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Study of the cloud point of $C_{12}E_n$ nonionic surfactants: effect of additives

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Abstract

Nonionic surfactants are useful in the formation of emulsions. The aqueous solutions of these surfactants show complex phase behaviour including liquid–liquid phase separation at higher temperature. Addition of foreign substance to surfactant solutions does change the temperature at which the clouding phenomena occurs. In this article, we report the effect of electrolytes as well as nonelectrolytes on the cloud point (CP) of a series of nonionic surfactants of the poly(oxyethylene)ether type $C_{12}E_n$ ($n = 6, 9, 10$). It was observed that NaI and KI have different effect on the CP from that of NaCl, NaBr, KCl and KBr. Tetra butyl ammonium iodide (TBAI) acts differently on the CP from the Tetra methyl ammonium bromide (TMAB). Overall the electrolytes and nonelectrolytes have a large amount of effect on CP of nonionic surfactants, because of their effect on water structure and their hydrophilicity.
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1. Introduction

Nonionic surface active agents are prepared by reacting a water insoluble material, such as an alkyl phenol with ethylene oxide to give a product which has an oil soluble group attached to a water soluble polyoxyethylene chain. The high water solubility of polyoxyethylene chain is due to hydrogen bonding between the solvent and the ether oxygen atoms in the chain. Since hydrogen bonding is temperature sensitive phenomenon, for each nonionic emulsifier molecule, there exists a temperature at which the degree of hydration of the hydrophilic portion is just insufficient to solubilize the remaining hydrocarbon portion, which is called the 'Cloud Point' [1]. At this temperature, surfactant is no longer soluble in water and solution becomes hazy or cloudy. This instant separation of nonionic surfactant upon heating into two phases, one surfactant rich and other aqueous, containing surfactant close to cmc at that temperature is the characteristic of non-ionic surfactant which differentiates it from ionic surfactant. Nonionic surfactants are widely used as solubilizers, emulsifiers and detergents in many industrial processes. Therefore, the cloud point data are of considerable practical interest. For

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instance, the stability of O/W emulsions solubilized by nonionic surfactant has been related to CP [3–5]. In preparing emulsions, the CP is very important in selection of the most suitable surfactant for a given oil [3,6,7]. Moreover, pharmaceutical dosage forms consist of nonionic surfactant as stabilizer [8]. Several factors have been considered to be responsible for the CP phenomenon like structure of surfactant molecule, concentration, temperature and a third component (additive). CP is very sensitive to the presence of additives in a system, even at a very low concentration. The additives modify the surfactant–solvent interactions, change the cmc, size of micelles and phase behavior in the surfactant solutions [9]. Many efforts have been made to investigate the effect of various additives e.g. inorganic electrolytes [10,12–20], organic compounds [7,8,11,21–25], ionic surfactants [10,24–29], cationic surfactants [24,29] and zwitterionic surfactants on the cloud point of a nonionic surfactant. Some authors have also reported the CP of ionic surfactants [30–32]. This paper presents experimental results of the effect of various additives like inorganic electrolytes (NaX, KX, $Ca(NO_3)_2$ where X is halide ion) and nonelectrolytes (PEG-4000, carboxy methyl cellulose, glucose, sucrose) on the cloud points of aqueous solutions of a series of $C_{12}E_n$ ($n = 6$, 9, 10) nonionic surfactants. We have also determined the cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ in presence of Triton X-100 (TX-100), which is widely used as a detergent in molecular biology [33].

2. Materials and methods

Hexa oxyethylene monododecylether, $C_{12}E_6$–[$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$], and nona oxyethylene mono dodecylether, $C_{12}E_9$–[$CH_3CH_2)_{11}(OCH_2CH_2)_9OH$], of Lion Corporation, Tokyo, Japan were used as received. Deca oxyethylene monododecylether, $C_{12}E_{10}$–[$CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$], and Triton X 100 of Sigma, USA were used without further purification. The electrolytes used in all experiments were of analytical grade. Glucose and sucrose were obtained from Qualigens, India.

Carboxy methyl cellulose (M.W. $\sim 100,000$) and PEG-4000 (M.W. 4000) were obtained from Suvidinath Laboratories, Baroda, India. Doubly distilled water was used to prepare sample solutions.

Cloud points of surfactant solutions were determined visually by noting the temperature at which the turbidity was observed. The temperature at which the turbidity disappeared on cooling was also noted. Cloud points presented in this article are averages of the appearance and disappearance temperatures of the clouds. These temperatures did not differ by more than 0.4 °C.

3. Results and discussion

In Fig. 1 the variation of CP as a function of $C_{12}E_{10}$ concentration are shown. For $C_{12}E_{10}$ (1% w/v) solution the CP is 88 °C [2,34]. The cloud point increases as concentration decreases from dilute to very dilute solution (less than 1%, inset in Fig. 1). However CP decreases as the concentration becomes greater than 1% up to about 10% (w/v). Above 10% (w/v), the CP increases with increasing concentration (Fig. 1). A number of studies of CP of aqueous nonionic surfactants are reported but most of them are limited to reasonably dilute solutions [1]. The decrease in CP with increase in $C_{12}E_{10}$ concentration is due to increase in micelle concentration. The phase separation results from micelle–micelle interaction. However,
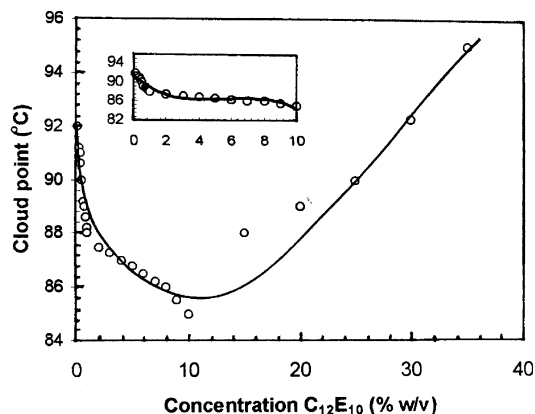

Fig. 1. Cloud point of $C_{12}E_{10}$ as a function of wt.% of $C_{12}E_{10}$ in solution.

at higher concentration (> 10%) the CP increases. This is because, at high surfactant concentration, a structured water surfactant system is present [10,35]. With increase in temperature, this structure breaks, though the molecules are not free of the surfactant effect. That is, some water molecules are not attached to a micelle in particular, but to micelle system in general, forming buffers between micelles. It has been suggested earlier that in polyglycol ether surfactant systems, the water molecules are available for total tenside molecules [36]. Thus higher temperature is required to remove these 'floating' water molecules which are barriers for micellar interaction. Thus CP is a higher temperature and at this temperature the bridge water molecules are released [10].

In Fig. 2, the effects of NaF, NaCl, NaBr and NaI on the cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) are reported. NaF, NaCl and NaBr decrease the cloud point of both surfactants, whereas NaI increases the cloud point. In the lyotropic series, it is expected that the effect of $F^- > Cl^- > Br^- > I^-$ on the decrease in CP, because the ionic sizes increase along the group consequently decreasing the formal charge density on anion, thus lowering the attraction on anion and thereby lowering the attraction of water. However, NaI is considered as water structure breaker, resulting in an increase in CP. Similar results for $C_{12}E_6$ were observed earlier

also [37]. However, there is not much difference in the CPs of $C_{12}E_9$ and $C_{12}E_{10}$ both in the presence and absence of electrolytes. This is probably because of the polydispersity in these surfactants. The error in CPs being less than 2%.

Fig. 3 represents the change in cloud point, ΔCP (°C) of $C_{12}E_6$, and $C_{12}E_{10}$ (1% /v) in presence of KCl, KBr and KI. These electrolytes also had similar impact on the CP as did NaF, NaCl, NaBr and NaI had on $C_{12}E_6$, $C_{12}E_9$, and $C_{12}E_{10}$. NaX has more pronounced effect than KX, baring an exception of KBr, which decreased the CP to a large extent compared to NaBr.

Figs. 4 and 5 represent the effect of tetra butyl ammonium iodide (TBAI) and tetra methyl ammonium bromide (TMAB) on the cloud points of $C_{12}E_n$ ($n = 6$, 9, 10), respectively. It is clear from Fig. 4 that CP of $C_{12}E_n$ increases with increase in concentration of TBAI. The cloud point increase in this case is attributed to the mixed micelle formation of TBAI with nonionic surfactant predominating over water structure formation. Thus the mixed micelles with their cationic components have greater intermicellar repulsions and stronger interaction with water and consequently higher cloud point than the corresponding POE nonionic micelle [16]. TMAB however, decreases the CP of all three surfactants. TMAB is water structure former, thereby decreases the availability of non-
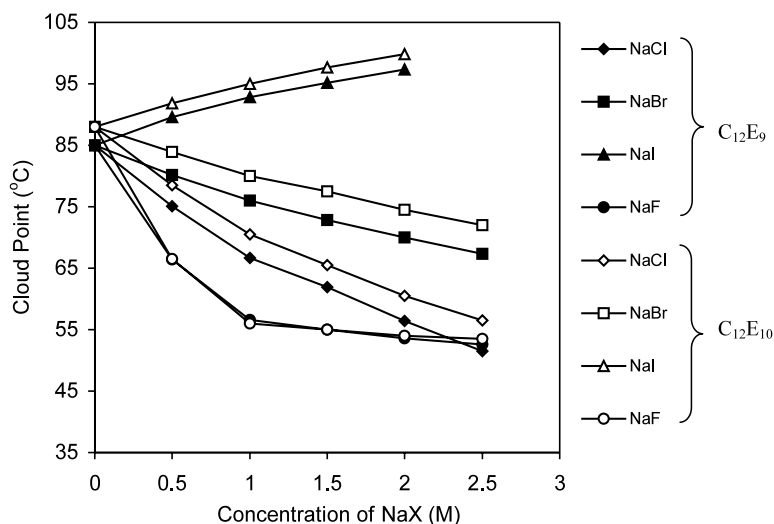

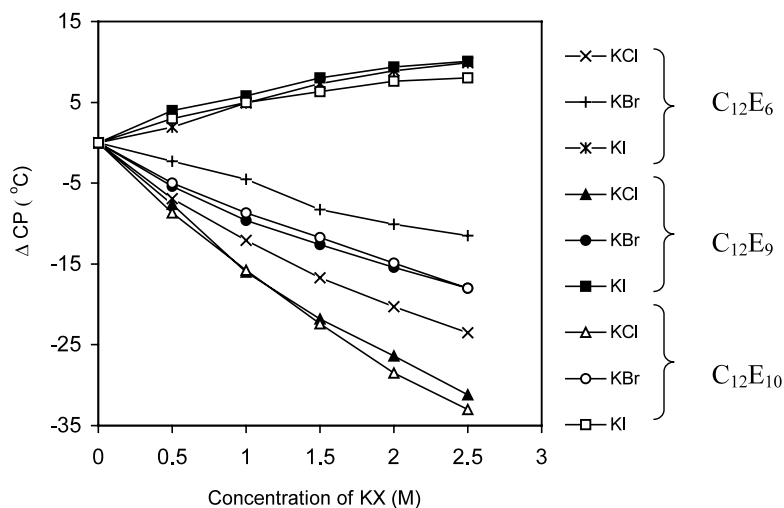Fig. 2. Cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) in presence of NaX.

Fig. 3. Change in cloud point (ΔCP, °C) of $C_{12}E_n$ in presence of KX.

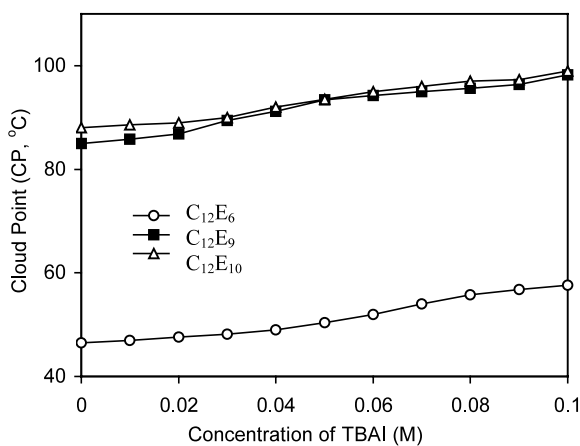Fig. 4. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra butyl ammonium iodide.

Fig. 5. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra methyl ammonium bromide.

associated water molecules to hydrate the ether oxygens of the POE chain [2] and thus lowering the cloud point.

In Fig. 6, the cloud point of $C_{12}E_n$ (1% w/v) solution in presence of glucose, sucrose and $Ca(NO_3)_2$ is illustrated. It is clear that, glucose and sucrose both decrease the cloud point, whereas $Ca(NO_3)_2$ has negligible effect on the CP of $C_{12}E_n$. This indicates that glucose and sucrose remove nearby water molecules surrounding the micelle and helping the micelles to approach each
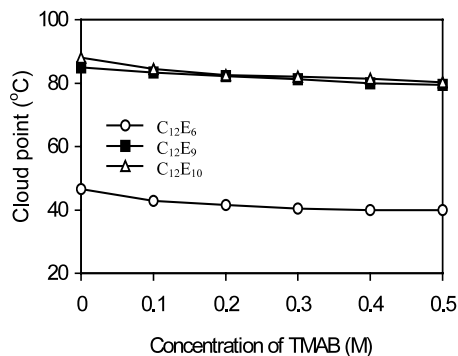
other easily. It was suggested by Kjellander and Florin [38] that, appearance of cloud point is entropy dominated. The ethylene oxide group of POE nonionic surfactant is highly hydrated. When the additives (glucose and sucrose) are added, the water of hydration of the micelles decreases, as these additives compete for water molecules associated with the micelle. Thus with two relatively less hydrated micelles approaching each other, the hydration spheres overlap and some of the water molecules are freed to increase the entropy of the system. At the cloud point, the water molecules get totally detached from the micelles. However, some researchers [3] have suggested that the hydropho-
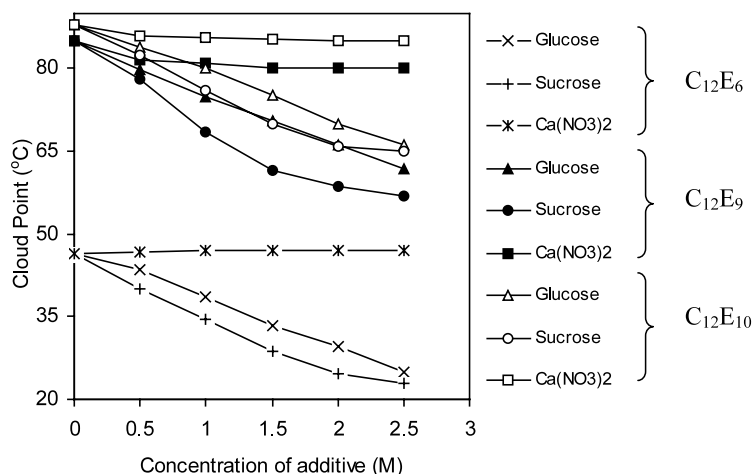
Fig. 6. Cloud point of $C_{12}E_n$ (1% w/v) in presence of different additives.

bic and hydrophilic parts of the micelle interact with water differently where temperature dependent interaction parameters come in to play. At CP the hydrophobicity has relative dominance over hydrophilicity and complete removal of water may not be necessary. With our study it is difficult to make a choice between the two ideas. In any case the overall entropy is high and hence the free energy change is relatively more negative and the appearance of cloud point is facile [39].

In Table 1, the cloud points of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) as function of concentration of KSCN are presented. It is evident that, thiocyanate anion being a very soft lewis base and water structure breaker increases the cloud point by

making more water molecules available to interact with POE chain.

We have also determined the CP of $C_{12}E_9$ and $C_{12}E_{10}$ mixed with TX-100 i.e. nonionic–nonionic surfactant system. Also the CP of $C_{12}E_{10}$/TX-100 (1:1, 1% w/v) mixture in presence of NaX and KX (Fig. 7) were determined.

The cloud points of $C_{12}E_9$/TX-100 (2% w/v) as well as $C_{12}E_{10}$/TX-100 (2% w/v) mixed in various mole ratios are presented in Table 2. It is clear that, the CP of mixed surfactant system at all mole fractions in both the systems are intermediate

Table 1
Cloud point for $C_{12}E_9$/TX-100 and $C_{12}E_{10}$/TX-100 (2% w/v) as a function of mole fraction of TX-100

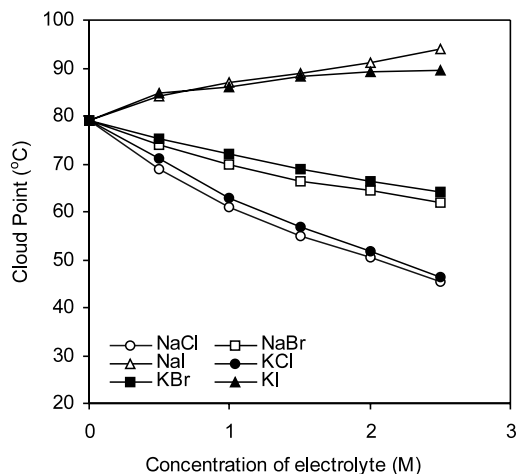| N_{TX-100}	Cloud point (°C)	
	$C_{12}E_9$/TX-100	$C_{12}E_{10}$/TX-100
0.0	84.2	88
0.1	82.4	84
0.3	80	80.4
0.5	77.2	77
0.7	73.6	72.5
0.9	72.8	70
1.0	65.4	65.4

Fig. 7. Cloud point of $C_{12}E_{10}$/TX-100 (1:1, 1% w/v) in presence of electrolytes.

Table 2
Cloud point of $C_{12}E_n$ in presence of KSCN

Concentration of KSCN (M)	Cloud point (^oC)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88
0.1	48	87.2	89
0.2	50.6	89	91
0.3	52.8	90.2	92.5
0.4	54.2	91.6	93.3
0.5	55.4	92.8	94

between either of the pure surfactant. From Fig. 7, it is evident that the cloud point of $C_{12}E_{10}$/TX-100 mixed surfactant system in presence of NaX and KX (where $X = Cl^-$, Br^-) decreases CP whereas in presence of NaI and KI the CP increases. This is expected, because the mixed nonionic–nonionic micelle formed by adding TX-100 to $C_{12}E_{10}$ is chargeless similar to that of a pure nonionic surfactant. Thus the addition of NaX and KX will have similar effect on the CP of mixed nonionic–nonionic surfactant system, as it had on pure nonionic surfactants. Reasons for such behaviour have been described earlier in this article.

We also investigated the effect of carboxy methyl cellulose and PEG-4000 on the CP of $C_{12}E_n$ (1% w/v) solution (Table 3, Fig. 8a and b). It was suggested earlier that the solutes, which get solubilized in the POE mantle of the micelle decrease the cloud point [40]. Hence we believe that, both carboxy methyl cellulose and PEG-4000 do enter the core of the micelle, consequently decreasing the cloud point. Similar result for TX-

114 on addition of PEG-200, -300 and -400 has been reported earlier [10]. However, as carboxy methyl cellulose and PEG-4000 are expected to be reasonably hydrated it is difficult to visualize these molecules in core of the micelle which is oil type but may be present at the palisade layer. Moreover, they will affect the water structure as well as the number of water molecules available for POE groups of the surfactants to be hydrated and hence the CP decreases (cf. discussion of the effect of glucose, sucrose etc., Fig. 6).

Clouding phenomenon is dependent on the structure of poly oxyethylenated nonionic surfactant. The results reported in this article also support the above-mentioned hypothesis. We have studied the effect of various foreign substances on the CP of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$. That is, the hydrophobic group is same, only the ethylene oxide content is changing ($n = 6$, 9, 10). Higher the percentage of oxyethylene (hydrophilic) group, higher will be the cloud point, though the relation between oxyethylene percentage and cloud point is not linear. Hence the decreasing order of cloud point of CP is $C_{12}E_{10} > C_{12}E_9 > C_{12}E_6$ [2].

4. Conclusion

The effects of various electrolytes and nonelectrolytes on the cloud points of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$ were studied. The CP of $C_{12}E_{10}$ showed a minimum in variation with concentration. Sucrose, glucose, KCl, KBr, NaCl, NaI, $(CH_3)_4NBr$ and $(C_4H_9)_4NI$ do change the cloud point to a large extent. Water structure breaking property of

Table 3
Cloud point (^oC) of $C_{12}E_n$ in presence of CMC and PEG-4000

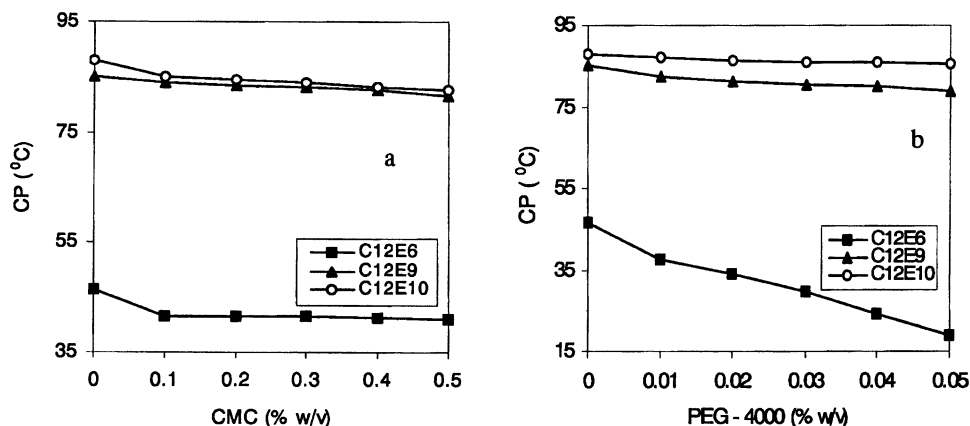| CMC (% w/v)	Cloud point ($^\circ C$)			PEG-4000 (% w/v)	Cloud point ($^\circ C$)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$		$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88	0.0	46.5	85	88
0.1	41.4	83.8	85	0.01	37.4	82.4	87
0.2	41.4	83.4	84.5	0.02	34.2	81	86.4
0.3	41.4	83	84	0.03	29.6	80.4	86
0.4	41.2	82.6	83	0.04	24	79.8	85.7
0.5	41	81.4	82.5	0.05	18.8	78.8	85.4

Fig. 8. (a) Cloud point of $C_{12}E_n$ in presence of CMC; (b) cloud point of $C_{12}E_n$ in presence of PEG-4000.

NaI and KI makes its effect different from that of NaCl, NaBr as well as KCl and KBr. $(C_4H_9)_4NI$ has different effect on CP than $(CH_3)_4NBr$, because of mixed micelle formation of $(C_4H_9)_4NI$ with nonionic surfactant predominating over water structure formation. Mixed nonionic–nonionic surfactant system shows clouding phenomenon at temperatures, which are intermediate to that of corresponding pure surfactants.

Acknowledgements

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