

Influence of various series of additives on the clouding behavior of aqueous solutions of triblock copolymers

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Abstract The cloud point (CP) studies on aqueous solutions of two ethylene oxide-propylene oxide triblock copolymers $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and $(EO)_{13}(PO)_{30}(EO)_{13}$ with varying number of ethylene oxide (EO) units were carried out in the presence of series of additives, such as alkali, acids, ionic surfactants, alcohols, salts, and hydrotropes. The results of this study show that sodium hydroxide decreases the CP of the two copolymers. Acids increase the CP in the order hydrochloric acid > acetic acid > formic acid for both the triblock copolymers. Hydrotropes increase the CP, whereas salts decrease or increase the CP based on their salting-out/salting-in nature. Alcohols, which are polar organic additives, affect the CP of the two copolymers differently. The change in the CP of the triblock copolymers depends upon the structure and concentration of the additives and on the number of EO units of the two triblock copolymers.

Keywords Cloud point · Hydrotropes · Triblock copolymers · Ionic surfactants

Introduction

Block copolymers containing hydrophilic and hydrophobic polymeric moieties have been of interest in recent years for their surfactant characteristic, which can be optimized by tailoring their molecules. The most extensively examined block copolymers are polyethylene oxide–polypropylene oxide based surfactants (PEO–PPO–PEO) marketed under

different trade names, Pluronics (BASF), Synperonics (ICI), and Poloxamers or generic names like EPE polyols as flakes, liquids, and pastes [1–3]. Triblock copolymers possess symmetrical structure $(EO)_x(PO)_y(EO)_x$ where x and y denote the number of ethylene oxide (EO) and propylene oxide (PO) monomers per block, which are available in a range of x and y values. Pluronics due to their unique aggregational characteristics are extensively used for a variety of applications such as in cosmetics, pharmaceuticals, and textile industries [4].

PEO–PPO–PEO triblock copolymers are macromolecular surfactants that exhibit micelle formation and clouding behavior in water similar to other non-ionic surfactants. As the temperature increases, the aqueous solubility of the block copolymers decreases because of the decreased interaction of both moieties, EO and PO, with water and instant separation into two phases occurs. The temperature at which this phase separation occurs is known as the cloud point (CP). The phase separation results into polymer- and water-rich phases, and its occurrence reflects the balance between polymer–polymer and polymer–water interaction. The phenomenon can be explained on the basis that EO segments assume a conformational change at higher temperature [5, 6]. This less polar conformation decreases the polymer solvation, leading to the predominance of polymer–polymer interactions. The CP temperatures are relatively independent of the polymer concentration suggesting that phase separation phenomenon is controlled by the solvation capacity of water rather than by the probability of molecular encounters. Therefore, it can be said that, at certain temperature, water becomes a poor solvent to the polymer possibly due to the new and less polar polymer conformation, causing the aggregation of the copolymer.

For EO/PO copolymers solutions, the cloud points depend strongly on the copolymer composition, with high

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values for those containing a large percentage of EO units. It has been noticed that copolymers with more than 70% EO present cloud points above 100 °C. CP separation is an innovative technique used to recover various substances from aqueous samples [7–9]. The CP is very sensitive to the presence of additives in the system even at very low concentrations. The additives modify the surfactant–solvent interactions, which lead to the change in the critical micelle concentration, the size of the micelles, and the phase behavior in the surfactant solutions. Because the triblock copolymers are widely used in many industries, therefore, the cloud point data are of considerable practical interest. In the preparation of emulsion, the CP and the phase inversion temperature is a very important factor in the selection of the most suitable surfactant for given oil [10–12].

Lad et al. [13] have carried out studies on the clouding behavior of EO–PO block copolymers in the presence of ionic surfactants. Mixed copolymers systems were also examined for their phase behavior. Pandya et al. [14] have described the effect of electrolytes on the CP of Pluronic L64, identifying the “salting in” and “salting out” effects. For electrolytes, these effects were observed to follow the Hofmeister series. The larger effects were verified with additives presenting surface activity, which has attributed to the formation of a polyelectrolyte-like complex.

Prasad et al. [15] have studied the clouding of the surfactants, Triton-X 100 and Brij 56 as well as the polymers, polyvinylmethyl ether and triblock copolymer, Pluronic 85 in the presence of a number of hydrotropes, glycols, and polyethylene oxides. The clouding temperatures with the additive concentration have been determined, and the energetics of the process were estimated. They observed that the enthalpic behavior of TritonX 100 was different from that of polyvinylmethyl ether and Pluronic 85. The hydrotropes on the whole, decreased the CP of Triton-X 100, polyvinylmethyl ether, and Pluronic 85.

In view of the importance of the effect of additives on the CP of triblock copolymers, we report the clouding behavior of $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and $(EO)_{13}(PO)_{30}(EO)_{13}$ with varying number of EO units. This study includes the determination of CP with varying concentration of some oil field chemicals, such as salts, alkalis, acids, ionic surfactants, hydrotropes (urea, nicotinamide, etc.), and alcohols. The effects are analyzed regarding the structure and interaction of the additives and the triblock copolymers.

Experimental

Materials

The two triblock copolymers $(EO)_{13}(PO)_{30}(EO)_{13}$ (MW=2900), $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (MW=2036), alcohols and

anionic surfactant sodium dodecyl sulfate (SDS) were purchased from Aldrich. The simple inorganic and organic salts, acids, and alkali used were obtained from CDH, Mumbai (India) and were of analytical grade. Hexadecyltrimethylammonium bromide (HTAB) was obtained from Lancaster Synthesis, UK. All the chemicals were used as received. Water was purified by deionization followed by double distillation. All the solutions were prepared by mass with an accuracy of ± 0.01 mg.

Methods

The CP measurements were made visually for the onset of turbidity by controlled heating (about 1 °C/min) of the well-stirred samples and then cooling of the solutions until they cleared. The temperatures were measured with a precision of 0.1 °C. The values determined are the mean of three separate determinations. The method has a reproducibility of better than ± 0.5 °C. The concentrations of both the triblock copolymers used for measurements were 1% (w/v), as after 1% (w/v), the CP becomes almost constant with increasing concentration of the polymer but varies significantly below 1% (w/v) as is evident from the Fig. 1.

Results and discussion

Effect of different concentrations of the two triblock copolymers on CP

The CP of the two triblock copolymers is a function of their concentration. Figure 1 shows the effect of concentration of

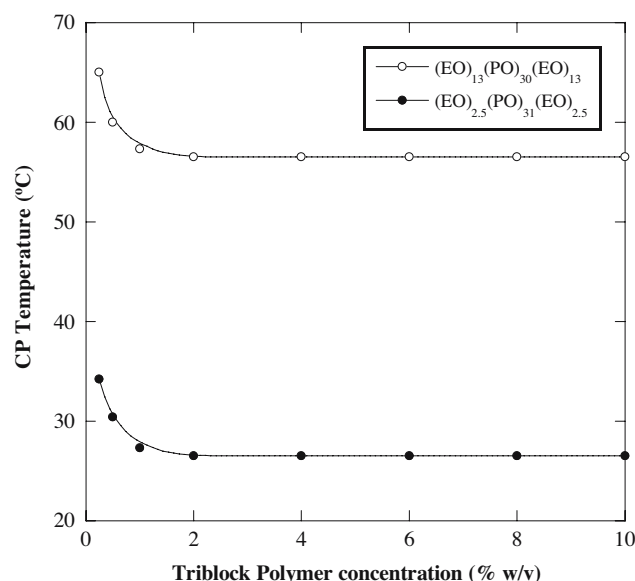


Fig. 1 Clouding behavior of aqueous solutions of the two triblock copolymers

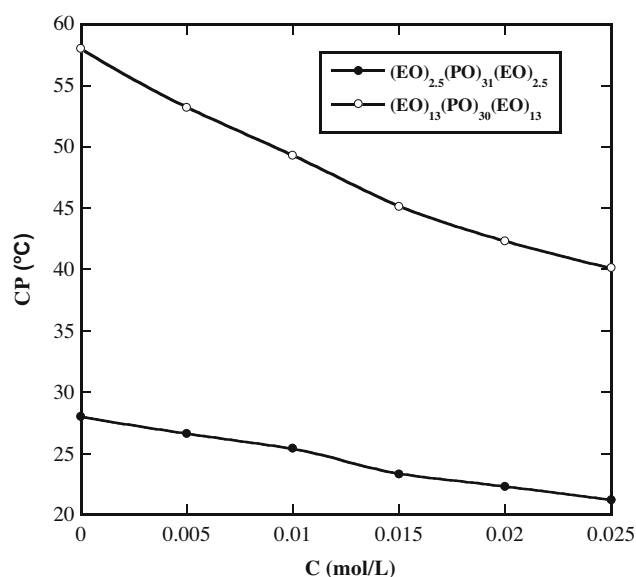


Fig. 2 Effect of NaOH on the CP of the two triblock copolymers

the two triblock copolymers on their CPs. In Fig. 1, we observe a small dependence of the CP with varying copolymer concentration. A decrease in the CP with the copolymer concentration was observed, from 1–2% (w/v), and these values remaining almost constant up to 10% (w/v) copolymer concentration. At the concentration of 1%, the CP of $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ is 27.2 °C and the CP of $(EO)_{13}(PO)_{30}(EO)_{13}$ is 57.3 °C, which is close to the value earlier reported in literature [16]. We find that increase in the EO content produced increase in clouding temperature.

Effect of alkali

Alkali are used with surfactants in processes like oil recovery, so the effect of NaOH on the CPs of two copolymers was studied. Figure 2 shows that the CP of both the copolymers decreased as the concentration of NaOH increased. The results can be explained on the basis of the salting-out effects. Here, both sodium and hydroxide ions caused salting-out effects, as a result of which the CP was significantly depressed at low NaOH concentration.

Effect of acids

Some inorganic acids like hydrochloric acid are used together with triblock copolymers in carbonate reservoirs in oil field operations [17]. Organic acids are known to be used in stimulation process [18]. In this paper, we have studied the effect of hydrochloric, formic, and acetic acids on CP of the two triblock copolymers. With the increase in the concentration of these acids, the CP of the two triblock polymers also increases as can be seen from Fig. 3a,b. The

increasing effect of the acids on CP follows the order hydrochloric acid > acetic acid > formic acid. The results can be explained on the basis that the hydrogen ions cause salting-in effect, which increases the CP. The anion causes salting-out effect, which decreases the CP, but in case of HCl, the salting-in effect is dominant. Formic acid ($pK_a=3.54$) is more acidic than acetic acid ($pK_a=4.76$), but the reverse is true for their effect on the CP of two copolymers. This can be explained on the basis of the fact that acetic acid provides less polar medium and causes difficulty in phase separation [19].

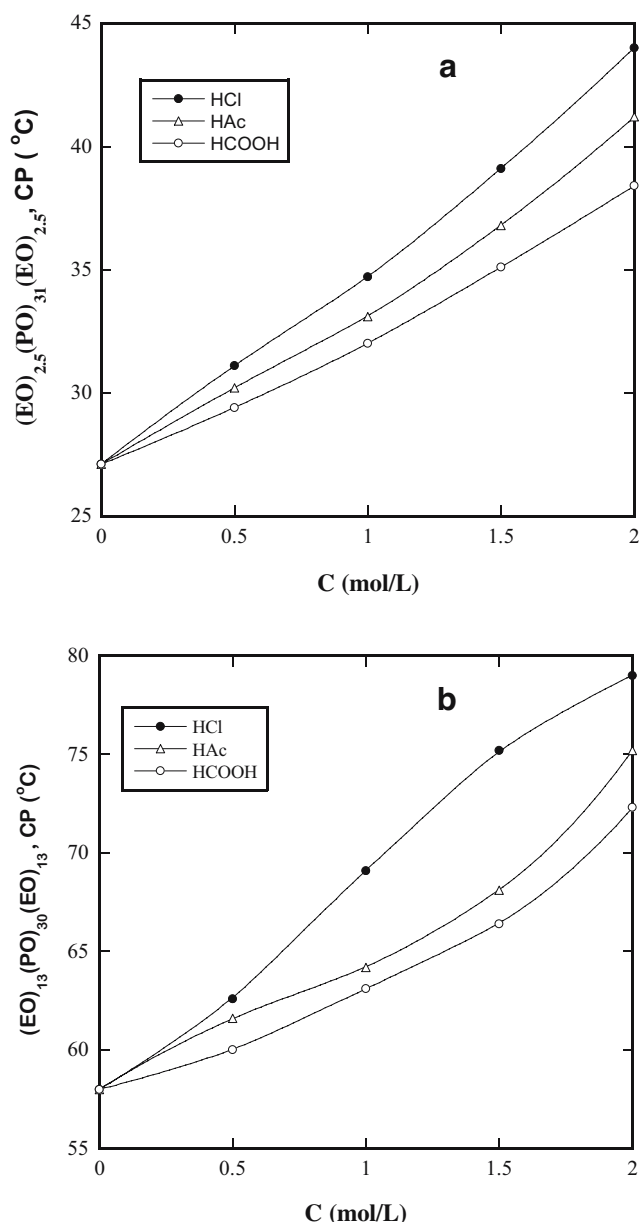


Fig. 3 Effect of acids on the CP of **a(EO)_{2.5}(PO)_{31}(EO)_{2.5} and **b(EO)_{13}(PO)_{30}(EO)_{13}****

Effect of ionic surfactants

The CP of a non-ionic surfactant can be drastically increased in the presence of small concentrations of ionic surfactants [20–22]. The clouding behavior of Pluronic L64 in the presence of various additives like electrolytes and ionic surfactants was reported earlier [14]. Similar studies of the behavior of EO–PO block copolymers in the presence of ionic surfactants have been reported [13]. It has already been proved that, for a particular class of non ionic surfactant, the number of ethylene oxide units in the molecule has a dramatic effect on the CP. Figure 4a and b shows the effect of anionic surfactant, SDS, and cationic surfactant, HTAB, on the CP of the two triblock copolymers. From these figures, we find that the addition of ionic surfactants caused a significant increase in the CP of the two copolymers. The results can be explained by taking into account the fact that ionic monomers are charged, and when they are added to the copolymer solutions, they form mixed micelles. The mixed micelles formed are also charged and generate electrostatic repulsion between different micelles and make the micelles more hydrophilic. The mixed micelle studies on L-64 $[(EO)_{13}(PO)_{30}(EO)_{13}]$ has been earlier reported by our lab [23]. However, the other triblock polymer, $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$, does not show ideal mixed micelle formation with conventional surfactants because of the high PPO/PEO ratio, but it does show mixed micelle formation to some extent, which results in the increase of the cloud point as is evident from Fig. 4. The increase in hydrophilicity raises the CP. It was found that the ionic surfactants interact more strongly with $(EO)_{13}(PO)_{30}(EO)_{13}$ as compared to $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$.

Effect of alcohols

It is well known that the stability of oil/water emulsion incorporating non-ionic surfactants is correlated to the CPs of the non-ionics. In majority of emulsion preparations, medium chain *n*-alkanol is used as a co-surfactant. There are many works that deal with the effect of added alcohols on the micellization of ionic surfactants [24, 25], but only less work deal with the effect of added alcohols on the micellization of non-ionic surfactants [26, 27]. In this study, we have seen the effect of four alcohols, namely, methanol, ethanol, propanol, and 1-butanol on the CP of the two triblock copolymers, Fig. 5a,b. We find that, for both polymers, the addition of small chain alcohols (methanol- C_1 and ethanol- C_2) increases the CP, whereas the addition of longer chain alcohol (butanol- C_4) decreases the CP. The effect of propanol- C_3 is different for the two polymers; its addition results in a decrease of the CP of $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$, whereas it increases the CP of $(EO)_{13}(PO)_{30}(EO)_{13}$. The results can be explained on the basis of the less hydrophobic nature of

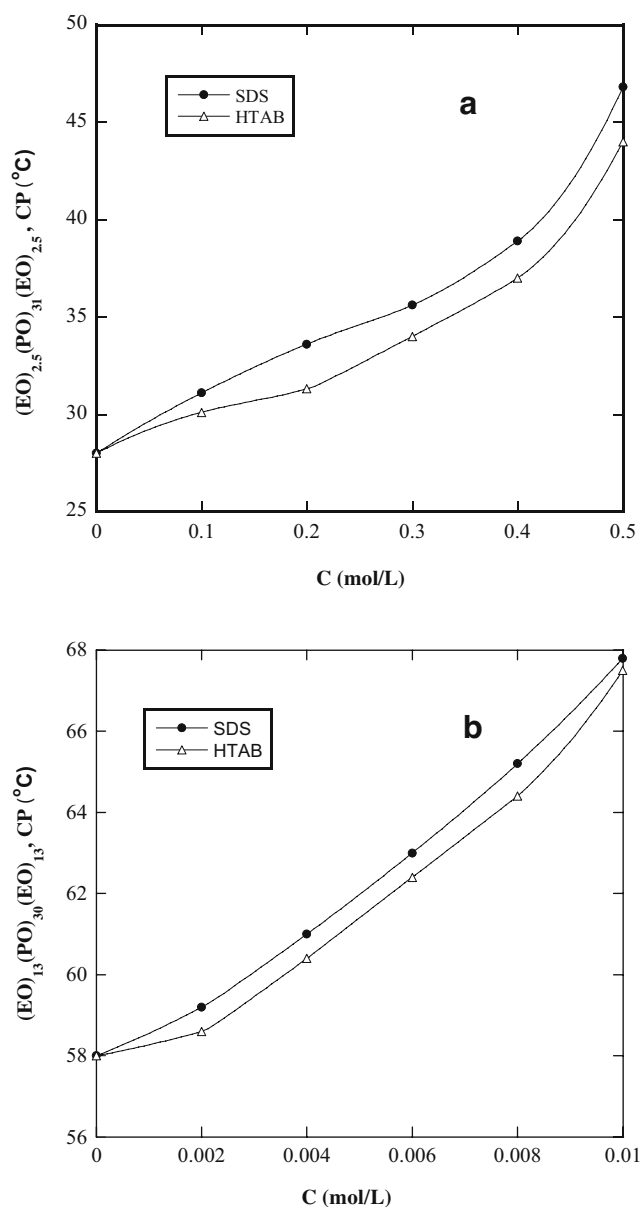


Fig. 4 Effect of ionic surfactants on the CP of **a** $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and **b** $(EO)_{13}(PO)_{30}(EO)_{13}$

small chain alcohols, which are highly soluble in water, and therefore, they increase the CP. 1-Butanol being more hydrophobic is less miscible in water, and it decreases the CP of the two polymers.

Effect of the electrolytes

The effect of five inorganic salts NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4 , and Na_3PO_4 has been studied on the two triblock copolymers. The electrolytes are known to increase (salting in effect) or decrease (salting out effect) the CP due to individual ions [28–31]. In this study, it is seen that the

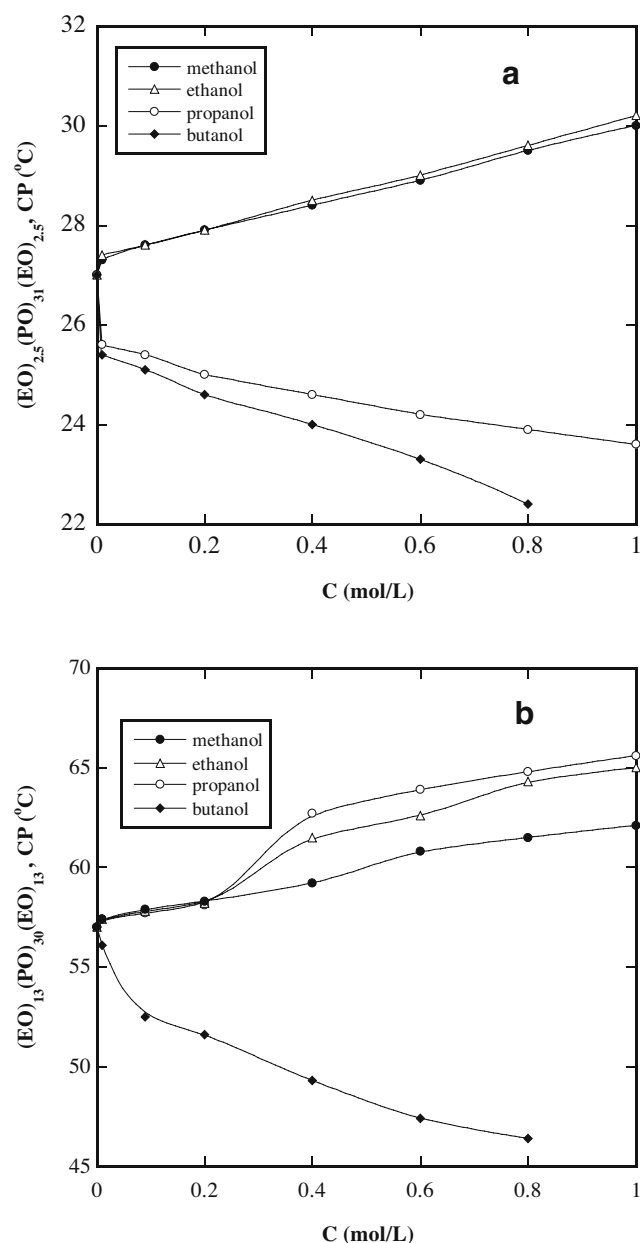


Fig. 5 Effect of alcohols on the CP of **a** (EO)_{2.5}(PO)₃₁(EO)_{2.5} and **b** (EO)₁₃(PO)₃₀(EO)₁₃

addition of all the five electrolytes decreased the CP as shown in Fig. 6a,b. Various ions modify the water structure and influence the hydration of PEO and PPO blocks. The order of CP depression is as follows: NaCl > CaCl₂ > MgCl₂ and Na₃PO₄ > Na₂SO₄ > NaCl. The results show that trivalent anion, i.e., PO₄³⁻ containing salt is more effective at salting out the PEO chain than that containing divalent anion SO₄²⁻, which in turn is more effective than monovalent anion Cl⁻. All the three anions lower the CP of the polymers because they enhance structure of water and promote association among the water molecules and compete with the surfactant for water of hydration. The

salts containing monovalent cations like Na⁺ are more effective at salting out the PEO chains than those containing the cations Ca²⁺ and Mg²⁺. It has been shown that divalent and trivalent cations form complexes with the ether linkage of non-ionic surfactant, increasing their solubility in water and hence raising the CP [32]. The decrease in CP is due to an increase in water structure.

Effect of hydrotropes

Hydrotropes, chaotropes, or antihydrophobic agents are the compounds that increase the aqueous solubility [33]. The

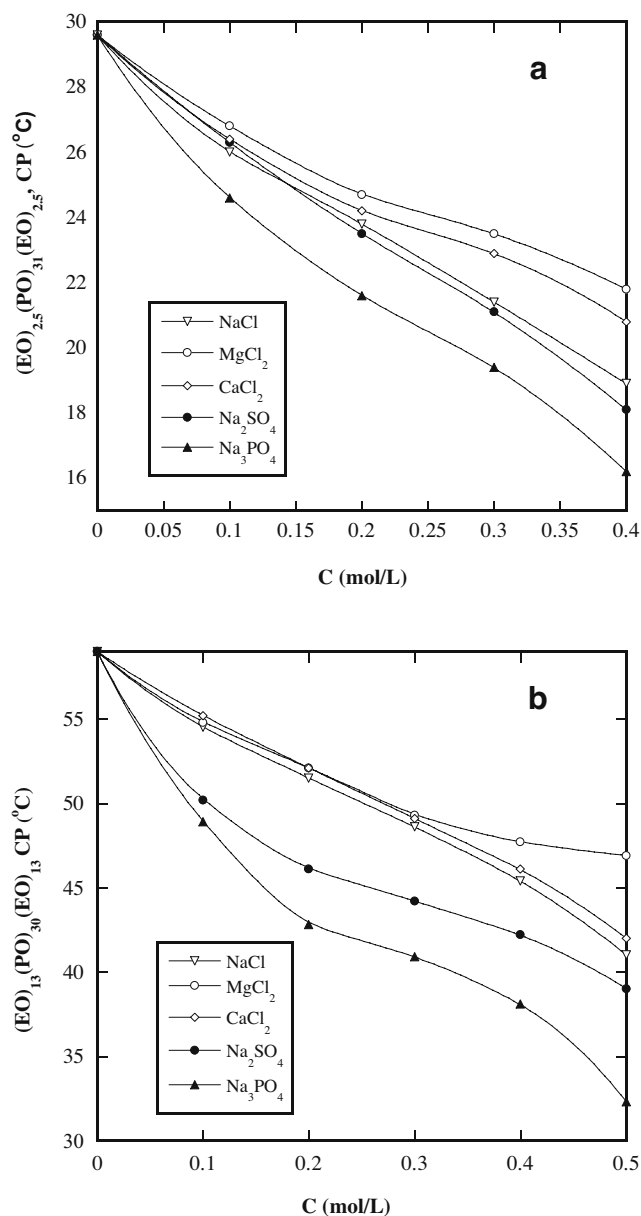


Fig. 6 Effect of salts on the CP of **a** (EO)_{2.5}(PO)₃₁(EO)_{2.5} and **b** (EO)₁₃(PO)₃₀(EO)₁₃

effect of hydrotropes on aqueous solution is observed for a variety of processes, such as solubilization of apolar compounds [34], protein stability [35], micelle formation, and solute binding to the micelles [36, 37]. In this paper, we have studied the effect of four hydrotropes, urea, dimethylurea, nicotinamide, and sodium-*p*-toluenesulfonate on the CP of the two triblock copolymers, Fig. 7a,b. It was found that all four additives increase the CP of the polymers and rate of increase follows the order: sodium-*p*-toluenesulphonate > nicotinamide > dimethylurea > urea. The additives for which self-association occurs are most effective in increasing the CP. For sodium-*p*-toluenesulphonate and

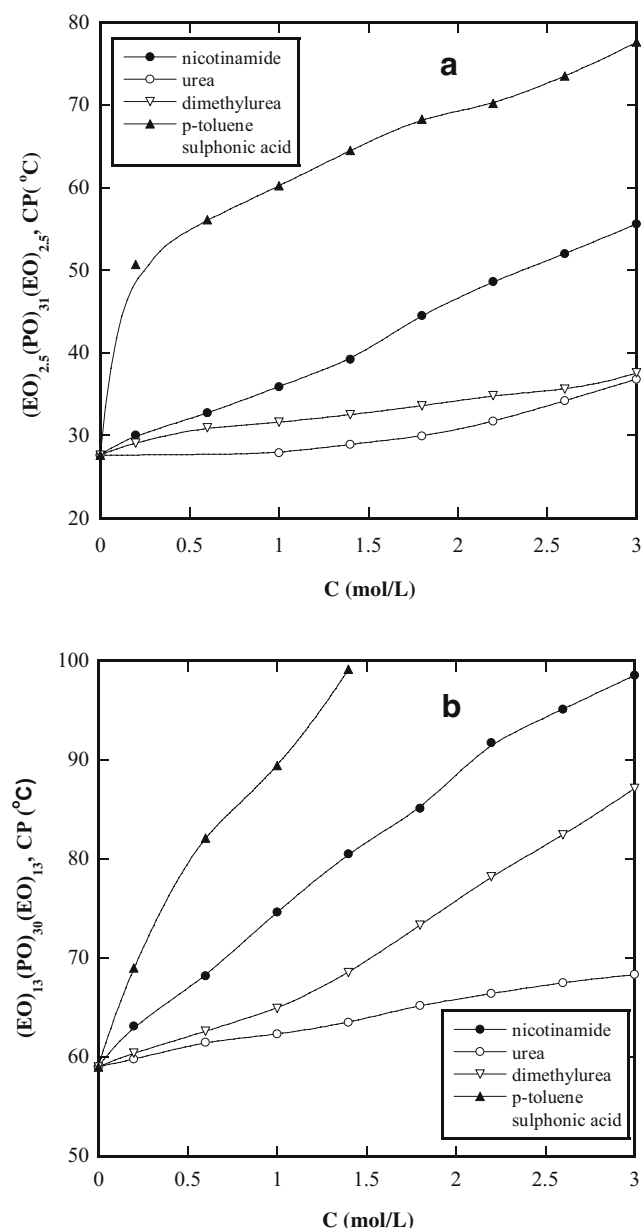


Fig. 7 Effect of hydrotropes on the CP of **a** $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and **b** $(EO)_{13}(PO)_{30}(EO)_{13}$

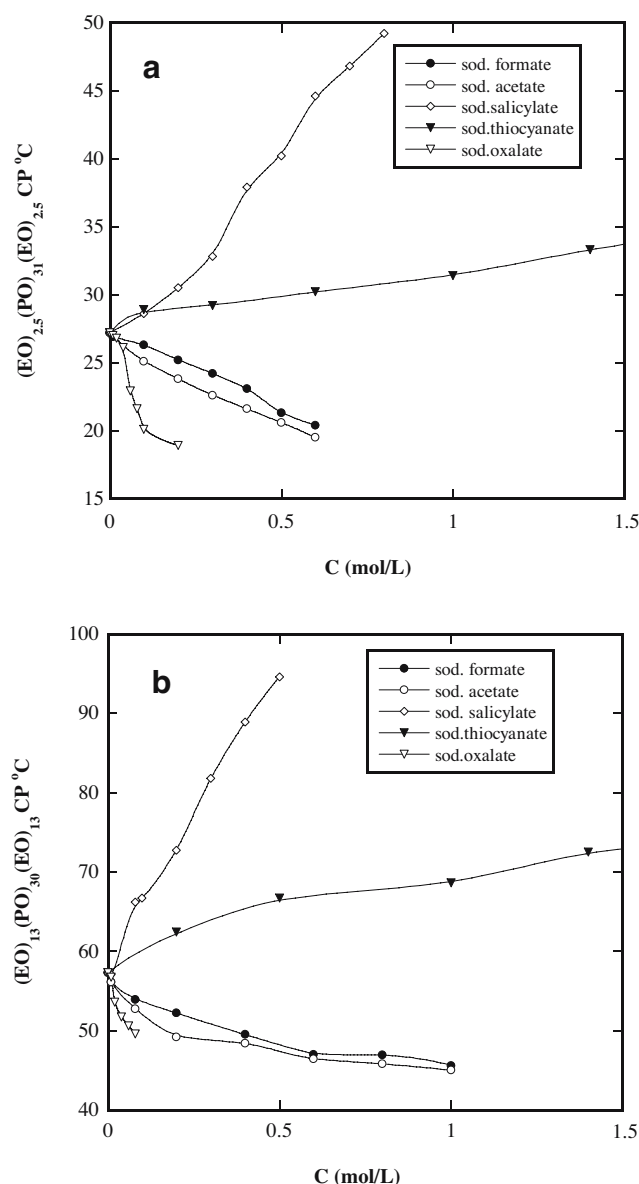


Fig. 8 Effect of sodium salts on the CP of **a** $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and **b** $(EO)_{13}(PO)_{30}(EO)_{13}$

nicotinamide, small amount of aggregation is known to occur, whereas for dimethylurea and urea, no such aggregation takes place. These additives arrange themselves around the EO units of the two polymers in a way to prevent their dehydration at higher temperatures and affect the EO–water interaction and therefore increase the solubility capacity. The effectiveness of different additives is different because of their different tendencies to aggregate. Also from the figures, we can see that effect of the hydrotropes is more drastic on $(EO)_{13}(PO)_{30}(EO)_{13}$, which contains greater number of EO units as compared to $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$, and its CP can be raised to the boiling point of water.

Effect of the sodium salts

Salts change the CP of the water soluble copolymers, and the effect of some inorganic salts on the two copolymers has already been reported in the earlier section. In this study, we see effect of some sodium salts on the two copolymers as shown in Fig. 8a,b. Anions with low lyotropic number, high hydration, or a strong structure-making tendency decreases the CP. The two sodium salts of thiocyanate and salicylate bring about an increase in the CP of the two triblock copolymers. Special interactions of the thiocyanate anion and PEO head groups have been proposed to explain the behavior. Sodium salicylate, which is a hydrotrope, increases the solubility of triblock copolymers, and this raises the CP. It can be seen from the figures that very small amount of sodium salicylate is required to give sufficient rise to the CP of the two copolymers, whereas large amount of sodium thiocyanate is required to give noticeable changes in the CP of the two copolymers. The other sodium salts of oxalate, formate, and acetate decreased the CP of the two copolymers.

Conclusions

The effect of seven kinds of additives, which are alkali, acids, ionic surfactants, alcohols, salts, and hydrotropes, on the CP of $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and $(EO)_{13}(PO)_{30}(EO)_{13}$ in aqueous solution has been investigated. The results obtained show that alkali decreases the CP of the two triblock copolymers. Acids increase the CP and order of increasing effect is hydrochloric acid > acetic acid > formic acid. The results with the alcohols indicated that the addition of small chain alcohols methanol and ethanol lead to a significant increase of the CP of two copolymers, whereas the longer chain alcohol, butanol, decreases the CP. On the other hand, propanol decreases the CP of $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$, whereas it increases the CP of $(EO)_{13}(PO)_{30}(EO)_{13}$. The two ionic surfactants and hydrotropes both increase the CP of two triblock copolymers. Various salts used also decrease/increase the CP of the two triblock copolymers, and the effect has been attributed mainly due to the salting-out/salting-in nature. We also observed that the effect of additives on the CP depends on the number of EO units of triblock copolymers and also on the structure of the additives. In all cases, we find that additives affect the CP of $(EO)_{13}(PO)_{30}(EO)_{13}$ more than $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$. This is because the additives modify the solvation capacity of water in relation to the EO units.

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