Chapter VI A

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

Preview

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 phenomenon occurs. In this chapter, 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, and 9).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 Tetramethyl ammonium bromide (TMAB). Overall the electrolytes and non-electrolytes have a large amount of effect on CP of nonionic surfactants, because of their effect on water structure and their hydrophilicity.

Keywords: Nonionic Surfactants; Cloud Point; Electrolytes; Non-electrolytes; Hydrophilicity.

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 nonionic 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 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 eg. 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 chapter incorporates experimental results of the effect of various additives like inorganic electrolytes (NaX, KX, $Ca(NO_3)_2$ where X is halide ion) and non-electrolytes (PEG-4000, carboxy methyl cellulose, glucose, sucrose) on the cloud points of aqueous .

solutions of a series of $C_{12}E_n$ (n=6, and 9) nonionic surfactants. We have also determined the cloud point of $C_{12}E_9$ in presence of TX 100, which is widely used as a detergent in molecular biology [33].

2. Materials and methods

Hexaoxyethylene monododecylether,$C_{12}E_6$–[CH_3 $(CH_2)_{11}(OCH_2CH_2)_6OH$], and nonaoxyethylene mono dodecylether, $C_{12}E_9$-[CH_3 $CH_2)_{11}(OCH_2CH_2)_9OH$], of Lion Corporation, Tokyo, Japan were used as received. The electrolytes used in all experiments were of analytical grade. Glucose and sucrose were obtained from Qualigens, India. Carboxy methyl cellulose (M.W.~100,000) & 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 chapter 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 effects of NaF, NaCl, NaBr and NaI on the cloud point of $C_{12}E_9$ 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 [34].

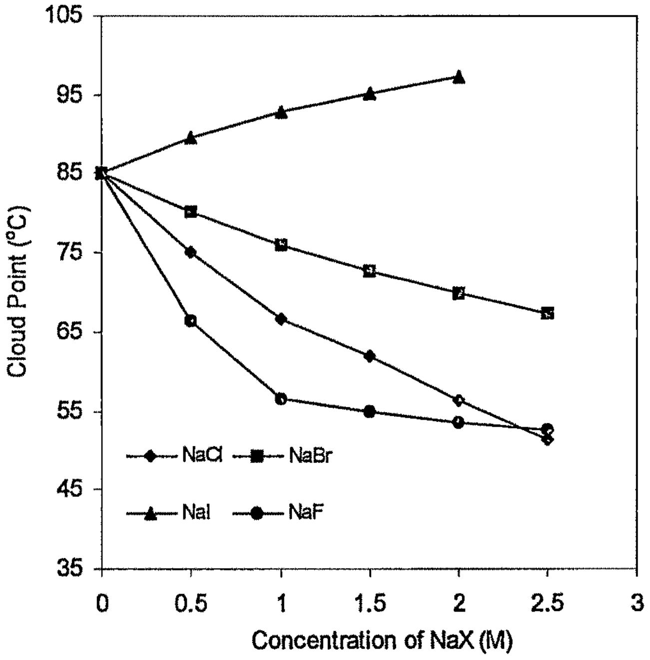

Fig. 1. Cloud point of $C_{12}E_9$ (1% w/v) in presence of NaX.

Figure 2 illustrates the change in cloud point, Δ CP (°C) of $C_{12}E_6$, and $C_{12}E_9$ (1%w/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 $C_{12}E_6$ and $C_{12}E_9$. NaX has more pronounced effect than KX, baring an exception of KBr, which decreased the CP to a large extent compared to NaBr.

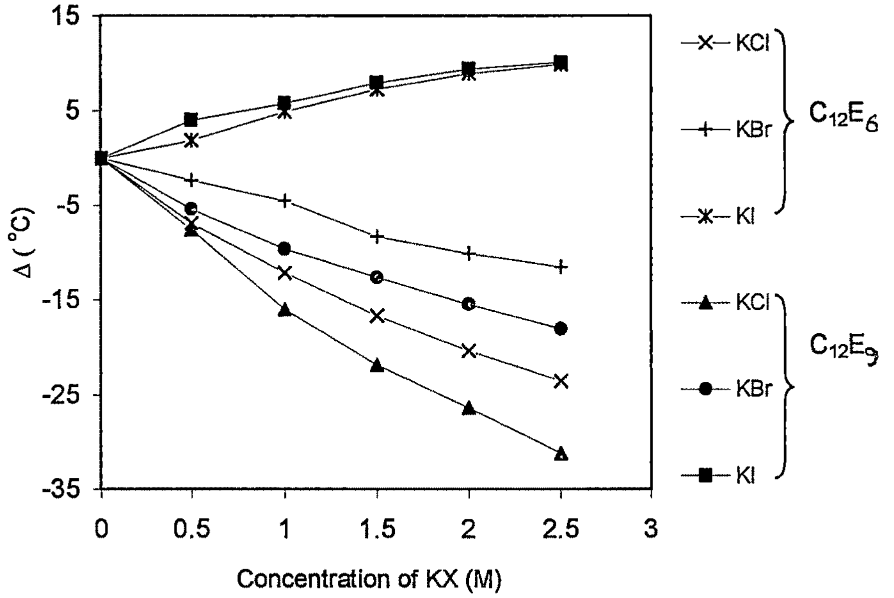

Fig. 2. Change in cloud point (Δ CP, °C) of $C_{12}E_n$ in presence of KX.

Figs. 3 and 4 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, and 9) respectively. It is clear from Fig. 3 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 nonassociated water molecules to hydrate the ether oxygens of the POE chain [2] and thus lowering the cloud point.

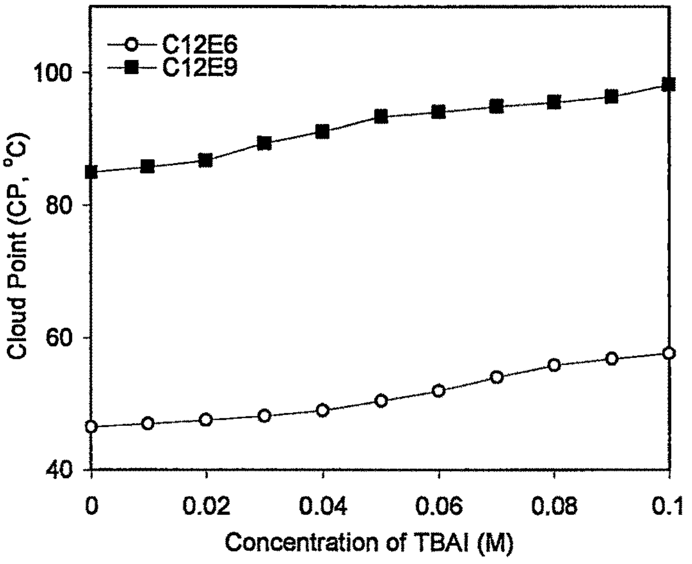

Fig. 3. Cloud Point of $C_{12}E_n$ (1% w/v) in presence of Tetra butyl ammonium iodide.

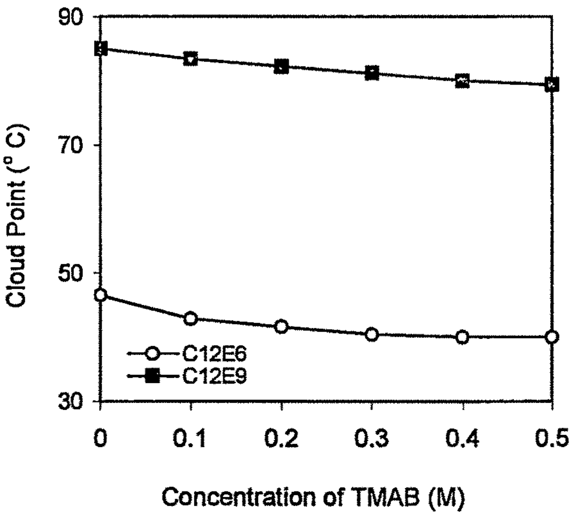

Fig. 4. Cloud Point of $C_{12}E_n$ (1% w/v) in presence of Tetra methyl ammonium bromide.

In Fig. 5, 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.

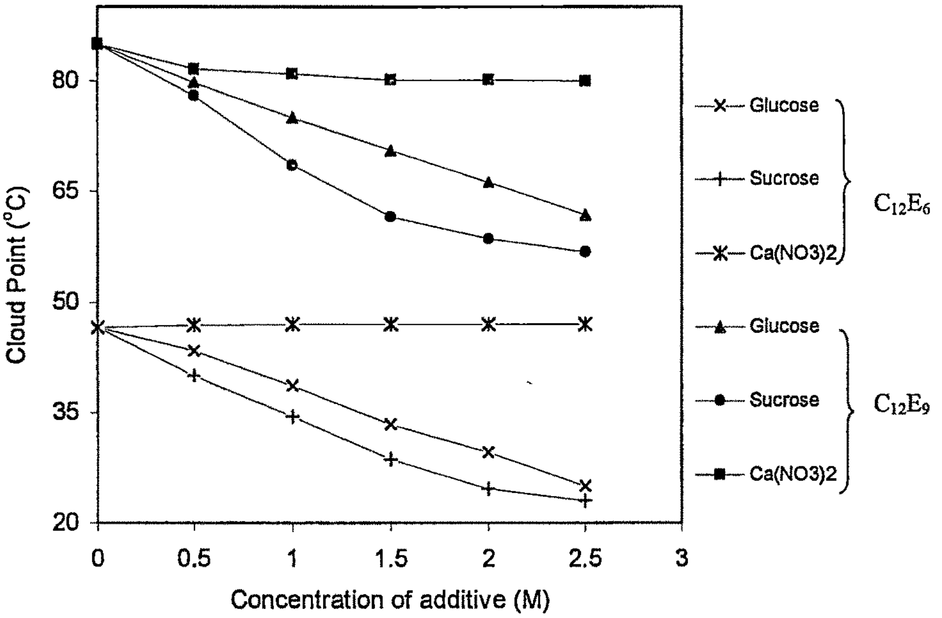

Fig. 5. Cloud Point of $C_{12}E_n$ (1% w/v) in presence of different additives.

It was suggested by Kjellander et al [35] 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 hydrophobic 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 [36].

In Table 1, the cloud points of $C_{12}E_6$, and $C_{12}E_9$ (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.

Table 1.

Cloud Point of $C_{12}E_n$ in presence of KSCN

Concentration of KSCN (M)	Cloud Point (°C)	
	$C_{12}E_6$	$C_{12}E_9$
0.0	46.5	85
0.1	48	87.2
0.2	50.6	89
0.3	52.8	90.2
0.4	54.2	91.6
0.5	55.4	92.8

We have also determined the CP of $C_{12}E_9$ mixed with Triton X 100 i.e. nonionic-nonionic surfactant system. The cloud points of $C_{12}E_9$/TX100 (2%w/v) mixed in various mole ratios and are illustrated in Fig. 7. It is clear that, the CP of mixed surfactant system at all mole fractions in both the systems are intermediate between either of the pure surfactant.

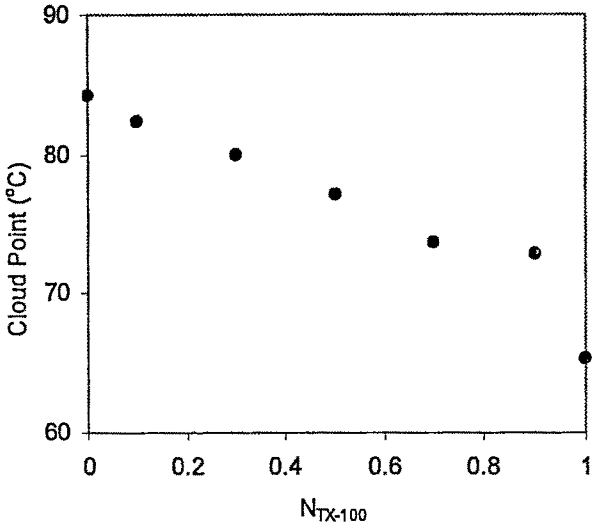

Fig. 7. Cloud Point for $C_{12}E_9$/TX-100 (2% w/v) as a function of mole fraction of TX-100

Table 2.

Cloud Point (°C) of $C_{12}E_n$ in presence of Carboxy methyl cellulose (CMC) and PEG-4000.

CMC (% w/v)	Cloud Point (°C)		PEG- 4000 (% w/v)	Cloud Point (°C)	
	$C_{12}E_6$	$C_{12}E_9$		$C_{12}E_6$	$C_{12}E_9$
0.0	46.5	85	0.0	46.5	85
0.1	41.4	83.8	0.01	37.4	82.4
0.2	41.4	83.4	0.02	34.2	81
0.3	41.4	83	0.03	29.6	80.4
0.4	41.2	82.6	0.04	24	79.8
0.5	41	81.4	0.05	18.8	78.8

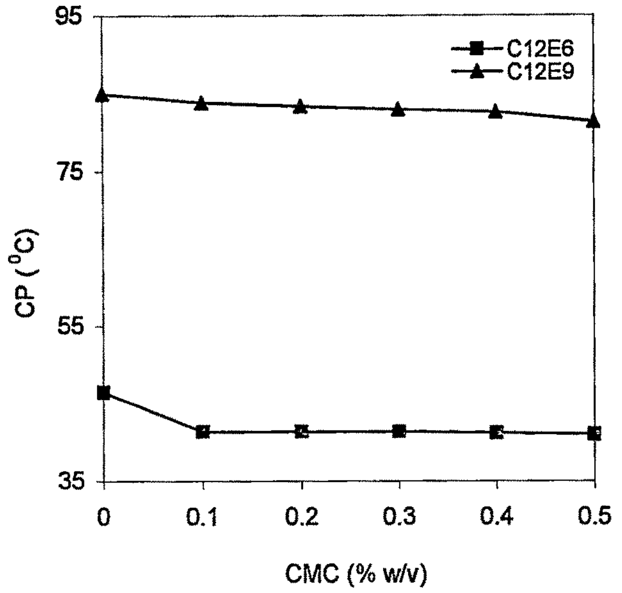

Fig. 8. Cloud Point of $C_{12}E_n$ in presence of CMC.

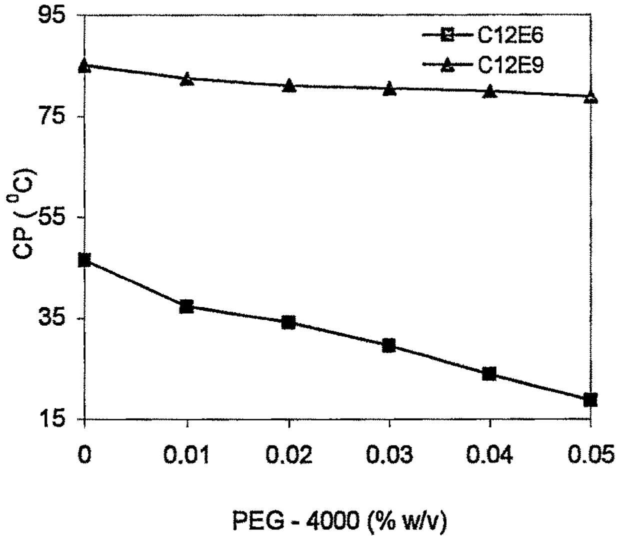

Fig. 9. Cloud Point of $C_{12}E_n$ in presence of PEG – 4000.

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 2, Figs. 8 and 9). It was suggested earlier that the solutes, which get solubilized in the POE mantle of the micelle decrease the cloud point [37]. 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 TX114 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 $C_{12}E_6$, and $C_{12}E_9$. That is, the hydrophobic group is same, only the ethylene oxide content is changing (n=6, and 9). 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 nonionic surfactants is $C_{12}E_9 > C_{12}E_6$ [2].

4. Conclusion

The effects of various electrolytes and non-electrolytes 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, $(CH_3)_4$ NBr and $(C_4H_9)_4$ NI do change the cloud point to a large extent. Water structure breaking property of NaI and KI makes its effect different from that of NaCl, NaBr as well as KCl and KBr. $(C_4H_9)_4$ NI has different effect on CP than $(CH_3)_4$ NBr, because of mixed micelle formation of $(C_4H_9)_4$ NI 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.

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Chapter VI B

Membrane Electrode Sensitive to a Cationic Surfactant in Aquo-Organic Media

Abstract

An electrode originally sensitive to dodecyltrimethylammonium ions (DTA^+) was proven to be sensitive to tetradecyltrimethylammonium ions (TTA^+) and was used for determination of critical micelle concentration of tetradecyltrimethylammonium bromide (TTAB) in water. Moreover the response of the electrode was tested in presence of non-aqueous polar solvents i.e. dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) in water and was observed to be Nernstian within the concentration range studied (up to 40% v/v of DMF and DMSO). The validity of this electrode, for electrochemical measurements, was checked by comparing the critical micelle concentration values of TTAB obtained by using the electrode, with those obtained by conductivity measurements in mixed polar solvents. The effect of solvent on the micellization of TTAB has been discussed.

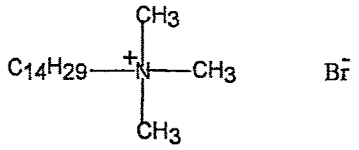
Key words: Ion selective electrode, Tetradecyltrimethylammonium bromide, Critical micelle concentration, Hydrophobic effect

1. Introduction

Surfactants are important in various phenomena of interfacial science and continue to be critical in many applications in agrochemicals, emulsion polymerization, paper manufacturing, water treatment, oil recovery, fire fighting and plastic manufacturing [1]. Handling of surfactants for use, formulation or production needs simple and reliable analytical technique to determine their quantity in reaction media [2]. Hence ion selective electrodes for surfactants have been developed in the last three decades [3-6] and have been used to study biomolecule-surfactant interactions [7]. The principle of these electrodes is based on a selectively permeable membrane between two electrolyte phases across which only a single ion can penetrate. Polymeric membranes are easy to handle and also prevent rapid loss of expensive electro active material dissolved in a plasticizer. Complexing agents having selectivity towards ions of interest are dissolved in it, and they provide the mechanism for selective charge transport across the boundaries of the membrane. Different associative behavior of surfactants in water and other solvents have stimulated the interest to elucidate how solvent properties influence aggregation and many studies have been performed to gain information on the role of solvent in the aggregation process [8]. Hence, in order to understand – a) the behavior of polymeric membrane electrodes in aquo-organic medium and b) the role of solvent on aggregation of surfactant, we determined the critical micelle concentration (cmc) of a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), in H_2O/DMF as well as in H_2O/DMSO medium using the cationic surfactant ion selective electrode (ISE). We have also compared the cmc values of TTAB obtained by electrochemical measurements using ISE with those obtained by conductivity measurements at the same temperature to determine the response nature of surfactant electrode in mixed aquo-organic medium.

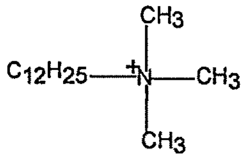
2. Experimental

2.1 Materials. Tetradecyltrimethylammonium bromide procured from Lancaster, U. K. was recrystallized thrice in acetone prior to use. Dimethyl formamide (DMF), tetrahydrofuran (THF) (Qualigens, India) and dimethyl sulfoxide (DMSO) (E. Merck, India) were purified as per standard methods reported in the literature [9]. Dodecyltrimethylammonium bromide (DTAB) obtained from Acros Organics was recrystallized twice from methanol and then dried under vacuum at room temperature. Sodium tetraphenylborate ($NaB\phi_4$) was obtained from E. Merck, Germany and used as received. Dioctyl phthalate (plasticizer) was purchased from Suvidinath Laboratories, India. Doubly distilled water, having conductivity < 6 μS cm^{-1} was used in all the experiments. The structures of TTAB and DTA^+ are presented below.



$$C_{14}H_{29}-\overset{+}{N}(CH_3)_3 \quad Br^-$$

a) Tetradecyltrimethylammonium bromide (TTA^+Br^-)



$$C_{12}H_{25}-\overset{+}{N}(CH_3)_3$$

b) Dodecyltrimethylammonium ion (DTA^+)

2.2 Methods.

a) Electrochemical measurements.

The cationic surfactant ion selective electrode was prepared in our laboratory as detailed below. Membranes were made from low molecular weight poly (vinyl Chloride) (PVC) mixed with a large quantity of plasticizer. PVC (0.8 g) and Dioctyl phthalate (DOP, 1.2 g) were mixed in 10 mL of THF until PVC was completely soluble (Solution A). $DTAB\phi_4$ was used in order to have $B\phi_4^-$ ion as mobile anionic site in the membrane for TTA^+ detection, which was prepared by mixing equimolar aqueous solutions of two salts: dodecyltrimethylammonium bromide (DTAB) and sodium tetraphenylborate ($NaB\phi_4$). The solution obtained was extracted three times in dichloromethane. After evaporation of solvent, the precipitate was recrystallized twice from ether-methanol mixture. A 10^{-2} M solution (Solution B) of $DTAB\phi_4$ in THF was made. 3 mL of solution A was mixed with 0.2 mL of solution B and the clear solution was spread on clean and clear glass surface of a flat dish, which lost THF by evaporation at room temperature forming the membrane in the form of thin film (~0.1 mm thick). If the plasticizer (i.e Dioctyl phthalate) exceeded 1.2 g, the resultant membrane used to be too much flexible, sticky, having low mechanical strength and thus very difficult to handle. Whereas, if the DOP content was lower than 1.2 g, the resultant film was stiff, less flexible and it was difficult to fix up on the narrow end of the glass tube. Even if such membrane was glued at the end of the narrow glass tube, it used to leak and thus unfit for experimental purpose. Thus the

method mentioned above at the beginning of the paragraph incorporates the optimized contents of various ingredients required for preparation of the membrane suitable for the electrochemical measurements. The membrane was removed and cut into small pieces and fixed on the open end of a narrow glass tube of 1 mm diameter using PVC-THF paste as glue. The membrane was conditioned with the reference solution (very dilute solution of TTAB) prior to electrochemical measurements. The experimental setup for electrochemical measurements is as shown in Scheme 1.

Scheme 1.

Cu	Calomel reference electrode	KCl saturated agar agar salt bridge	Reference solution (very dilute solution of TTAB)	Membrane electrode	Aqueous unknown solution	KCl saturated agar agar salt bridge	Calomel reference electrode	Cu

The reference electrode of the KCl-saturated calomel was protected from amphiphile diffusion by a saline agar-agar gel made of saturated KCl. Moreover, to limit the diffusion speed of surfactant, the gel was contained in a teflon capillary tube. Aliquot addition of known concentration of surfactant solution to a fixed quantity of solvent [water/DMF or water/DMSO mixture (max. 40% v/v)] was done and the corresponding emf values were recorded.

The aquo-DMF and aquo-DMSO solutions were neutral to 0.001 M aquo-NaOH solution. Stable emf values (mV, ± 2%) were recorded at regular interval of 3 minutes after each aliquot addition. The emf values thus obtained were plotted as a function of logarithm of surfactant concentration and the break in emf-log concentration of

surfactant profile was considered as the critical micelle concentration (cmc) of the surfactant (Fig. 1). Total duration to complete one set of experiment was ~ 3 h. The reproducibility of the emf measurements and hence cmc determinations was crosschecked by carrying out duplicate runs and the cmc values were reproducible within ± 4%. The membrane showed good resistance and stable electrochemical response in aquo-organic solvent and was unaffected by the solvent medium [water/DMF or water/DMSO mixture (max. 40% v/v of DMF or DMSO)]. No leaching/leakage of the polymeric membrane was observed and the polymeric film remained intact throughout the experimental duration (~3 hrs and more). The same electrode was used for atleast 6 times or more covering 3 days or more with prior rinsing followed by conditioning with reference solution before each experimental run. However our attempt to work with water–ethylene glycol mixed solvent was unsuccessful at any concentration of ethylene glycol. In the DMF-water and DMSO-water medium, the lower limit of detection of cation was found to be $1x10^{-5}M$, accuracy of detection of cation was ±4 %, the emf vs $log_{10}C$ plot was linear althrough from lower limit of $1x10^{-5}M$ to desired higher concentration. The thermodynamic background of such electrode has been discussed in detail by Turmine et al. [10].

b) Conductivity measurements.

The conductance (k) measurements were done with Welltronix (India) conductivity bridge. A dip type cell of cell constant 1.01 cm^{-1} was used. The conductance of different solutions, which were obtained on aliquot addition of a known concentrated surfactant solution to a given volume of the thermostated solvent, was measured. Conductance (k) vs concentration of surfactant (mole/litre) plots are shown in Figure 2, for TTAB. The break in conductance-concentration profile was considered as the critical micelle concentration [11].

3. Results and discussion

The critical micelle concentration is probably the simplest means of characterizing the colloid and surface behavior of a surfactant, which in turn determines its industrial usefulness and biological activity and also gives a measure of solute-solute interactions [12]. Electrochemical measurements were carried out to study the micellization of the cationic surfactant in aquo-organic medium using ISE selective to a surfactant ion, as this will be then an additional tool of characterization of micellar aggregates in aquo-organic medium, besides the existing conventional techniques (surface tension, conductivity etc.). Potentiometric measurements were carried out with ISE sensitive to TTA^+ ions using a Systronics, India, multimeter. The EMF values were reproducible and had ± 0.5mV stability. Figure 1. shows the representative potentiometric curve obtained for TTAB in aqueous as well as aquo-organic medium at 35°C. Initially the potential response was linear, however as the concentration of surfactant increased, a break corresponding to critical micelle concentration of TTAB was observed. The potential response of this membrane was equal to (59 ± 3mV) per decade indicating a reasonably good Nernstian slope.

The cmc values of TTAB obtained in aquo-organic medium (containing varying amount (%v/v) of DMF and DMSO by electrochemical as well as conductivity measurements are reported in Table 1. It is evident from Table 1, that the critical micelle concentration value of TTAB in aqueous medium is lower than that in

presence of DMF and DMSO. The micelle formation is dependent on the hydrophobic effect and London dispersion forces [13, 14]. The increase in cmc values of TTAB in presence of DMF and DMSO, can be attributed to the increase in solvation of the hydrocarbon chains of the surfactant by DMF (ε=36.7) and DMSO (ε= 46.6). Thus lowering of hydrophobic effect- the driving force for micellization leads to higher values of cmc in presence of DMF and DMSO and in aquo-DMF medium more than in aquo-DMSO. We observed that the electrode potential (mV) plotted against the $\log_{10}C$ of the ion (i.e [TTA^+]) gave a straight line of gradient $2.3RT/z_iF$, where z_i and F are the charge of ions (i.e TTA^+) and Faraday constant respectively. This means that the response of the electrode for the studied system in aquo-organic medium is Nernstian. Though the electrode showed Nernstian response, it lost its sensitivity at higher concentrations of DMF and DMSO in the solvent [> 40% v/v], and could not be used for cmc determination using electrochemical measurements. Also the membrane made of $DTAB\phi_4$ could be successfully used for the detection of TTA^+ ions in water, suggesting the possibility of their use as cation selective electrode irrespective of the chain length of the cation as well as in aquo-organic medium.

4. Conclusions

A surfactant ion selective electrode (ISE) originally sensitive to dodecyltrimethylammonium ions (DTA^+) was proved to be sensitive towards tetradecyltrimethylammonium ions (TTA^+) and successfully employed for evaluation of critical micelle concentration of tetradecyltrimethylammonium bromide. The electrode was also used for determination of critical micelle concentration of tetradecyltrimethylammonium bromide in aquo-organic medium i.e. water/dimethyl formamide and water/dimethyl sulfoxide mixture, up to 40% v/v of the organic liquid]. The validity of this ISE, for electrochemical measurements, was substantiated by comparable values of critical micelle concentration of tetradecyltrimethylammonium bromide obtained by using this electrode, with those obtained by conductivity measurements in aquo-organic media. The ISE showed good resistance towards the mixed solvent system (within the concentration range studied) and hence it can prove to be an important tool for studying the self-aggregation of cationic surfactants in aquo-organic medium.

Table 1. Critical micelle concentration (mM) values of tetradecyltrimethylammonium bromide (TTAB) at 35°C using different methods.

Organic solvent %v/v	Critical micelle concentration (mM)			
	DMF		DMSO	
	Conductance	Potentiometry	Conductance	Potentiometry
0	3.80 ± 0.04	3.70 ± 0.03	3.80 ± 0.04	3.70 ± 0.03
10	6.65 ± 0.13	6.45 ± 0.13	5.20 ± 0.10	5.01 ± 0.07
20	8.50 ± 0.22	8.32 ± 0.24	6.10 ± 0.16	6.02 ± 0.14
30	11.10 ± 0.27	10.96 ± 0.26	8.80 ± 0.19	8.91 ± 0.22
40	14.30 ± 0.31	14.40 ± 0.36	12.50 ± 0.29	12.58 ± 0.26

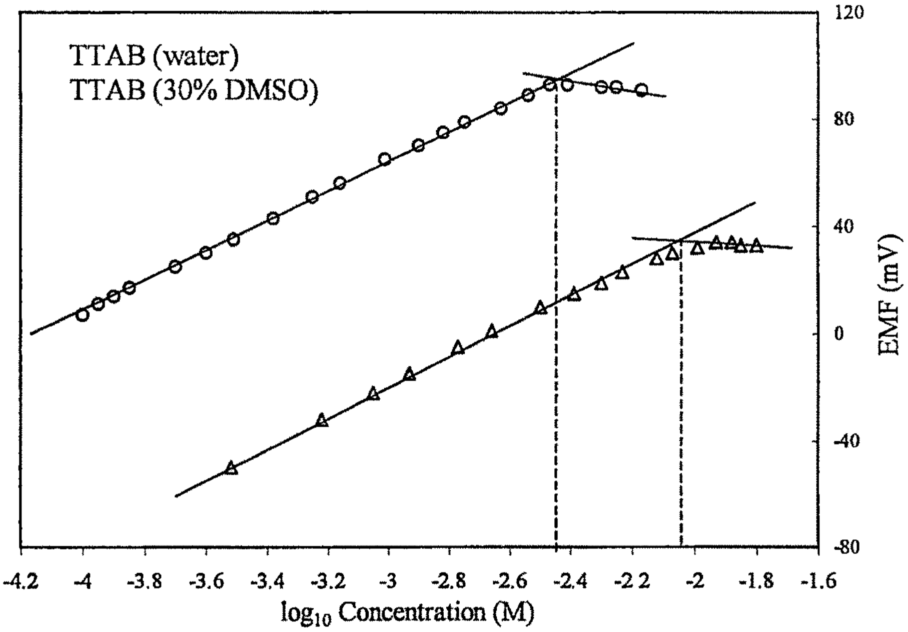


Figure 1. Representative emf vs log [TTAB] plots at 35°C for various systems.

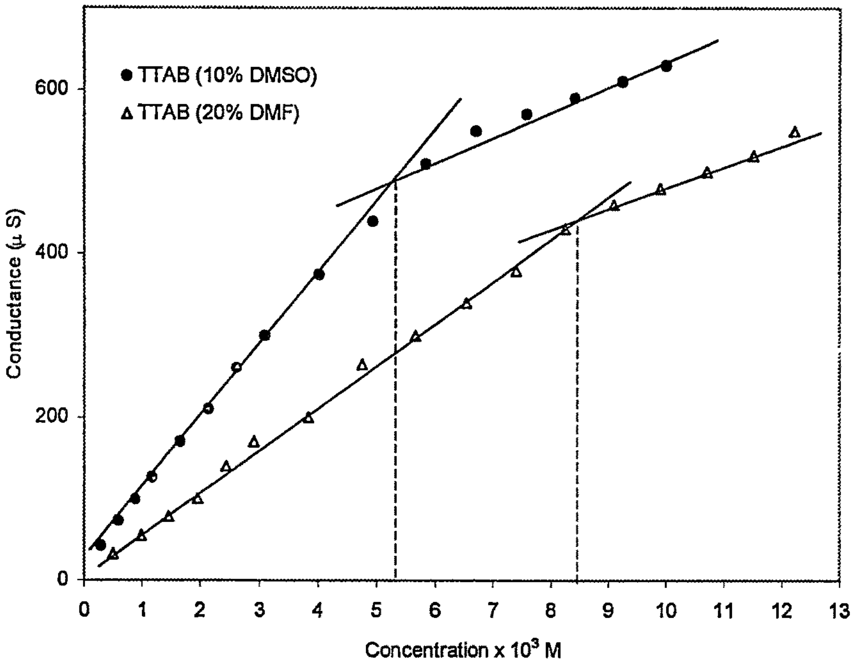


Figure 2. Representative conductivity vs concentration plots at 35°C for various systems.

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