyrene fluorescence measurements were carried out using a Perkin–Elmer MPF 66 fluorescence spectrophotometer. The experiments were done as a function of surfactant concentration. The polymer and probe concentrations were fixed. The fluorescence intensity of the pyrene solutions was followed over the range 360–500 nm. The fluorophore was excited at a wavelength of 340 nm. The excitation slit width was maintained at 1.5 nm, while the emission slit was 2.0 nm wide. The spectra were scanned at a rate of 30 nm/min.

The fluorescence studies with auramine-O were performed on the Aminco Bowman Series 2 luminescence spectrometer. In the auramine-O fluorescence experiments, an excitation wavelength of 368 nm was employed. Both the excitation and emission slit widths were maintained at 16 nm. The fluorescence intensity was scanned over a range 450–600 nm, with a scan speed of 1 nm/s.

2.5. Solubilization

The extent of the solubilization of Sudan III was determined with visible absorbance. The analysis was carried out using a Hewlett-Packard 8452A diode array spectrophotometer. Absorbance at 512 nm was monitored to determine the solubility of the Sudan III dye. Arrows in the plots indicate these deviations.

3. Results and discussion

Fig. 2 is a representative plot of the specific conductivities of the alkyl pyridinium chloride salts in aqueous solutions of varying concentrations of LM200. The deviation of the conductivity plots from linearity in the pre-cmc region is indicative of the presence of association and surfactant molecules with polymer (cac). The shift in the cmc values to higher concentrations also suggests the existence of polymer–surfactant associations.

The cac and cmc concentrations so determined for the alkyl pyridinium chloride surfactants in LM200 solutions are summarized in Table 1.

Conductivity measurements were also carried out using a

Table 1
CMC and CAC values for the alkyl pyridinium chloride salts

Surfactant	Solvent (g/l)	CAC (mol/l)	CMC[a] (mol/l)	CMC[b] (mol/l)	CMC[c] (mol/l)
$C_{10}PC$	Water	–	6.8×10^{-2}	6.8×10^{-2}	6.8×10^{-2}
$C_{10}PC$	0.05 LM200	1.4×10^{-2}	7.1×10^{-2}	–	–
$C_{10}PC$	0.10 LM200	2.6×10^{-2}	7.4×10^{-2}	–	–
$C_{10}PC$	0.25 LM200	1.4×10^{-2}	7.1×10^{-2}	7.2×10^{-2}	7.2×10^{-2}
$C_{10}PC$	0.50 LM200	1.0×10^{-2}	6.9×10^{-2}	–	–
$C_{10}PC$	1.00 LM200	1.0×10^{-2}	6.9×10^{-2}	–	–
$C_{12}PC$	Water	–	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}
$C_{12}PC$	0.05 LM200	2.6×10^{-3}	1.7×10^{-2}	–	–
$C_{12}PC$	0.10 LM200	5.3×10^{-3}	1.7×10^{-2}	–	–
$C_{12}PC$	0.25 LM200	3.8×10^{-3}	1.7×10^{-2}	1.7×10^{-2}	1.8×10^{-2}
$C_{12}PC$	0.50 LM200	2.5×10^{-3}	1.6×10^{-2}	–	–
$C_{12}PC$	1.00 LM200	2.4×10^{-3}	1.6×10^{-2}	–	–
$C_{14}PC$	Water	–	3.7×10^{-3}	3.7×10^{-3}	3.7×10^{-3}
$C_{14}PC$	0.05 LM200	3.6×10^{-4}	3.7×10^{-3}	–	–
$C_{14}PC$	0.10 LM200	5.0×10^{-4}	4.0×10^{-3}	–	–
$C_{14}PC$	0.25 LM200	4.1×10^{-4}	3.9×10^{-3}	3.9×10^{-3}	3.8×10^{-3}
$C_{14}PC$	0.50 LM200	3.8×10^{-4}	3.8×10^{-3}	–	–
$C_{14}PC$	1.00 LM200	3.5×10^{-4}	3.8×10^{-3}	–	–
$C_{16}PC$	Water	–	9.0×10^{-4}	9.0×10^{-4}	9.0×10^{-4}
$C_{16}PC$	0.05 LM200	2.3×10^{-4}	9.1×10^{-4}	–	–
$C_{16}PC$	0.10 LM200	3.7×10^{-4}	9.3×10^{-4}	–	–
$C_{16}PC$	0.25 LM200	2.0×10^{-4}	9.3×10^{-4}	9.3×10^{-4}	9.4×10^{-4}
$C_{16}PC$	0.50 LM200	2.0×10^{-4}	9.2×10^{-4}	–	–
$C_{16}PC$	1.00 LM200	Too low	9.2×10^{-4}	–	–

[a] Conductometric titration.
[b] Fluorescence of pyrene.
[c] Fluorescence of auramine-O.

systematic series of ammonium-based surfactants (C_nTAB, C_nDAB, and C_nAB). The substituents attached to the central nitrogen atom of the head group region clearly influenced the mechanism and extent of interaction in the polymer–surfactant systems. The conductivity plots for the C_nTAB salts in LM200 solvent blends all show a displacement in the cmc values from the aqueous values. Although this evidence supports the concept of polymer–surfactant association, the apparent lack of a second break point (cac) in the conductivity plot suggests that the interaction of these surfactants with LM200 was not as strong as in the case of the C_nPC salts with LM200. This may be due to the nature of the head group of these surfactants. The three methyl groups make the head group region quite bulky, thus the interactions with the polymer molecules may be sterically hindered due to the inability of the monomers to closely pack in a micelle-like aggregate (Ananthapadnabhan, 1993). The head group region of the C_nPC salts is also quite large, but it contains a pi cloud that may enhance the possibility of an association of LM200 and the surfactant monomers.

The alkyldimethyl ammonium bromide and the alkyl ammonium bromides have a more intense association with LM200 than the C_nTAB salts, indicating by a larger difference in the cmc values (Δcmc), as well as the presence of a cac break point in the conductivity plots. The effect was more pronounced in the case of the alkyl ammonium bromide surfactants. However, a slight turbidity was observed in the $C_{10}AB$ / LM200 solution before the cmc. The solution remained turbid even after the cmc was reached. Goddard and Leung (1992) observed similar phase behavior in the case of $C_{10}TAB$ with LM200.

There are two possible explanations for the increase in the polymer–surfactant association with a decrease in the number of methyl substituents on the polar head of the ammonium-based surfactants. The replacement of the methyl group(s) with a hydrogen atom(s) makes the head group region less bulky, thus the association of the surfactants with LM200 molecules is less sterically hindered. The presence of the hydrogen atom(s) on the head group also allows for the possibility of hydrogen bonding with the oxygen atoms of the polymer backbone. The critical concentrations obtained through specific conductance studies of the ammonium-based surfactants are summarized in Tables 2 and 3.

The interaction between the LM200 molecules and the families of surfactants investigated was found to be more prominent for surfactants with smaller surfactant tail lengths. This may be due to a higher cmc values of these surfactants. One further note regarding the interaction of LM200 with the cationic surfactants considers the dependence of the association on the polymer concentration (Tables 1–3). For a given surfactant, the maximum shift

Table 2
CMC Values for the alkyl trimethylammonium bromide salts

Surfactant	Solvent (g/l)	CMC[a] (mol/l)	CMC[b] (mol/l)	CMC[c] (mol/l)
$C_{10}TAB$	Water	6.8×10^{-2}	6.8×10^{-2}	6.8×10^{-2}
$C_{10}TAB$	0.05 LM200	6.9×10^{-2}	–	–
$C_{10}TAB$	0.10 LM200	7.2×10^{-2}	–	–
$C_{10}TAB$	0.25 LM200	7.0×10^{-2}	7.1×10^{-2}	7.2×10^{-2}
$C_{10}TAB$	0.50 LM200	7.0×10^{-2}	–	–
$C_{10}TAB$	1.00 LM200	6.9×10^{-2}	–	–
$C_{12}TAB$	Water	1.6×10^{-2}	1.6×10^{-2}	1.6×10^{-2}
$C_{12}TAB$	0.05 LM200	1.6×10^{-2}	–	–
$C_{12}TAB$	0.10 LM200	1.9×10^{-2}	–	–
$C_{12}TAB$	0.25 LM200	1.8×10^{-2}	1.8×10^{-2}	1.8×10^{-2}
$C_{12}TAB$	0.50 LM200	1.8×10^{-2}	–	–
$C_{12}TAB$	1.00 LM200	1.6×10^{-2}	–	–
$C_{14}TAB$	Water	3.5×10^{-3}	3.5×10^{-3}	3.5×10^{-3}
$C_{14}TAB$	0.05 LM200	3.5×10^{-3}	–	–
$C_{14}TAB$	0.10 LM200	3.8×10^{-3}	–	–
$C_{14}TAB$	0.25 LM200	3.7×10^{-3}	3.8×10^{-3}	3.8×10^{-3}
$C_{14}TAB$	0.50 LM200	3.7×10^{-3}	–	–
$C_{14}TAB$	1.00 LM200	3.6×10^{-3}	–	–
$C_{16}TAB$	Water	9.2×10^{-4}	9.2×10^{-4}	9.2×10^{-4}
$C_{16}TAB$	0.05 LM200	9.3×10^{-4}	–	–
$C_{16}TAB$	0.10 LM200	9.4×10^{-4}	–	–
$C_{16}TAB$	0.25 LM200	9.3×10^{-4}	9.4×10^{-4}	9.4×10^{-4}
$C_{16}TAB$	0.50 LM200	9.3×10^{-4}	–	–
$C_{16}TAB$	1.00 LM200	9.3×10^{-4}	–	–

[a] Conductometric titration.
[b] Fluorescence of pyrene.
[c] Fluorescence of auramine-O.

in the cmc was found to occur at a concentration of 0.1 g/l of LM200. One would assume that this was the concentration of the polymer corresponding to the maximum possible interactions between the polymer and the surfactant. However, the cac region begins at a higher surfactant concentration in this solvent system. The most likely explanation for the delay of polymer–surfactant and surfactant–surfactant interactions may be due to the domination of polymer–polymer interactions at this concentration of polymer (Winnik & Regismond, 1996). The conductivity data obtained for the C_nTAB and C_nPC surfactants were used to estimate the free energy of transfer of a methylene unit of the surfactant tail from the bulk phase to the micelle phase. The free energy value can provide some valuable information about the effect of the polymer on the micellization process (Zana, 1996). The Gibbs free energy of micellization was calculated using Eqs. (1) and (2).

$$\Delta G_{\mathrm{mic}} = \Delta G_{\mathrm{mic}}(\text{–CH}_3) + n\Delta G_{\mathrm{mic}}(\text{–CH}_2\text{–}) + \Delta G_{\mathrm{mic}}(\text{–X}) \tag{1}$$

$$\Delta G_{\mathrm{mic}} = (2 - \alpha)\mathrm{R}T \ln(\mathrm{X}_{\mathrm{cmc}}) \tag{2}$$

In Eq. (1), the Gibbs free energy has been broken down into the component parts of the surfactant ($CH_3(CH_2)_nX$). In this case X represents the head group of the surfactant. In the second equation the effective degree of dissociation of the micelle and the mole fraction of the cmc are represented by α and X_{cmc}, respectively. From the plots of free energy of micellization as a function of the number of carbon atoms in the surfactant tail, it can be concluded that there is virtually no difference in the free energy for transferring a methylene unit in the presence of LM200 for both series of surfactants (within the experimental error of 0.5 kJ). The presence of polymer in solution may have inhibited the micellization process by reducing the amount of free surfactant monomer in solution, but once the critical micelle concentration is reached, the polymer had little influence on the surfactant association.

3.1. Fluorescence spectroscopy

The pyrene emission spectrum is a well-known tool utilized in the determination of micropolarity of the media. The polarity of the microenvironment is probed with a change in the ratio I_1/I_3 of the relative intensities of the (0,0) and (0,3) bands, respectively. The ratio increases with increasing polarity (Dong & Winnik, 1985). This chemical tool was first employed in the field of surfactant chemistry by (Kalyanasundaram & Thomas, 1977), and has been more recently used to study polymer–surfactant systems (Winnik & Regismond, 1996). The cmc and cac of surfactants can be obtained from measurements of the changes in I_1/I_3 as a function of surfactant concentration. The ratio of I_1/I_3 decreases sharply at the onset of micellization, as a

Table 3
CAC and CMC for the alkyl dimethylammonium bromide salts and the alkyl ammonium bromide salts

Surfactant	Solvent (g/l)	CAC (mol/l)	CMC[a] (mol/l)	CMC[b] (mol/l)	CMC[c] (mol/l)
$C_{12}DAB$	Water	–	1.2×10^{-2}	1.3×10^{-2}	1.3×10^{-2}
$C_{12}DAB$	1.00 LM200	4.1×10^{-3}	1.3×10^{-2}	1.4×10^{-2}	1.4×10^{-2}
$C_{10}AB$	Water	–	6.5×10^{-2}	6.6×10^{-2}	5.8×10^{-2}
$C_{10}AB$	1.00 LM200	3.0×10^{-3}	7.5×10^{-2}	7.8×10^{-2}	8.1×10^{-2}
$C_{12}AB$	Water	–	1.4×10^{-2}	1.4×10^{-2}	1.4×10^{-2}
$C_{12}AB$	1.00 LM200	3.8×10^{-3}	1.5×10^{-2}	1.6×10^{-2}	1.6×10^{-2}

[a] Conductometric titration.
[b] Fluorescence of pyrene.
[c] Fluorescence of auramine-O.

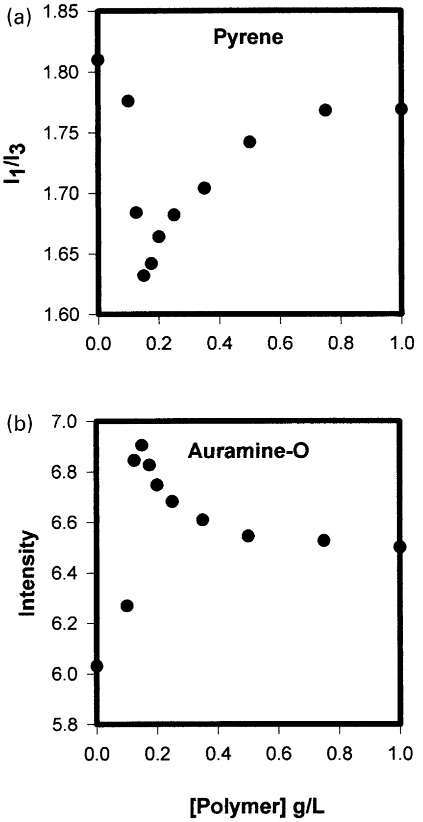

Fig. 3. Micropolarity and microviscosity of aqueous solutions of LM200.

result of the preference of pyrene to reside in the nonpolar regions of the aggregates (Thomas, 1990).

Auramine-O is a fluorescent probe often used to detect the microviscosity of its immediate solution environment (Miyagishi, Asakawa & Nishida, 1987). The fluorescence quantum yield of the probe decreases by dissipation of electronic energy through intramolecular rotation (Mwalupindi, Rideau, Agvaria & Warner, 1994). Hence, the fluorescence intensity of the probe indicates the effective microviscosity of its environment. A major peak in the fluorescence spectra at approximately 510 nm is followed for the studies.

The fluorescence studies were first carried out for aqueous polymer solution. It was found that the polymer did not possess the ability to fluoresce on its own. Pyrene was added to these LM200 solutions, and the I_1/I_3 ratio was followed as a function of the polymer concentration. Winnik et al. (1996) conducted a similar study, but only reported the findings at 0.5 g/l ($I_1/I_3 = 1.74$), and 1.5 g/l ($I_1/I_3 = 1.61$). The results are in good agreement in the region of concentration overlap. A plot summarizing the dependence of micropolarity on polymer concentration is shown in Fig. 3a. The minimum micropolarity occurred at 0.15 g/l of LM200. This result suggests the presence of inter- and intramolecular polymer interactions thereby creating nonpolar regions in solution. It is well known that LM200 can form hydrophobic microdomains with its alkyl chain units, (Guillement & Piculell, 1995), and these may provide preferential solubilization sites for pyrene molecules.

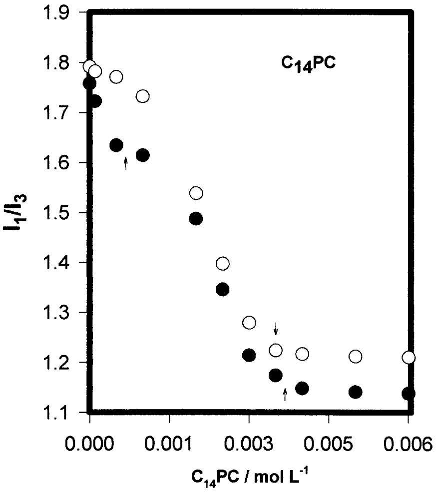

Fig. 4. Micropolarity plot for $C_{14}PC$ in water (○), and 0.25 g/l of LM200 (●).

The fluorescence of auramine-O was also studied in the presence of LM200. The plot of intensity as a function of the polymer concentration shows a maximum microviscosity at 0.15 g/l of LM200 (Fig. 3b). The critical point corresponds to the concentration at the minimum in the micropolarity plot for LM200. This observation reinforces the argument in favor of the existence of hydrophobic regions created by the interactions between the polymer chains. Since auramine-O is a cationic probe, it will not reside near the charged regions of the polymer substituent groups. It will prefer to be located close to the sugar residues of the polymer backbone. The probe molecules could also situate themselves in the water filled spaces in the microdomain structures of aggregates of LM200 molecules. These aggregates may represent a loose association of molecules that has an increased resistance to flow; hence, the probe senses the highest microviscosity in their presence.

The interaction between the alkyl pyridinium chloride salts and the polymer were investigated using pyrene as a fluorescence probe. Fig. 4 depicts a comparison of the micropolarity sensed by the probe in $C_{14}PC$ system in the presence and absence of polymer–surfactant associations. The deviation occurred in the fluorescence intensity prior to the cmc was taken as evidence for the association of surfactant molecules with the polymer (cac). There is also a notable shift in the cmc values. The cmcs obtained from the fluorescence experiments are presented in Table 1. The results are in good agreement with the values obtained from specific conductance.

The fluorescence experiments were also conducted using the ammonium-based family of surfactants. The focus was initially placed on the C_nTAB salts in LM200. A study of $C_{12}TAB$ and $C_{16}TAB$ in 1.0 g/l of LM200 was conducted by Winnik et al., 1996. This group observed a difference in the shape of the I_1/I_3 plots before the cmc in the presence and

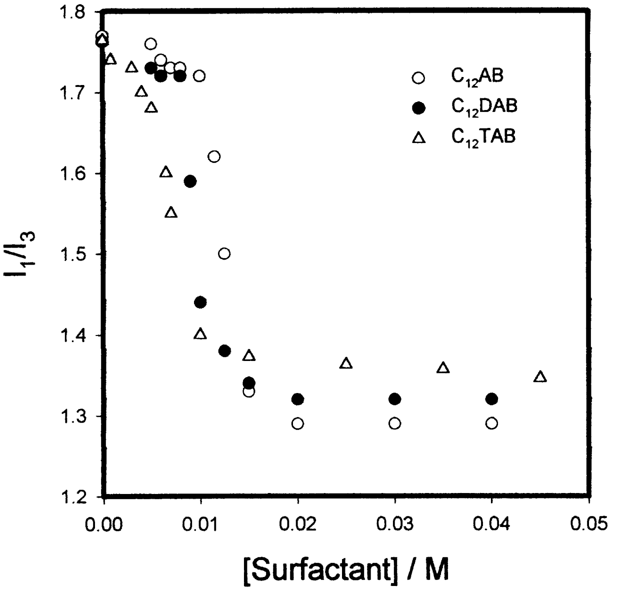

Fig. 5. Pyrene probe studies on the interactions of LM200 with $C_{12}AB$,$C_{12}DAB$ and $C_{12}TAB$.

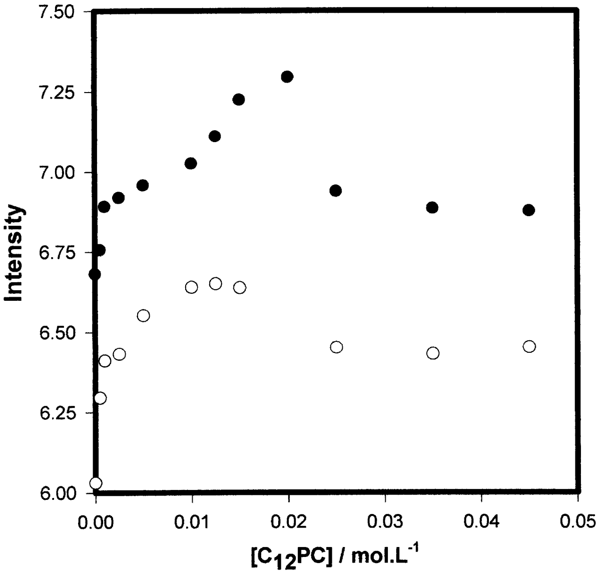

Fig. 6. Microviscosity plot for $C_{12}PC$ in water (○), and 0.25 g/l of LM200 (●).

absence of polymer. This was attributed to an interaction driven by hydrophobic forces between the polymer and the surfactant monomers. A slight shift in the cmc value to a higher surfactant concentration was also noted in the presence of polymer, due to this association.

Similar results were obtained in this study, which was carried out on the family of C_nTAB salts in a solvent of 0.25 g/l of LM200. These observations are noteworthy since the cac region was not distinguishable from the conductivity plots. The cmc values for the TABs correlated well with the values obtained through conductometric titration experiments and are summarized in Table 2.

Fig. 5 depicts the micropolarity studies of the ammonium-based surfactant systems in a LM200 solvent blend as a function of the surfactant concentration. Although all families of surfactants appear to undergo some sort of association with the polymer molecules, the interaction appears to be intensified with a decrease in the number of methyl units of the head group region. Again, this is further evidence to support the concept of dual polymer–surfactant interactions composed of hydrophobically driven aggregation and hydrogen bond formation.

The microviscosity of the polymer–surfactant systems was studied by following the fluorescence of auramine-O in these systems. The auramine-O fluorescence reached a maximum value at the cmc of each surfactant in both aqueous and LM200 solvent systems (Figs. 6 and 7). This trend is well documented in the literature; it reflects the dynamic nature of the micellar system that leads to an increase in the resistance to flow (Methernitis, Morcellet, Sabbadin & François, 1986).

The maximum microviscosity occurred at a higher surfactant concentration in the LM200 solution than in water. The shifts in the cmc values closely resembled those obtained from conductivity and micropolarity studies (Tables 1–3). The intensity of the maximum microviscosity for each member of a given family of surfactants was not dependent on the chain length of the surfactant, but did show a weak dependence on the polymer concentration. This suggests that probe molecules do not reside inside the aggregates, but rather situate themselves somewhere around the periphery of the aggregates. Thus, the number of surfactant monomers composing the aggregates does not influence the intensity of the fluorescence.

A representative plot of the microviscosity sensed by the probe in the C_nPC salt solutions is shown in Fig. 6. The anomaly present prior to the cmc in the plot of these surfactants in the LM200 blends is more prominent in the case of the pyridinium chloride salts than the other family of surfactants. This phenomenon may be a result of the unique ability of this family of salts to undergo pi cloud interactions with the hydrophobic part of the polymer molecules, thus leading to stronger associations between the polymer and surfactant.

Fig. 7 provides a comparison of the microviscosity sensed by the probe in the ammonium-based surfactants in the presence and absence of LM200. Although there is an obvious difference in the microviscosity plots for each member of the surfactant families in water, the presence of LM200 in solution increases the differences in the microviscosity plots. The most notable variation is the shift in the maximum. The greatest change in the cmc for a given chain length of surfactant occurred with the C_nAB salts. The smallest change in the cmc value was observed in the C_nTAB salts. This was attributed to the ability of the C_nDAB and C_nAB surfactants to form hydrogen bonds with the polymer. Hence, dual polymer–surfactant interactions intensify the association between the two species in the case of these two surfactant families.

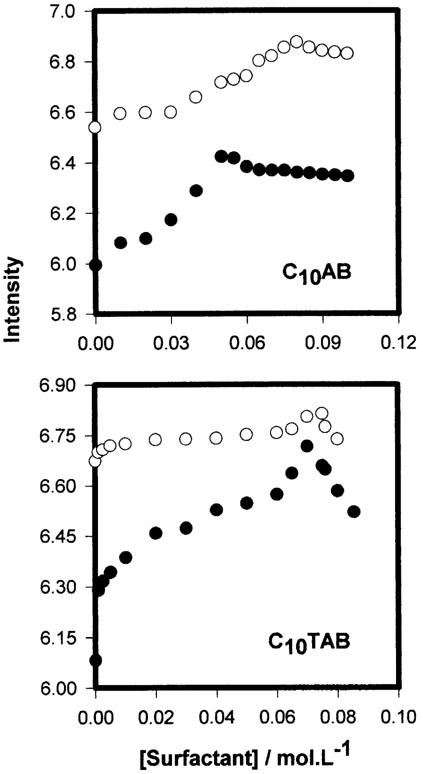

Fig. 7. Comparison of the change in the cmc detected by auramine-O fluorescence for $C_{10}AB$ and $C_{10}TAB$ in water (○), and in 1.0 g/l of LM200 (●).

3.2. Fluorescence quenching

The pyridinium ion present in the alkyl pyridinium chloride surfactants is a known quencher of the excited single state of pyrene (Davis, 1973). Fluorescence quenching is the reduction of the fluorescence emission by competing deactivating processes, resulting from the specific interactions between an excited chromophore and another substance present in the system (Rosenbluth, Weiss-Lopez & Olea, 1997).

Quenching can occur through a dynamic or a static mechanism (Chang & Forcé 1995). For a dynamic mechanism, the ratio of the fluorescence intensity in the absence (I_0) and presence (I) of quencher is equal to the ratio of fluorescence lifetimes in the absence (τ_0) and presence (τ) of quencher. It is common practice to follow the first vibronic peak in the pyrene spectrum to obtain the intensities. The ratios are related to the Stern–Volmer constant (K_{SV}) and quencher concentration as shown below:

$$I_0/I = \tau_0/\tau = 1 + K_{SV}[Q] \qquad (3)$$

where [Q] is the quencher concentration, K_{SV} is equal to the product of the quenching rate constant (k_q) and τ_0.

When static quenching occurs in addition to dynamic quenching, the ratio of the intensities is given below:

$$I_0/I = \tau_0/\tau = 1 + (K_{SV} + K_{eq})[Q] \qquad (4)$$

K_{eq} is the equilibrium constant for the fluorophore–quencher complex.

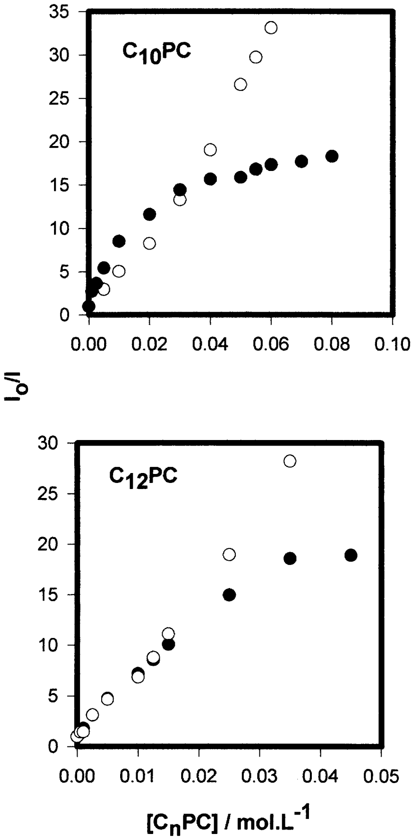

Fig. 8. Stern–Volmer plots for pyrene for $C_{10}PC$ and $C_{12}PC$ in water (○) and in 0.25 g/l of LM200 (●).

The quenching ability of the pyridinium chloride surfactants was investigated to obtain additional information about the interaction of the salts with LM200. Stern–Volmer plots were obtained. The plots for $C_{10}PC$ and $C_{12}PC$ are shown in Fig. 8. Each of the surfactants in the C_nPC series had a Stern–Volmer plot that curved in a slightly upward manner in pure water. This observation suggests that for the aqueous surfactant systems both static and dynamic quenching were occurring simultaneously. The upward curvature indicates that the dominant quenching mechanism was static in nature. This is a viscosity independent quenching process (Rosenbluth et al., 1997).

The Stern–Volmer plots in the presence of LM200 displayed a downward curvature. This deviation from the linear model is characteristic of a quenching mechanism that is mostly dynamic in nature. Overall, the process is quite dependent on the viscosity of the solution. The more prominent deviation from linearity occurred in the presence of LM200. This observation indicates that the secondary quenching process was more intense in the polymer solution than in water. The extent to which these mechanisms take place in a given system can only be determined by time resolved fluorescence studies (Chang & Forcé, 1995).

Table 4
Stern–volmer constants for the alkyl pyridinium chloride salts

Surfactant	Solvent (g/l)	K_{SV} (l/mol)
C_{10}PC	Water	363
C_{10}PC	0.25 LM200	428
C_{12}PC	Water	804
C_{12}PC	0.25 LM200	863
C_{14}PC	Water	566
C_{14}PC	0.25 LM200	599
C_{16}PC	Water	1364
C_{16}PC	0.25 LM200	1492

The initial linear portion of the Stern–Volmer plots was used to obtain the Stern–Volmer constant (K_{SV}). The magnitude of this value is a direct indication of the quenching efficiency (Rosenbluth et al., 1997). The larger the K_{SV} value, the more efficient is the quenching process. The Stern–Volmer constants are summarized in Table 4. There are two notable trends in these values. The quenching efficiency increased with an increase in the chain length of the surfactant. This has been reported in the literature to be the case for the alkyl pyridinium chloride salts in water (Blackburn, Lockwood & Solan, 1976). The other interesting trend was the increase in the quenching efficiency in the presence of LM200 for all surfactants under investigation. For polyelectrolyte– or polysoap–surfactants systems, quenchers with a long linear alkyl chain were found to be very inefficient and in some case unable to quench the pyrene fluorescence (Cohin, Candau & Zana, 1993). In the present study it is observed that the all alkyl pyridinium salts were able to quench the pyrene fluorescence efficiently contradicting earlier findings.

Table 5
Aggregation numbers of the ammonium-based salts

Surfactant	Solvent (g/l)	Aggregation number
C_{10}TAB	Water	39
C_{10}TAB	1.00 LM200	32
C_{12}TAB	Water	57
C_{12}TAB	0.10 LM200	56
C_{12}TAB	0.15 LM200	53
C_{12}TAB	0.25 LM200	52
C_{12}TAB	0.50 LM200	51
C_{12}TAB	1.00 LM200	49
C_{14}TAB	Water	68
C_{14}TAB	1.00 LM200	64
C_{16}TAB	Water	88
C_{16}TAB	1.00 LM200	85
C_{12}DAB	Water	60
C_{12}DAB	1.00 LM200	54
C_{10}AB	Water	39
C_{10}AB	1.00 LM200	58
C_{12}AB	Water	56
C_{12}AB	1.00 LM200	49

3.3. Aggregation numbers

A comparison of the size of a surfactant's micelles in the presence and absence of polymer can be used to further investigate the nature of the polymer–surfactant interactions above the cmc. Aggregation numbers can be determined using a fluorescence method. The use of static quenching for the determination of micellar size was first employed by Turro and Yekta (1978). The quencher is maintained at a concentration low enough not to disturb the self-assembly of the surfactant monomers. The fluorescence intensity (I_1) in the presence of quencher is represented by the following equation:

$$I_1 = I_0\, e^{(-[Q]/[M])} \tag{5}$$

The I_0 is the fluorescence intensity in the absence of quencher. The concentration of micelles is given by [M]. This value is equal to the slope of the line obtained from a plot of $\ln(I_0/I)$ as a function of the quencher concentration. The aggregation number (N_A) can then be calculated from the equation provided below:

$$N_A = (C_{surf} - cmc)/[M] \tag{6}$$

The surfactant concentration (C_{surf}) was maintained at a concentration that was at least double the cmc. The experimentally determined cmc or cac values for the surfactants in different solvents were used to determine the aggregation numbers.

In this particular study, pyrene was used as the probe. Two quenchers chosen were hexadecyl pyridinium chloride (C_{16}PC) and benzophenone (Nilson et al., 1995). Benzophenone was used to verify the aggregation numbers obtained by C_{16}PC as a quencher. It was found that the numbers obtained by employing these two quenchers were in agreement. Since the C_nPC salts are able to quench the fluorescence of pyrene, the aggregation numbers for this family were not determined in this study. The experiments were repeated several times to ensure reproducibility.

A study of the influence of the concentration of LM200 on the aggregation number of C_{12}TAB was carried out at five different concentrations of the polymer (Table 5). It was found that the aggregation number decreased slightly with an increase in the LM200 concentration. This suggests that with an increase in the number of polymer hydrophobic side chains present in solution these chains may become incorporated into the surfactant micelles, hence forming mixed micelles. Thus, as the polymer concentration was increased the polymer–surfactant interactions were enhanced.

The study was also carried out as a function of the chain length of the C_nTAB surfactants. It was determined that the

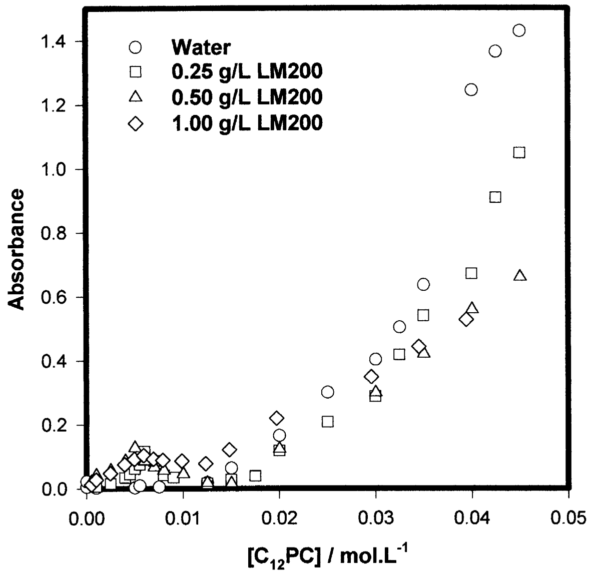

Fig. 9. Solubility of Sudan III in C_{12}PC–LM200 systems as a function of polymer concentration.

difference between the aggregation number in 1.0 g/l of LM200 and the values in aqueous solution increased as the chain length decreased. This may be due to a greater difficulty fitting into the compact micelles formed by the surfactants with higher chain lengths.

The effect of the head group size of the surfactant and the possibility of hydrogen bond formation was also examined using the ammonium-based surfactants. The results are also summarized in Table 5. A comparison of the results for the dodecyl version of each family of surfactants in 1.0 g/l of LM200 suggests that the above mentioned factors had very little influence on the aggregation number for each surfactant. Although the size of the head group would influence the size of the micelle, each different micelle must have similar spacing, thus accommodating a similar number of polymer side chains. It was also apparent that the ability of the surfactant head group to form hydrogen bonds with the polymer backbone does not affect the composition of the micelles.

3.4. Dye solubilization

Sudan III was the organic molecule of choice for the solubility section of the study. It is a highly conjugated azo dye, which is insoluble in water. In typical aqueous surfactant systems solubilization of organic compounds, such as Sudan III, is thought to occur either deep in the palisade layer of the micelle, or in the inner core of the micelle (Rosen, 1978).

Both UV and NMR studies indicate that such probes reside in a predominantly nonpolar environment on solubilization (Eriksson, 1963; Reigelman, Allawala, Hrenoff & Strait, 1958). The solubilization process is influenced by a number of factors such as the structure of the surfactant, the structure of the organic additives, the temperature, as well as the presence of polymeric additives. The two varied factors in this study were the structure of the surfactant and the presence of a polymer in solution.

Dye solubilization experiments were performed at various concentrations of LM200 in order to confirm the presence of polymer–polymer associations. Micropolarity studies have indicated that relatively nonpolar regions exist at given concentrations of the polymer, but there was no significant solubilization of Sudan III at any concentration of LM200 in the absence of surfactant. The difference can be attributed to the fact that dye solubilization is a bulk phenomenon while fluorescence studies are restricted to the microenvironment of the polymer solutions.

Fig. 9 depicts the solubilization plots for C_{12}PC as a function of LM200 concentration. There was an increase in absorbance due to the dye solubilized prior to the cmc in the presence of polymer compared to the absence of absorbance in aqueous surfactant solutions. The onset of the increase in absorbance corresponded to the cac value found with the conductivity studies. It can be concluded that micelle-like aggregates are formed between the alkyl chain of the polymer substituents and the hydrocarbon tail of the surfactant monomers. This results in the creation of a favorable nonpolar region for dye solubilization. The absorbance attained a maximum in the cac region due to the saturation of the substituent sites on the polymer backbone, followed by a decline in the amount of dye solubilized in the system until the micellization occurred. This type of pre-micellar absorbance was observed for all surfactant–LM200 systems investigated. There was little difference in the absorbance of the dye over the cac region with a variation in the LM200 concentration. At higher concentrations of surfactant (>cmc), the amount of dye solubilized decreased with an increase in the polymer concentration for a given concentration of surfactant. The decrease in the dye solubility at higher concentrations of polymer may be due to the formation of mixed micelles, in which an alkyl chain of the polymer became incorporated into a micelle. This would decrease the amount of space available in the micelle for the solubilization of a dye molecule.

The absorbance due to the dye solubilized does show some dependence on the alkyl chain length of the surfactant due to the difference in monomer concentration prior to the cmc.

Similar results were obtained with the ammonium-based surfactants. It is observed that the polymer–surfactant interaction becomes more intense with a decrease in the size of the polar head group and an increase in the ability of the head group region to form hydrogen bonds with the polymer. Overall, the C_nDAB and C_nAB ammonium bromide surfactants interact more strongly with the polymer compared to C_nTAB. The cac and cmc values obtained for

C_nDAB and C_nAB surfactants from the solubility studies correlate well with those obtained from other experimental means.

4. Conclusions

There are several important conclusions that can be drawn from the present investigation of the cationic cellulose ether derivatized Quatrisoft® LM200 polymer and surfactants of like charge. The results indicate that the hydrophobically modified polymer interacts significantly with all families of surfactants studied. This includes the alkyl pyridinium chlorides, the alkyltrimethyl ammonium bromides, the alkyldimethyl ammonium bromides, and the alkyl ammonium bromides. It is believed that at a particular concentration (cac), prior to the cmc, the polymer molecules began to partake in an association with the surfactant monomers in solution. Micelle-like aggregates are thought to form from an association of the hydrophobic tails of the surfactant monomers and the alkyl chain of the LM200 polymer. Such an interaction is hydrophobically driven. In addition to the above interaction, it is also possible for the C_nDAB and C_nAB surfactants to interact with the polymer backbone through hydrogen bonding. The C_nPC salts and the C_nAB salts appear to have the most intense interaction with the LM200 polymer compared to the other ammonium-based salts. This may be due to the pi cloud of the head group region in the case of the C_nPC salts, and the great hydrogen bonding ability of the C_nAB surfactants. The steric hindrance associated with the bulky head groups of the C_nTAB inhibits interaction with the polymer molecules. This restriction is also prevalent in the C_nDAB–LM200 systems.

The interactions between the polymer and the surfactant appeared to be intensified with a decrease in the alkyl chain length of the surfactants. It was concluded that this was a result of the higher concentration of free surfactant monomer in solution at lower chain lengths before the cmc is reached (Guveli, 1989).

A study of the behavior of LM200 in solution was also performed. The results indicated that an association of the polymer molecules is dependent on the polymer concentration. At a particular concentration of 0.15 g/l of LM200 the polymer molecules form loosely associated, viscous aggregates.

Overall, this study has proven that a polymer and surfactants of the same charge can interact in more than a repulsive manner. Such interactions may prove useful for industrial applications.

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