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Probing the association behavior of poly(ethyleneglycol) based amphiphilic comb-like polymer in the presence of cationic surfactant

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Abstract

The interaction between an amphiphilic comb-like polymer—poly(styrene–maleic anhydride) copolymer esterified with brij-35—and a cationic surfactant, *N*-cetyl-*N*,*N*-diethanolyl-*N*-methyl ammonium bromide (CDMAB), was investigated at pH 6.2. Our earlier experiments (Polymer 42, 7801, 2001) revealed that at this pH the polymer forms intramolecular aggregates and these self-aggregates behave as polyelectrolyte due to the partial ionization of the backbone of the polymer. When surfactant is gradually added to the polymer solution in the present study, binding of the surfactant to the polymer takes place even at lowest surfactant concentration. Initially binding occurs due to electrostatic interaction, leading to compact aggregates. After complete charge neutralization of the polymer backbone, the surfactant hydrophobes are adsorbed into the microdomains formed by the polymer due to hydrophobic interactions. An exothermic enthalpy change is associated with both kinds of interactions, electrostatic as well as hydrophobic. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Comb-like polymer; Intramolecular aggregates; Polymer–surfactant interaction

1. Introduction

Hydrophobically modified water-soluble polymers show unusual rheological features and high solubilization properties in aqueous media [1,2]. These properties arise from inter- or intra-molecular association among hydrophobic groups, providing hydrophobic microdomains in an isotropic aqueous solution. Self-assemblies of block copolymers or hydrophobically modified polymers have been investigated in the field of biotechnology and pharmaceutics [3,4]. In aqueous media, such polymeric amphiphiles are assumed to form self-assemblies, consisting of inner core of hydrophobic segments and the outer shell of hydrophilic segments, due to the preference for the formation of free-energy minimized structures. These self-assemblies of polymeric amphiphiles with core–shell morphology are potential drug carriers because the inner core can solubilize hydrophobic bioactive agents [3]. In addition to hydrophobic interactions, the driving force for the aggregation of these systems may include ionic interactions and intra- and/or inter-molecular hydrogen bonding. A very minor alteration in the chemical structures modifies these interactions to a very large extent and in some cases show similar solution properties to those of surfactant molecules [1,2].

Comb-like polymer is a special architectural variation of conventional block copolymer [5–24]. Very recently a new class of associative comb-like polymers, in which an oligomeric PEG chain is sandwiched between the hydrocarbon backbone and an alkyl pendant segment, has been investigated by different techniques [8–24]. Studies of the association properties of one such polymer in an aqueous medium, prepared from methacrylic acid, ethyl acrylate and $C_{20}H_{41}O–E_{35}$ macromonomer with mole ratio 49.05:50.04:0.9, respectively, suggested that at low pH (<7.5) a large number of smaller aggregates are formed, which transform to larger structures at higher pH (>7.5) [8]. A detailed fluorescence probe study of this polymer at high pH revealed that the hydrophobic microdomains vary from nonionic micelle-like structures containing upward of 60 $C_{20}H_{41}$ groups, mixed structures containing $C_{20}H_{41}$ and ethyl acrylate, and some protonated methacrylic acid groups [8–10]. Interactions between sodium dodecyl sulphate and this class of associative polymer at high pH have also been studied using isothermal titration calorimetric techniques by varying both the degree of polymerization of PEG part and

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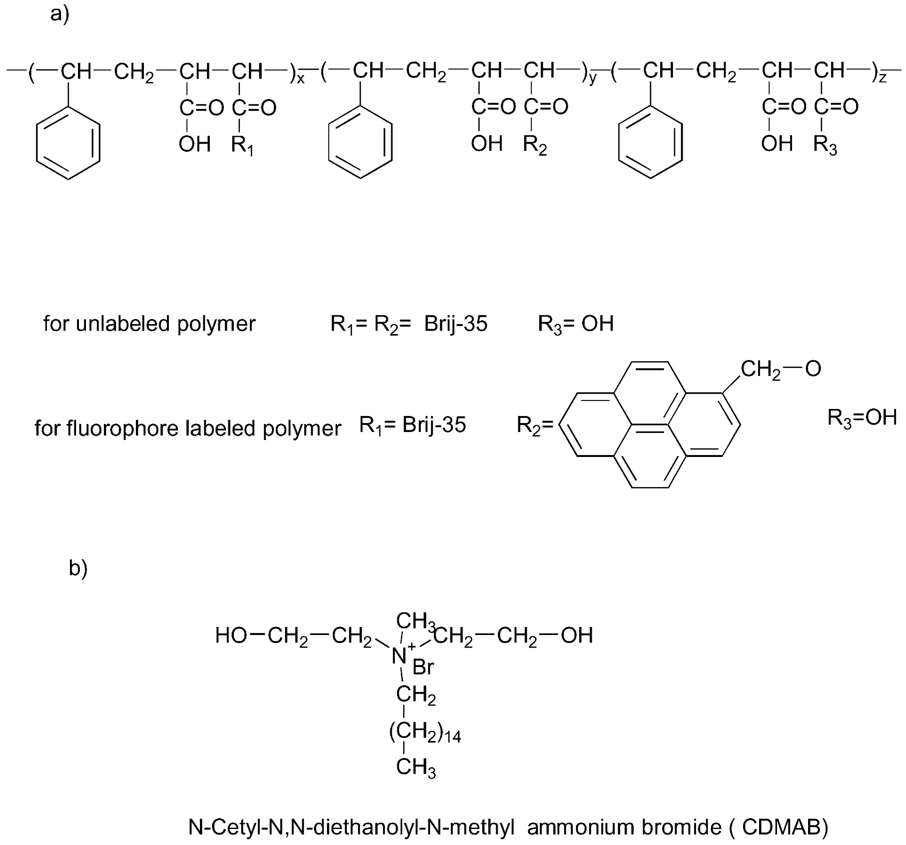
hydrophobic chain length of the pendant group [16,17]. It has been observed that, with increase in hydrophobic chain length, both the change in Gibbs free-energy of aggregation and the critical aggregation concentration (cac) decrease, while the enthalpy becomes less negative. Very recently, Noda and coworkers [21–24] have studied association behavior of polyAMPS-bound $C_{12}E_{25}$ moieties. They have shown that polymer-bound $C_{12}E_{25}$ moieties form aggregates via intra- and inter-polymer associations, and these polymer-bound aggregates are bridged by polymer chains. As a result a network structure is formed. The extent of such aggregate bridging strongly depends on polymer concentration and ionic strength of the solution. In a recent article [25], we reported the aggregation properties of a similar kind of comb-like polymer with poly(styrene–maleic anhydride) copolymer with high content (~34 mole%) of alkylated PEG grafts as pendent groups (Scheme 1). In that study, we used a combination of pyrene partition, surface tension, steady-state fluorescence, viscosity and light scattering experiments to examine the overall aggregation behavior of the polymer as a function of pH and salt concentration. Characterization results revealed that the surface activity, the nature and size of the aggregates formed by the polymer in water are very much pH dependent. At low pH the polymer forms intramolecular aggregates which behave as polyelectrolytes. As pH is raised, the intrachain aggregates are replaced by interchain aggregates with larger hydrophobic domain. Though the detailed picture of macroscopic and microscopic interactions played in the association behavior of such polymer are well documented as functions of concentration, ionic strength and pH, but in presence of surfactant have not been explored yet. In the present study, we used steady-state fluorescence, viscosity, dynamic light scattering and isothermal titration techniques to characterize the self-associating behavior of the anionic comb-like polymer in the presence of a cationic surfactant, *N*-cetyl-*N*,*N*-diethanolyl-*N*-methyl ammonium bromide (CDMAB), at low pH (6.2). The detailed structural features of the polymer and surfactant are presented in Scheme 1.

2. Materials and methods

Pyrene (Fluka) was recrystallized from ethanol. Double distilled water was used for all experiments. Detailed procedure for the synthesis of the comb-like polymer used in the present study has been described in our earlier report [25]. Briefly, brij-35 ($C_{12}E_{23}$) was grafted to styrene–maleic anhydride copolymer backbone by an esterification reaction in methyl ethyl ketone at 85 °C using *p*-toluene sulfonic acid as a catalyst. Pyrene labeled polymer was prepared by following identical reaction conditions except the addition



Scheme 1. Structures of (a) the comb-like poly(styrene–maleic anyhydride) copolymer esterified with brij-35 copolymer and (b) the cationic surfactant, *N*-cetyl-*N*,*N*-diethanolyl-*N*-methyl ammonium bromide (CDMAB) studied.

of 1-pyrenyl methanol. Average molecular weight polymers were 80,000–83,000 with a polydispersity of 2.9. The molar percentage of the grafted $C_{12}E_{23}$ in labeled and unlabeled was about 34 and of pyrene in the labeled polymer was 0.5 as calculated from ^{1}H NMR. The comb polymer yields a latex at $pH < 3.5$, gives a hazy solution at $pH > 3.5$ and dissolves completely at pH 4.8. CDMAB was synthesized by the reaction hexadecyl bromide with excess (1:1.2 mole ratio) *N*,*N*-diethanolyl-*N*-methyl amine in methanol–acetonitryl (30:70 volume ratio) mixed solvent under refluxing condition for 24 h. After removal of the solvent under reduced pressure, the product was recrystallized twice from ethylacetate and was characterized by ^{1}H NMR and mass spectroscopy.

All the experiments were done at pH 6.2 and 25 °C with polymer concentration of 0.1 wt%. For fluorescence measurements 3 ml of each solution was placed in a 10 mm rectangular quartz cell, and the spectra were run in a SPEX fluorolog spectrophotometer in right angle geometry. The emission spectra were collected with an integration time of 1 s/0.5 nm. As an extrinsic probe pyrene was used at a concentration of 1 μM wherever necessary. Isothermal calorimetric experiments were carried out using the Omega Titration Calorimeter from Microcal Inc. (Northampton, MA). In a typical experiment, 15–20 injections of 5–7 μl each were performed in a single step titration. Surfactant solution was used to titrate 2 ml (the active volume of the cell was 1.4 ml) of polymer solution using a 100 μl syringe. Complete mixing was achieved by stirring the syringe paddle at 400 rpm. The reference cell of the calorimeter was filled with water; the instrument was calibrated with a known standard electrical pulse. Precision in the measurement of enthalpy for each injection was within ±0.5 μcal. The electrophoretic mobility measurements were performed in a 'ZetaPlus' Zeta Potential Analyzer (Brookkhaven Instrument Co.) with a 15 mV solid-state laser operated at a wavelength of 635 nm. The ξ-potential of the aggregates was calculated from the EPM values using the Smoluchowski equation. Dynamic Light Scattering (DLS) measurements were performed in a Laser Light Scattering Spectrophotometer (Model DLS-700, Otsuka Electronics Co. Ltd, Japan) fitted with a 5 mW He–Ne laser, operated at 632.8 nm. All samples were filtered through membrane filter with pore size of 0.45 μm and the measurements were taken at 90° angle.

3. Results and discussion

We have previously reported that the polymer described in Scheme 1 forms intramolecular self-association at $pH < 7.4$ [25]. At this pH range, polymer associates intramolecularly and behaves as polyelctrolyte due to the hydrophobicity and partial ionization carboxyl groups of the polymer backbone. In the present study, we have chosen the experimental pH of 6.2 to identify the interaction behavior of a cationic surfactant with these kind of unusual intramolecular aggregates.

The interaction between the polymer and the cationic surfactant, CDMAB, is followed by steady-state fluorescence using pyrene as a probe. Pyrene is one of the few condensed aromatic hydrocarbons, which shows noticeable fine structure in the monomer fluorescence spectra in solution [26]. The intensity ratio between the first and third highest emission peaks of the pyrene spectrum, known as I_1/I_3 ratio, is related to the polarity of its immediate environment. The value of I_1/I_3 ratio in aqueous solution is about 1.8–1.9 while that in a nonpolar solvent such as hexane is around 0.6. In a typical surfactant solution below the critical micelle concentration (cmc), the I_1/I_3 value is the same as water [26,27]. When the concentration of surfactant exceeds the cmc, the I_1/I_3 ratio drops significantly, indicating the incorporation of pyrene molecules into the nonpolar interior of the micelle [26]. Fig. 1 presents the dependency of I_1/I_3 on CDMAB concentration in the absence and presence of the polymer. A sigmoid curve is obtained in surfactant solution in the absence of the polymer. The cmc calculated from the inflection point is 0.55 mM. The value of I_1/I_3 in polymer solution in the absence of the surfactant is 1.63, which is comparatively lower than that in water (1.84) revealing the presence of hydrophobic clusters formed by the polymer. This is consistent with our earlier studies where we have shown that the same polymer can form intramolecular aggregates at this pH range. A decrease in I_1/I_3 is observed on increasing the concentration of CDMAB, indicating the formation of domains of higher hydrophobicity in the system. The variation of I_1/I_3 is much more progressive, stretching over almost 2 decimal points of CDMAB concentration, which is attributed to a less cooperative association of hydrophobic moieties in the

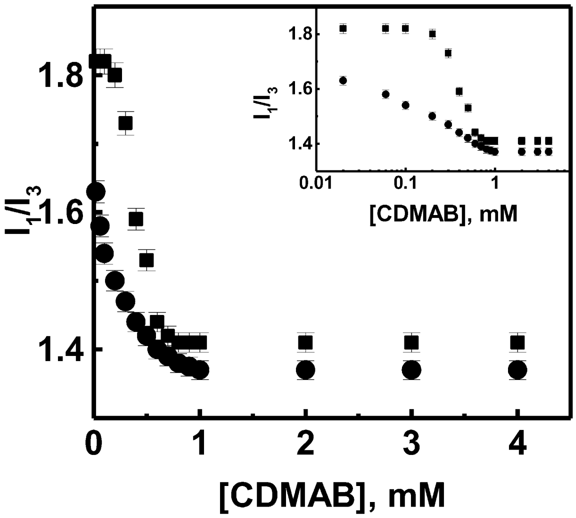


Fig. 1. Variation of I_1/I_3 in the steady-state fluorescence using pyrene as an extrinsic probe as a function of CDMAB concentration (■) in absence and (●) presence of 0.1 wt% polymer at pH = 6.2. The inset is the semi-logarithamic plot for the same curve.

presence of the polymer, as compared to micellization of CDMAB when the polymer is absent. However, starting from the first addition of the surfactant, the hydrophobic clusters present in the system are affected due to interaction with surfactant as revealed by the continuous decrease in I_1/I_3 value. The interaction levels off at the surfactant concentration of 1.0 mM and further addition of the surfactant causes the formation of free micelles.

It is logical to assume that the fluorescence behavior of pyrene used as an extrinsic probe characterizes the nature of hydrophobic domains present in the system, whereas the fluorescence behavior of an intrinsic probe attached to the polymer reflects the dynamics of the polymer chain where the probe is attached [28]. To monitor the dynamics of the polymer backbone, we have labeled the backbone by pyrene moiety. The emission spectrum of pyrene covalently attached to the polymer backbone (an intrinsic probe) shows an excimer band at 450 nm along with its monomer band. The ratio of intensity of excimer to monomer (I_E/I_M) can be used to follow the conformational changes of the polymer upon interaction with the surfactant [28]. Since pyrene moieties are randomly attached to the polymer backbone, a large value of I_E/I_M indicates contraction of the polymer backbone, whereas a small value suggests expansion of the backbone. Fig. 2 shows the effect of CDMAB concentration on the I_E/I_M ratio. Initially, with increasing concentration of CDMAB, there is an increase in the value of I_E/I_M. Above a CDMAB concentration of 0.22 mM, the I_E/I_M ratio starts to decrease and levels off at a concentration of 1 mM. The increase in I_E/I_M upon initial addition of CDMAB reveals the coiling of the polymer backbone. In our earlier study we observed that the backbone, though hydrophobic enough to promote the polymer to aggregate intramolecularly, is partially ionized at this pH (6.2) and behaves as a polyelectrolyte. Since the backbone is negatively charged, the cationic surfactant molecules interact electrostatically with the backbone neutralizing the charge present on it. As a result, the polymer backbone adopts more coiled conformation, giving smaller separation of fluorophore, and thus the I_E/I_M value increases. The decrease in I_E/I_M beyond the CDMAB concentration of 0.22 mM is attributed to the decrease in the number and the increase in the size of the hydrophobic domains resulting from adsorption of individual surfactant molecules onto intrapolymeric hydrophobic microdomains. This mixed microdomain formation leads to the separation of the pyrene moieties present in the backbone and causes decrease in I_E/I_M. The surfactant concentration, at which maximum value of I_E/I_M was observed, 0.22 mM can be considered as cac for this system since above this concentration interaction between the surfactant and the polymer leads to the formation of a mixed domain. I_E/I_M levels off at the CDMAB concentration of 1 mM, where all intrapolymeric hydrophobic domains are broken down to form mixed domains and further added surfactant molecules form free micelles. It is noticeable that the values of I_1/I_3 and I_E/I_M level off beyond 1 mM surfactant concentration. This confirms the interaction between the polymer and the surfactant completes at this CDMAB concentration.

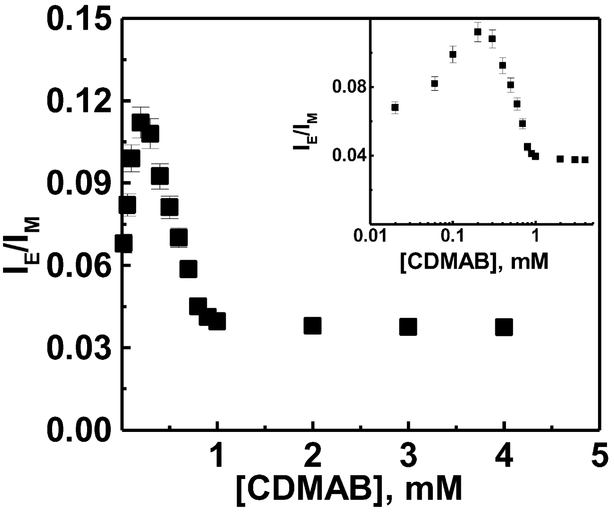


Fig. 2. Effect of CDMAB concentration on excimer-to-monomer (I_E/I_M) in the steady-state fluorescence using pyrene as an intrinsic probe at pH = 6.2. The polymer concentration is 0.1 wt%. The inset is the semi-logarithamic plot for the same curve.

Isothermal Titration Calorimetry (ITC) is a technique, which allows an investigator to study the heat of interaction between two molecules [29–37]. ITC has contributed significantly to the understanding of polymer–surfactant interactions and surfactant aggregation. Although the interpretation of the observed heat effects were generally not straightforward, the concentrations corresponding to the onset of micellization and saturation of the binding could be satisfactorily reproduced [37]. In a key development, the interactions of water-soluble polymers with different kinds of surfactants were studied by this technique [32–37]. These interactions closely resembled 'classical' polymer–surfactant interaction. Even though the degree of hydrophobic modification of the studied polymers were low (0.1–0.5 mol%), the surfactant molecules were able to interact with the polymer backbones in the usual 'bead-on-a-string' manner [16,17]. It would be interesting to investigate the present system by this technique, ITC, as the degree of hydrophobic modification of this polymer is high. Fig. 3(a) shows the thermogram of the isothermal titration of 12.5 mM CDMAB into water. The corresponding heat of enthalpy change per mole of surfactant is presented in Fig. 3(b). The enthalpy change at the initial stage of addition of surfactant solution (concentration is higher than cmc) in water essentially involves micellar dilution, demicellization, and dilution of monomer surfactant existing with the micelles and produced by the process of demicellization [30]. The enthalpy change at the final stage of addition of surfactant solution is mainly associated with micellar dilution, as the final concentration of surfactant in the cell is beyond cmc. Therefore, the inflection point in the enthalpy against concentration of CDMAB graph

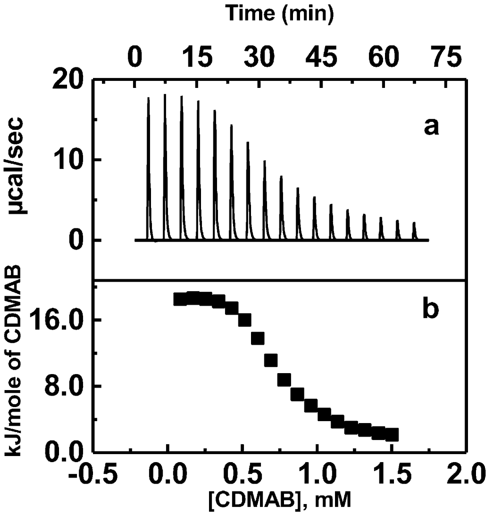


Fig. 3. (a) Thermograms showing the cell feedback versus time and (b) differential enthalpy vs. [CDMAB] curve for the isothermal calorimetric titration of 12.5 mM CDMAB into water.

(Fig. 3(b)) corresponds to the cmc (0.6 mM) and is consistent with the cmc obtained from the fluorescence experiment. The stiffness of the curve around the inflection point indicates that the process is highly cooperative. At a concentration close to the cmc, the dilution of monomer is minor; the enthalpy change between the initial and the final stage (Fig. 3(b)) essentially quantifies the enthalpy of demicellization [31], which is equal to 16.1 kJ/mol.

The picture became completely different when titration was done in the presence of the polymer. Instead of endothermic enthalpy change, an exothermic enthalpy change is observed throughout the titration process (Fig. 4). The enthalpy changes for the first few injections become more exothermic and become less exothermic steadily upon further injection of CDMAB. It is worth mentioning here that the highest exothermic enthalpy observed at a CDMAB concentration very close to the concentration at which we observed the highest I_E/I_M value. The overall enthalpy change in the presence of the polymer includes the enthalpy changes for all the processes where the polymer is absent as well as the additional enthalpy changes due to interaction of the surfactant with the polymer, and the various conformational changes of the polymer including the hydration change upon interaction. The overall enthalpy change is the sum of the contributions from each process and individual separation is not straightforward. However, the major contributions to the overall enthalpy change come from the enthalpy changes for the demicellization and the interaction between the surfactant and the polymer. At the initial stage of addition of the surfactant, the overall exothermic enthalpy change suggests that enthalpy change for the interaction is exothermic in nature since the change for demicellization is endothermic in nature. In the initial stage of surfactant addition, as we explained earlier, interaction occurs between polymer and surfactant monomer due to electrostatic attraction and is associated with exothermic enthalpy change.

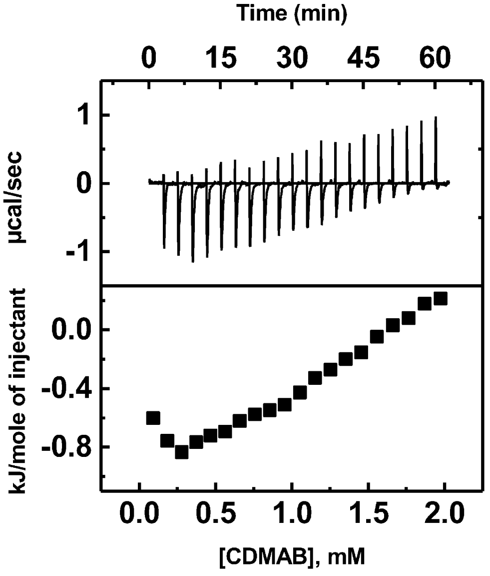


Fig. 4. (a) Thermograms showing the cell feedback versus time and (b) differential enthalpy vs. [CDMAB] curve for the isothermal calorimetric titration of 12.5 mM CDMAB into 0.1 wt% polymer.

In a recent report, on the interaction between SDS and a cationic polymer poly(ethylene imine) (PEI), it was observed that the initial interaction between surfactant and polymer causes an exothermic heat change [37]. That study has shown that in the initial stage of interaction individual surfactant binds to the polymer due to electrostatic interactions. The authors extensively reviewed recent reports on the interaction between surfactant and polymer studied by ITC technique in literature. It has been observed that the energetics of polymer–surfactant interaction is different for the different classes of polymer and surfactants and is very much dependent on the mechanism of their interaction. The exothermic enthalpy change observed for SDS–PEI system strengthens our argument that electrostatic interaction between surfactant and oppositely charged polymer is associated with exothermic enthalpy change. After complete neutralization of the charge present in the polymer backbone at CDMAB concentration, ~0.25 mM, surfactant monomer binds to the polymer due to hydrophobic interactions. As we mentioned earlier, this polymer aggregates yield intramolecular hydrophobic microdomains and offer the surfactant monomer to partition from bulk water. This partition process is also associated with exothermic heat change and predominantly contributes to the overall enthalpy change at this stage. On successive additions of surfactant, the amount of surfactant partition per injection decreases and the enthalpy change per injection, rather than per mole of surfactant, becomes less exothermic and finally reaches endothermic value of the dilution of micelles (Fig. 4). The ion–ion repulsions between mixed polymer–surfactant aggregates or free micelles may result in a decrease in enthalpy at this stage [37].

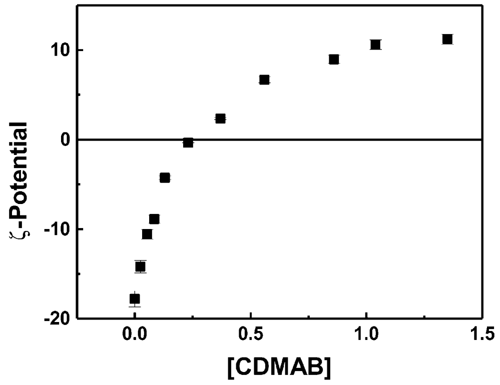


Fig. 5. Effect of CDMAB concentration on the ξ-potential of 0.1 wt% polymer solution at pH = 6.2.

The surface charge of the polymer–surfactant complex has been characterized using a laser microelectrophoresis apparatus. The ξ-potential of the complex is presented in Fig. 5 as a function of CDMAB concentration. In the absence of the surfactant, the negative ξ-potential of the aggregates suggests that they are negatively charged. This confirms our earlier observation that at this pH (6.2) the backbone is partially ionized, which makes the aggregates negatively charged. The increase in the amount of CDMAB added to the polymer solution results in the increase in the net positive charge of the aggregates. This provides evidence of the progressive neutralization of the polymer backbone by the surfactant cations upon interaction. Importantly, at [CDMAB] ~ 0.24 mM, ξ-potential value is approximately zero, suggesting that the charges of the backbone are completely neutralized. It can be mentioned here that the maximum value of I_E/I_M was observed at an almost similar concentration (0.22 mM) of CDMAB (Fig. 2).

One way to measure the size of aggregates in solution is by DLS [38]. The diffusion coefficient of the mobile species is determined by a cummulant analysis of the auto-correlation function decay, assuming a log–normal fit to the distribution of diffusing species. The diffusion coefficient obtained in this way depends on the polymer concentration [39]. As the polymer concentration increases, the diffusion coefficient tends to deviate from its value for a polymer chain completely isolated from others. This deviation arises from hydrodynamic and thermodynamic interactions among the interacting polymers. Thus the hydrodynamic radius R_H calculated using the Stokes Einstein equation, $R_H = kT/6\Pi\eta D_m$, where η is the solvent viscosity, D_m is the diffusion coefficient, k is the Boltzmann constant and T is the temperature, is apparent [39] and hence estimates higher value than the actual one. The effect of CDMAB concentration on the apparent diameter d_{ef} ($d_{ef} = 2R_H$) of the polymer aggregate, as measured by DLS are shown in the Fig. 6. The d_{ef} value decreases until a CDMAB concentration of ~0.25 mM. The CDMAB concentration at which aggregates adopt minimum d_{ef} is essentially similar to the concentration where we observed the maximum I_E/I_M ratio and zero ξ-potential. The reduction in size of the aggregates upon addition of cationic surfactant again supports our earlier argument that initially cationic surfactant monomer electrostatically binds to the polymer backbone resulting charge neutralization on it. This charge neutralization leads the polymer backbone to adopt a more compact structure. On further increase in concentration of the surfactant, the hydrodynamic size of the polymer–surfactant complexes increases due to formation of mixed hydrophobic domains. The rapid increase in the hydrodynamic size indicates that the mixed hydrophobic domains are shared by hydrophobe from both cationic surfactant, and individual and different polymer chains.

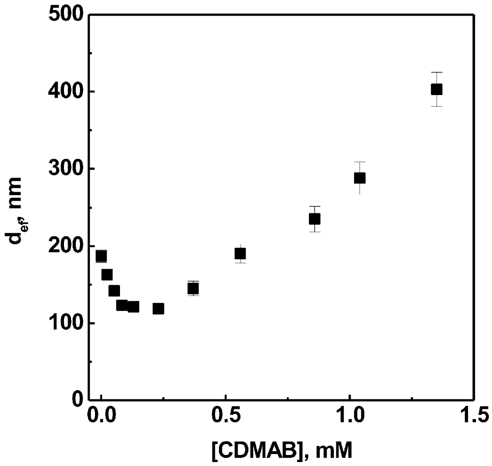


Fig. 6. Effect of CDMAB concentration on the apparent diameter (d_{ef}) of 0.1 wt% polymer solution at pH = 6.2.

4. Conclusions

The results presented here demonstrate that the interaction between a cationic surfactant and the hydrophobically modified comb-like polymer is fundamentally different from interactions between conventional surfactant and polymer such as PEO, PPO and PVP. Due to electrostatic interaction, individual surfactant molecules start to interact with the polymer from the initial stage of addition. This interaction leads the aggregates to adopt a compact size and such interaction is associated with exothermic enthalpy changes. In the second stage of interaction, individual surfactant monomers preferentially adsorb onto hydrophobic microdomains present in the system. Due to this hydrophobic interaction between the surfactant and the intramolecular hydrophobic domains of the polymer, mixed domains are formed which are eventually shared by the hydrophobe of both the surfactant molecules and individual and different polymer chains. As a result, these aggregates are larger in size. Such hydrophobic interactions are also associated with exothermic heat change.

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References

[1] Glass JE, editor. Water soluble polymers, Advances in chemistry series 213. Washington, DC: American Chemical Society, 1986.

[2] Glass JE, editor. Polymers in aqueous media, Advances in chemistry series 223. Washington, DC: American Chemical Society, 1989.

[3] Yokoyama M. Drug carriers system. Crit Rev Therap 1992;9:213.

[4] Glass JE. Hydrophilic polymers, performance with environmental acceptance, Advances in chemistry series no. 258. Washington, DC: American Chemical Society, 1996.

[5] Zhang H, Ruckenstein E. Macromolecules 2000;33:814.

[6] Heitz C, Pendharkar S, Prud'homme RK, Kohn J. Macromolecules 1999;32:6652.

[7] Tam KC, Jenkins RD, Winnik MA, Bassett DR. Macromolecules 1998;31:4149.

[8] Kumacheva E, Rharbi Y, Winnik MA, Guo L, Tam KC, Jenkins RD. Langmuir 1997;13:182.

[9] Araujo E, Rharbi Y, Huang X, Winnik MA, Bassett DR, Jenkins RD. Langmuir 2000;16:8664.

[10] Horiuchi K, Rharbi Y, Spiro JG, Yekta A, Winnik MA, Jenkins RD, Bassett DR. Langmuir 1999;15:1644.

[11] Vorobyova O, Lau W, Winnik MA. Langmuir 2001;17:1357.

[12] Horiuchi K, Rharbi Y, Yekta A, Winnik MA, Jenkins RD, Bassett DR. Can J Chem 1998;76:1779.

[13] Tan H, Tam KC, Jenkins RD. J Colloid Interface Sci 2000;231:52.

[14] Dai S, Tam KC, Jenkins RD, Bassett DR. Macromolecules 2000;33:7021.

[15] Tan H, Tam KC, Jenkins RD. Langmuir 2000;16:5600.

[16] Seng WP, Tam KC, Jenkins RD, Bassett DR. Macromolecules 2000;33:1727.

[17] Seng WP, Tam KC, Jenkins RD, Bassett DR. Langmuir 2000;16:2151.

[18] Dai S, Tam KC, Jenkins RD. Macromolecules 2000;33:404.

[19] Tirtaatmadja V, Tam KC, Jenkins RD. Langmuir 1999;15:7537.

[20] Tam KC, Jenkins RD, Winnik MA, Bassett DR. Macromolecules 1998;31:4149.

[21] Noda T, Hashidzume A, Morishima Y. Langmuir 2000;16:5324.

[22] Yusa S, Kamachi M, Morishima Y. Langmuir 1998;14:6059.

[23] Noda T, Hashidzume A, Morishima Y. Macromolecules 2001;34:1308.

[24] Noda T, Hashidzume A, Morishima Y. Macromolecules 2000;33:3694.

[25] Maiti S, Jayachandran KN, Chatterji PR. Polymer 2001;42:7801.

[26] Kalyansundaram K, Thomas JK. J Am Chem Soc 1977;99:2039.

[27] Hanson P, Almgren M. J Phys Chem 1995;99:16684.

[28] Winnik FM. Chem Rev 1993;93:587.

[29] Bijma K, Engberts JBFN, Haandrikman G, van Os NM, Blandamer MJ, Butt MD, Cullis PM. Langmuir 1994;10:2578.

[30] Bach J, Blandamer MJ, Bijma K, Engberts JBFN, Kooreman PA, Kacperska A, Rao KC, Subha MCS. J Chem Soc, Faraday Trans 1995;91:1229.

[31] Majhi PR, Moulik SP. Langmuir 1998;14:3986.

[32] Wang G, Olofsson G. J Phys Chem 1995;99:5588.

[33] Van Os NM, Daane GJ, Haandrikman G. J Colloid Interface Sci 1991;141:199.

[34] Bronich TK, Kabanov AV, Kabanov VA, Yu K, Eisenberg A. Macromolecules 1997;30:3519.

[35] Kevelam J, van Breemen JFL, Blokzijl W, Engberts JBFN. Langmuir 1996;12:4709.

[36] Bloor DM, Holzwarth JF, Wynjones EM. Langmuir 1995;11:2312.

[37] Winnik MA, Bystryak SM, Chassenieux C, Strashko V, Macdonald PM, Siddiqui J. Langmuir 2000;16:4495.

[38] Ou-Yang HD, Gao Z. J Phys II 1991;1:1375.

[39] Selser J. In: Brown W, editor. Light scattering: principle and development. New York: Oxford University Press, 1996. p. 232, chapter 7.