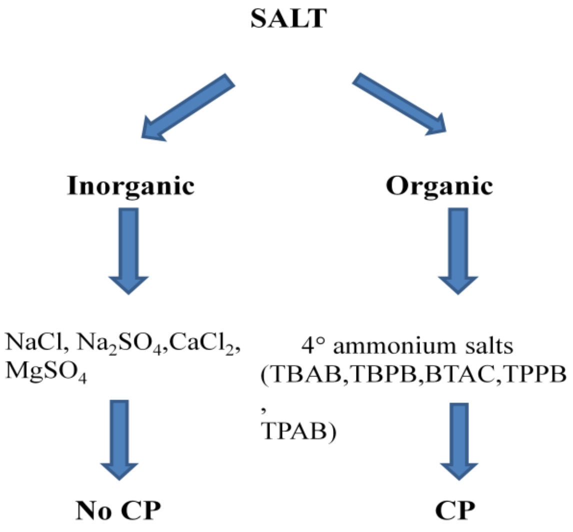
3.1 Introduction

Inspite of the clouding phenomenon easily seen in the non-ionic surfactant [38], main focus here is on the ionic surfactants because phenomenon is not well understood [43]. Conventional anionic surfactants having inorganic counterions as such are not prone to clouding. In the last decade, the structure of anionic surfactants showing clouding has been the subject of active interest [76, 87, 91, 98, 99, 101]. Clouding in ionic surfactant appears slowly than non-ionic ones. Therefore, such systems could be used to study micellar morphological changes on approaching CP.

In contrast to the inorganic counterions, symmetrical quaternary cations are essentially nonhydrated and the positive charge is buried in paraffin shell due to which the unusual phenomenon could be observed with these cations. In most of the studies on clouding phenomenon, in anionic surfactant solutions, has been appeared when tetra-*n*-butyl ammonium (TBA^+) counterion was driven from an added salt [79] or when it was attached to the anionic moiety (of the surfactant itself) [76,99,101]. Later on, the phenomenon was observed with other quaternary salts (TBPB, BTAC, TPAB, TPPB) [89-91]. Appearance of clouding phenomenon in presence of added salts has been shown in the following scheme.

In general,



Scheme: Clouding patterns of anionic surfactants in presence of different salts

It seems that quaternary counterion plays a dual role in initiating unusual clouding phenomenon in aqueous ionic surfactant: firstly, it can gradually discharge the micelle and tend the system towards pseudo nonionic and secondly, it can interact via hydrophobic interactions with the micellar surface. Recently, counterion effect with quaternary counterions is gaining recognition in micellar systems [146-148]. In above studies presence of quaternary counterion induces micellization (lower cmc), micellar growth (increase in Nagg) or micelle to vesicle transition, in the solution.

Further, additives modify the phase behaviour of surfactant solutions and therefore, it is of considerable importance to acquire knowledge of clouding phenomenon of such surfactant systems in presence or absence of additives in order to tune the phenomenon in desired way. The anionic surfactants could also be used to improve the accumulation of some electro active organic molecules [149]. Coumarin derivatives are excellent chromogenic and fluorogenic dyes that are widely utilized as reporters in chemosensors and as drug intermediates. These mixed solutions (if they show clouding) on heating may phase separate resulting in a surfactant rich phase having most of the organic compound. Therefore, effect of addition of coumarin derivatives on clouding behaviour of surfactant solutions has a potential to facilitate the methodology of chemosensing and drug delivery.

Among the ionic surfactants too, the anionic systems tend to be biodegradable and less toxic compared to cationic ones and therefore considered to be more environment friendly. The ability of salts to alter the cloud point has extensively been studied [91, 93, 99, 101]. However, correlations have not been established among the alterations in the CP and the nature of counterion/head group of ionic surfactants. Further, role of the magnitude of charge present on the added inorganic counterion has also not been addressed. The computation of the energetics of clouding phenomenon has gained importance, recently [65, 101, 102]. However, the thermodynamic parameters of clouding for the single ionic surfactant (in presence or absence of inorganic salts) have remained largely unexplored.

Based on the available literature on micellar systems containing quaternary counterions, following objectives were set.

To synthesize more anionic surfactants having quaternary counter ions.

To study the solution behaviour (micellization and clouding) of above synthesized surfactants.

To study the effect of inorganic additives on CP of synthesized surfactants.

In this work we have synthesized anionic surfactants with large counter ions. A detailed study on: i) micellization behaviour of ionic surfactants showing clouding, ii) effect of temperature on solution behavior, iii) CP determinations with varying concentration of surfactant iv) CP variation in presence of different concentration of inorganic salts and v) computation of thermodynamic parameters, has been undertaken.

The present work is intended to be a step towards the study of the connection between micellar structural properties (size and hydration) and macroscopic properties such as the *cloud point*. Different anionic surfactants having quaternary counterion: tetra-*n*-butylammonium dodecylsulphate (TBADS) and tetra-*n*-butylammonium dodecylbenzene sulfonate (TBADBS), tetra-*n*-butylphosphonium dodecyl sulphate (TBPDS) and tetra-*n*-butylphosphonium dodecylbenzene sulfonate (TBPDBS) are synthesized to compare the effects of alkyl headgroup (dodecylsulphate (DS^-) and dodecylbenzene sulfonate (DBS^-)) and the nature of counterion (TBA^+ and TBP^+) on clouding phenomenon. In continuation, a systematic study of clouding phenomenon, employing a variety of alkali salts and the representative anionic surfactants, **TBADS and TBADBS** is done.

3.2. Results and Discussion

Though all the surfactants are ionic in nature, they show clouding phenomenon on heating. Micellization and CP data for the synthesized surfactants are acquired by the procedure given chapter 2 (Materials and Methods).

3.2.1. Micellization

The cmc and α values for various conventional and synthesized anionic surfactants are compiled in Table 1. The perusal of data shows that cmc and α values are higher for surfactants having Na^+ counter ion than the surfactants containing quaternary counter ion (TBA^+ or TBP^+). This may be due to the nature of quaternary counterion in which a positive charge is buried in butyl chains. These counter ions can interact with anionic micellar surface electrostatically as well as hydrophobically due to butyl chains [98]. The interactions may force quaternary counterions to bind with the micellar surface and initiate the phenomenon of micellization at lower concentration. This indeed is observed in Table 1. Further, the cmc values of TBPDS and TBPDBS are higher than TBADS and TBADBS. This may be due to bigger size of phosphorus atom containing counter ion TBP^+ than nitrogen atom containing counter ion TBA^+. Therefore, electrostatic repulsive interaction between similar charged head groups will be less depleted with TBP^+ than TBA^+ resulting in higher cmc values in case of surfactants having TBP^+ counter ion.

Table 1: CMC and α values for different Anionic Surfactants

Surfactant	CMC. 10^3 (M)		α
	Conductometry	Tensiometry	
SDS	8.1	8.32	0.36
SDBS	2.3	2.0	0.75
MES	3.4	3.17	0.62
TBADS	1.21	1.12	0.39
TBADBS	0.485	0.46	0.53
TBAMES	0.85	0.7	0.51
TBPDS	1.375	-	0.43
TBPDBS	0.825	-	0.58

3.2.2. Effect of Temperature on Micellar Parameters

As micellization processes are known to be sensitive to temperature, TBADS is chosen for detailed micellization study at different temperatures. Figure 1 shows the plots of κ *vs* [TBADS] at various temperatures. These plots are used to determine cmc and α value at different temperatures, summarized in Table 2. CMC variation with temperature shows a U shaped behavior (Figure 2a) [150]. Two factors: i) dehydration of counterion and surfactant headgroup and ii) breakdown of structured water around the alkyl tails, with the increasing temperature may be responsible for such behaviour. CMC values decrease up to certain minimum temperature, as the initial heating causes a decrease in hydration of the hydrophilic head group and the counterion which favours micellization (Figure 2). However, when the surfactant molecules dissolve in the aqueous medium, water structure around the alkyl tail group gets distorted. The increasing temperature also causes a breakdown of structured water opposing micellization. Therefore, the CMC increases after the certain temperature resulting in the U shaped curve. Thus, micellization behaviour is supposed to be the resultant due to the competition between above two opposite effects. However, the temperature of minimum cmc (Tm) was found higher than that reported for conventional ionic surfactants (e.g. SDS) [151]. The α value shows a gradual decrease with temperature (Figure 2b). The reported α data on conventional ionic surfactant suggest a weak dependence of α on temperature [152]. In another study, an increase in α is also been reported with temperature [153]. Above two observations (higher Tm and decreasing α) indicate that TBADS responds differently on heating. A similar hint was intimated from the literature by Bales and Zana [76].

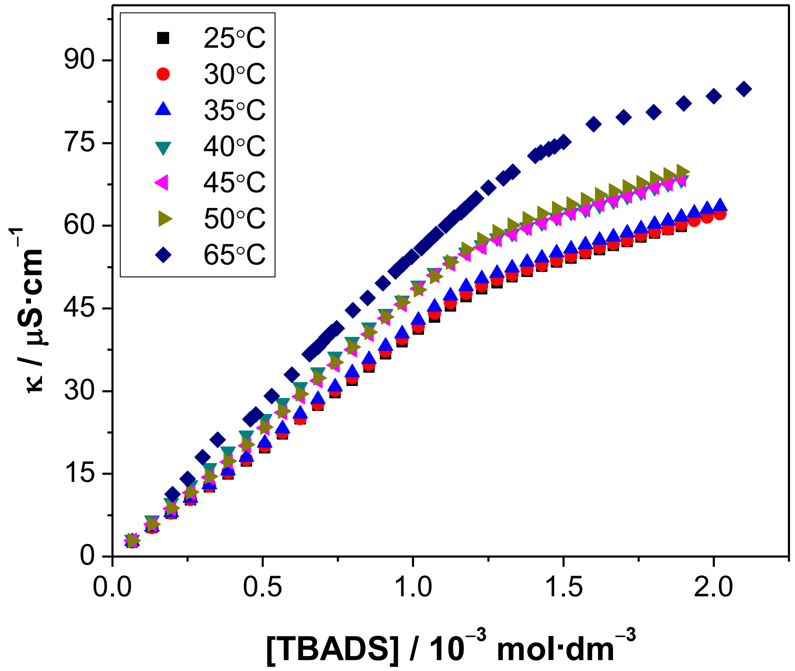


Figure 1: Variation of specific conductance (*κ*) *vs* concentration plots for TBADS at different temperatures

Table 2: cmc and α values for TBADS at different temperatures

Temperature (°C)	CMC (10^3.M)	α
25	1.22	0.42
30	1.21	0.39
35	1.19	0.37
40	1.16	0.37
45	1.18	0.37
50	1.25	0.37
65	1.42	0.23

To substantiate the heating response of quaternary surfactants conductivity data is collected at various temperatures for different TBADS concentrations as shown in Figure 3. Conductivity increases with the increase in temperature, for 0.005M TBADS concentration. This observation is in line to what we observed in Figure 1 as well as in earlier reports [152]. When the conductivity experiments were performed with 0.015M TBADS, κ values showed a weak dependence (nearly constant) on temperature. However, conductivity data for 0.03M TBADS showed a decrease in κ with temperature. This observation is in sharp contrast to the reported conductivity data for conventional ionic surfactants at higher concentration [152]. It is hard to understand the decrease in conductance of a solution with temperature which contains charged species.

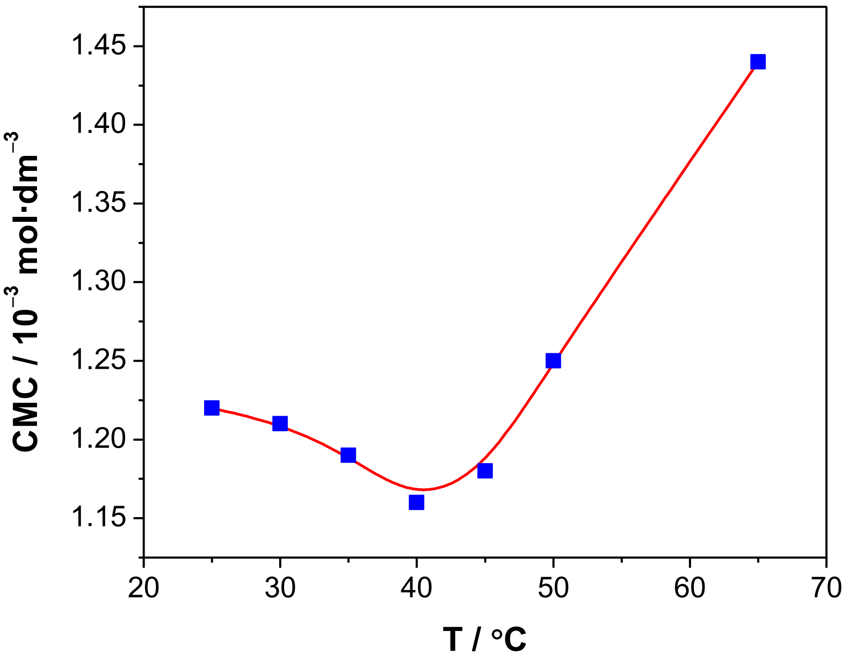


Figure 2a: Temperature effect on cmc

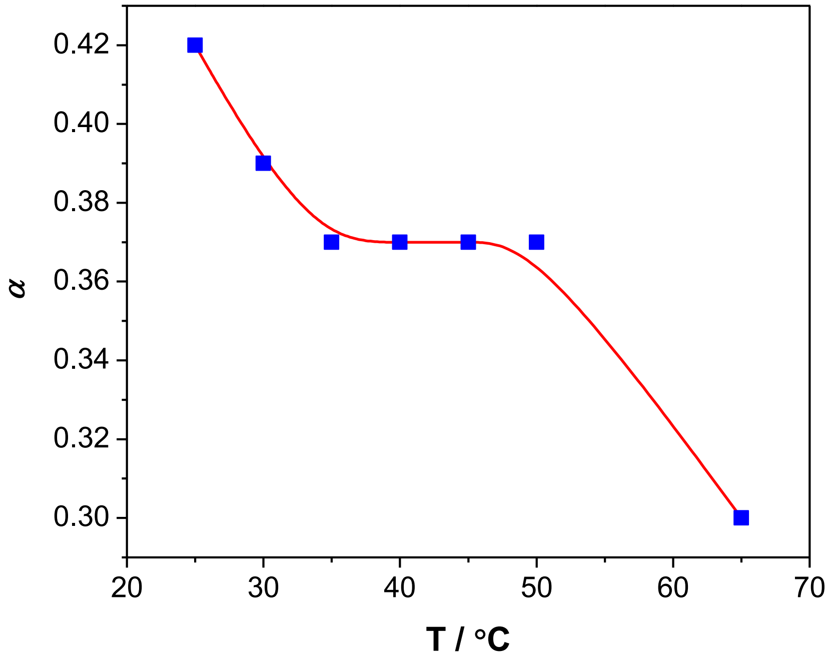


Figure 2b: Temperature effect on *α* of TBADS

Conductance in a typical solution generally depends upon mobility, number and ion sizes. The present decrease of κ with temperature (0.03M TBADS, Figure 3) can be understood in the light of the facts: a) both counterion (TBA^+) and headgroup will have certain degree of hydration which is expected to decrease on heating; b) this dehydration of counterion and headgroup causes effective charge neutralization c) due to these reasons the charge of the conducting species (counterion and headgroup) may neutralize with a concomitant conversion into nearly non-ionic species. It is already mentioned that quaternary counterions are less hydrated than inorganic counterions and the charge of the former is considered to be buried in a paraffin shell. This may facilitate quaternary counterion to interact with anionic micelle electrostatically and hydrophobically. Interestingly, such pseudo-nonionic micelles were proposed to explain the clouding behaviour of ionic surfactant system [74]. The above discussion seems sufficient to understand the peculiar behaviour (higher *Tm*, decrease in *α* and*κ*) of quaternary surfactants with respect to temperature.

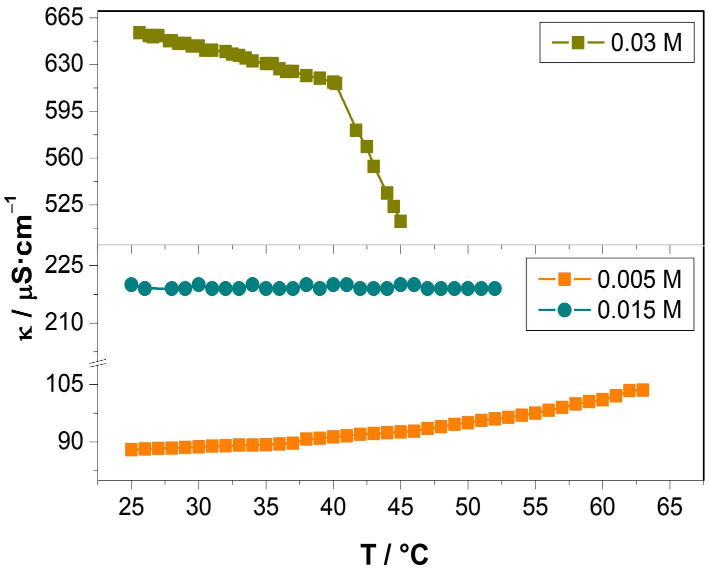


Figure 3: Variation of specific conductance (*κ) vs* temperature plot for TBADS at different concentrations.

3.2.3. Clouding phenomenon in anionic surfactant solution.

A perusal of CP data (Figure 4) indicates that CP follows the order: TBAMES>TBADS>TBADBS>TBPDS>TBPDBS. This order results from various combinations of counterion and alkyl head group part of the surfactant. Among the surfactants having TBA$^+$ counterion, TBAMES have higher CP than other surfactants of same class (TBADS or TBADBS). Looking at the structures (**scheme, chapter 2),** it is clear that TBAMES contains one ester group in addition to that of a sulfonate moiety in the head group. This extra ester group may form H-bond with water molecule owing to dipole-dipole interaction resulting in increased hydration and is responsible for higher CP. The CP data for TBADS are found in close agreement with the values given in literature [76]. CP for TBADBS was found lower than the corresponding values obtained with TBADS at different concentrations (Table 3). The lower CP values with TBADBS may be due to the presence of benzene ring in the dodecyl benzene sulfonate anion (DBS$^-$) that causes lengthening of hydrophobic chain as compared to TBADS. The structural difference is responsible for greater hydrophobic interactions between the DBS$^-$ and the alkyl chains of TBA^+. It has been reported that cmc of SDBS was found lower than SDS [154]. The same analogy can be drawn here and may be responsible for lower CP values with TBADBS (Table 3). Among the surfactants having TBP^+ counterion, the CP for TBPDS is found much lower than both TBADS and TBADBS. This may be due to the nature and bigger size of TBP^+ counterion due to which the surface dehydration is expected more. At equal concentrations of TBADS and TBPDS, faster saturation of micellar surface is expected with TBP^+ and thus more TBP^+ are left to facilitate the approach of various micelles close to each other resulting in lower CP. As [surfactant] increases, the number of TBA^+/ TBP^+ ions would increase and therefore the bridging (*vide supra*) of micelle is expected to facilitate clouding with a concomitant decrease in CP.

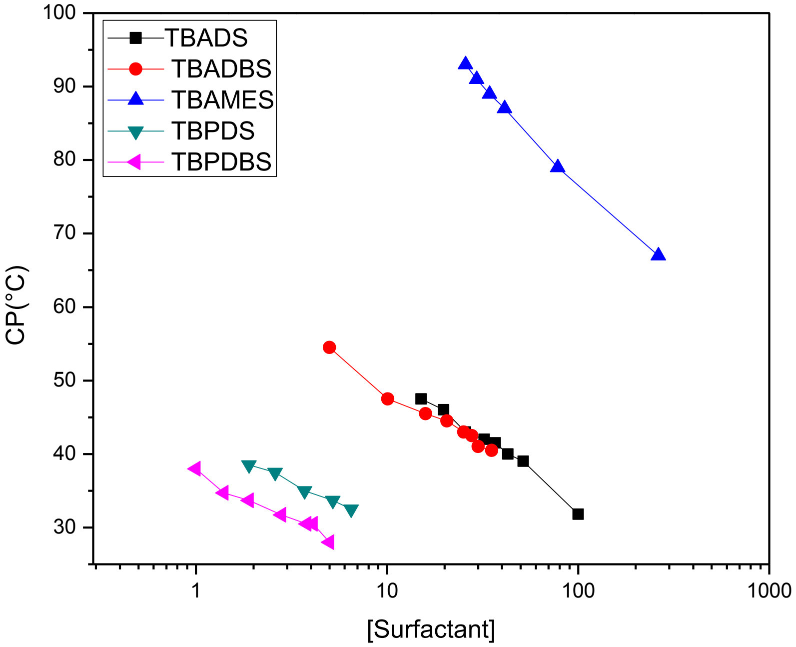


Figure 4: Variation in CP with surfactant concentrations

Generally, the non ionic surfactant solution at/or above CP separates into two isotropic liquid phases; one comprising of diluted surfactant solution, and the other as surfactant rich phase. The phase volume and distributed [surfactant] ratio in the two phases can be very high in such systems [155]. But for the present anionic surfactant systems showing clouding (and phase separation) on heating in a similar manner as non-ionic surfactants, a peculiar behaviour could be observed. Interestingly, it was visually observed that a turbid system on standing at CP, phase separates into two clear phases which on further heating gets cloudy again, which on standing at same temperature again separates into two isotropic liquid phases, now with the increased volume and [surfactant] in the surfactant rich phase (Figure 5). This is the reversible phenomenon. Thus, it is quite interesting to note that in present charged micellar solution the surfactant goes slowly in giant aggregates with increase in temperature beyond CP. To get the deeper insight for the obscure mechanism of CP, TBAMES is synthesized which due to increased hydration as discussed earlier gives clouding at higher temperature and at comparatively higher concentration. This provides enough temperature range to thoroughly study the clouding phenomenon.

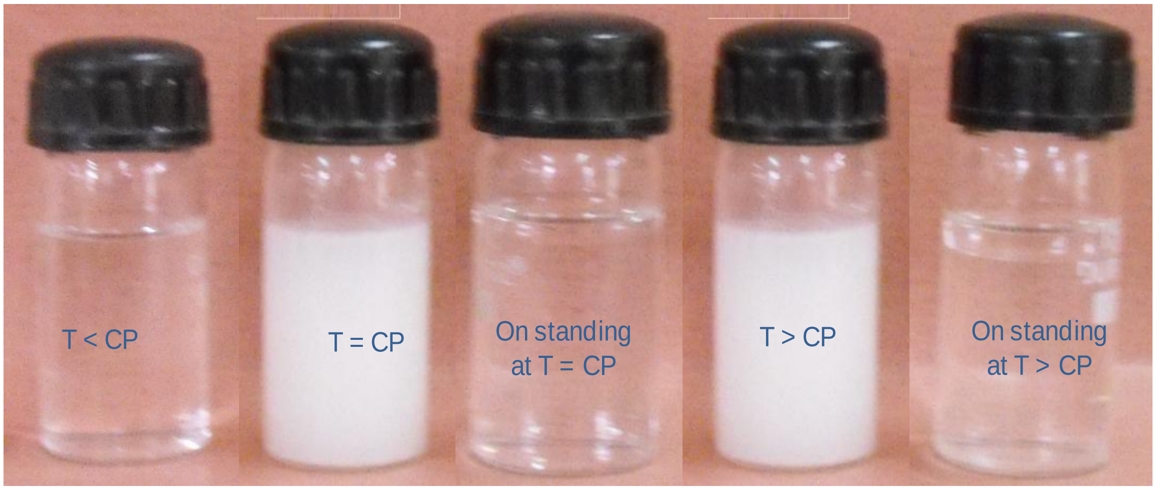


Figure 5: Variation of phase volumes at and beyond CP

It is observed that even at CP, the so called surfactant lean phase has sufficient fraction of individual micelles as observed by phase volume changes and concentration determination by tensiometry. The 0.1M TBADS solution on heating gives 0.023M in lean phase on separation at CP. Thus, the volume of one phase increases at the cost of other on standing at temperature beyond CP.

Table 3: CP data for anionic surfactants at different concentrations

TBADS		TBADBS		TBAMES		TBPDS		TBPDBS	
[TBADS]	CP	[TBADBS]	CP	[TBAMES]	CP	[TBPDS]	CP	[TBPDBS]	CP
10^3·M	°C	10^3·M	°C	10^3·M	°C	10^3·M	°C	10^3·M	°C
15.1	47.5	5.0	54.5	25.8	93.0	1.9	38.5	1.0	38.0
19.8	46.0	10.1	47.5	29.5	91.0	2.6	37.5	1.4	34.7
25.8	43.0	15.9	45.5	34.4	89.0	3.7	35.0	1.9	33.7
32.2	42.0	20.6	44.5	41.3	87.0	5.2	33.7	2.8	31.7
36.9	41.5	25.2	43.0	78.3	79.0	6.5	32.5	3.8	30.5
43.0	40.0	27.8	42.5	263.0	67.0			4.1	30.5
51.6	39.0	30.0	41.0					5.0	28.0
100.0	32.1	35.3	40.5						

3.2.3.1. Effect of inorganic counterion

Addition of salt can change the CP in either direction depending upon nature and concentration of the added salt. The CP data of TBADS and TBADBS in presence of salts $Ca(NO_3)_2$ and $Al(NO_3)_3$ are summarized in Table 4. Perusal of data indicates that the presence of salt counter ion increases and decreases the CP with continuous increase of [salt]. The initial increase may be due to exchange of monovalent TBA^+ counter ion with multivalent inorganic counter ion. In doing so the multivalent counter ion carries more water towards the micelle and hence needs higher temperature to observe CP. However, at higher [salt] a decrease in CP may be due to the fact that the above exchanged TBA^+ counter ion could be responsible for bridging of two or more micelles and hence facilitating clouding phenomenon and lowering of CP. Also, the water structure gets distrupted by the addition of inorganic electrolytes and hence promotes dehydration, the cause of decrease in CP in presence of higher [salts]. The similar salt effect on CP was reported earlier also with monovalent counter ions (e.g. Na^+) [99]. However, the increasing and decreasing effect on CP is observed at very low concentration of multivalent counter ions. This indicates that the charge of the added counter ion plays a significant role in observing the CP.

Table 4: CP data for 0.03M surfactants in presence of inorganic salts

TBADS				TBADBS			
$[Ca^{+2}]$	CP	$[Al^{+3}]$	CP	$[Ca^{+2}]$	CP	$[Al^{+3}]$	CP
10^3. M	°C	10^3. M	°C	10^3. M	°C	10^3. M	°C
4.5	42.5	1.3	36.1	0.3	39.5	0.05	40.5
7.2	44.0	1.5	36.5	0.47	40.3	0.1	40.4
10.2	44.8	2.0	37.0	0.52	39.8	0.2	39.2
15.3	45.5	2.7	35.5	1.0	33.5	0.3	38.6
20.4	43.5	3.2	33.9	1.5	30.5	0.42	38.1
24.5	42.0	4.0	28.8	2.0	24.5	0.5	37.5
30.6	40.0			2.4	20.5		
40.8	38.5						
50.0	37.0						

3.2.3.2. Effect of drug intermediate

CP variations of two representative anionic surfactants (TBADBS and TBPDS) with the addition of AHC are depicted in Figure 6. This addition causes a decrease in CP with the increase in the concentration of AHC. This may be due to the fact that AHC is a less polar organic compound with hydrophobic character. This character may facilitate micellar solubilisation due to hydrophobic interactions. Micelles are well known for presenting unique structural aspects consisting of a non-polar inner core and a polar outer surface. This structure allows micellar aggregates to enhance the solubility of hydrophobic materials and to modify environmental features such as micro-viscosity and micro-polarity. Therefore, the effect of addition of organic compounds depends on how they change the water structure and micellar structure. Here, this CP variation seems due to change in structure of micellar interior. Similar decrease in CP of anionic surfactant in presence of higher chain length alcohols/amines was explained in the light of hydrophobic interactions and micellar interior environmental changes [99]. One more advantage present CP variation has is that CP is moving towards physiological temperature (~ 37 °C).

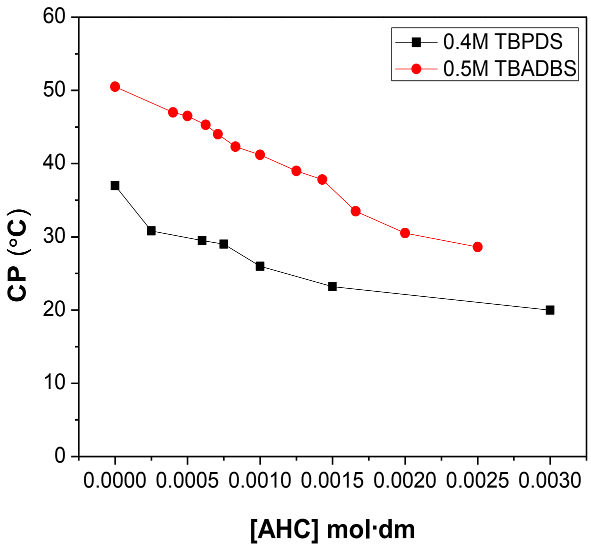


Figure 6: Variation of CP with concentration of AHC in TBADBS and TBPDS solutions.

3.2.4. Thermodynamics

The clouding in a surfactant solution can be considered as the solubility limit at or above which phase separation takes place. It is closely related to the way in which surfactant-water interactions occur. It is also relevant to evaluate and analyze the influence of additives. The CP shift may be explained as the resultant of attenuated H-bonding both in presence or absence of salt creating marked alteration in the hydration layer. The clouded fraction releases their solvated water and yields two phases.

The estimation of energetics of clouding process, standard Gibb's free energy change (ΔG°_{c}), standard enthalpy change (ΔH°_{c}) and standard entropy change (ΔS°_{c}), would offer an additional insight to energetically controlled clouding phenomenon. The standard free energy change (ΔG°_{c}) for clouding can be computed by the relation [156].

$$\Delta G^{\circ}_{c} = RT\ln x_{s} \tag{1}$$

where x_s is the mole fraction of the surfactant at which clouding species passes from the soluble state to an insoluble state, R is the gas constant (8.314 $J{\cdot}K^{-1}mol^{-1}$); and T is the clouding temperature.

The standard enthalpy change of clouding, ΔH°_{c} can be calculated from the slope of the $\Delta G^{\circ}_{c}/T$ versus $1/T$ plot

$$\Delta H^{\circ}_{c} = \partial\,(\Delta G^{\circ}_{c}/T)/\partial\,(1/T) \tag{2}$$

From relation (1) and (2) we can estimate the value of standard entropy change (ΔS°_{c}) using the relation

$$(\Delta S^{\circ}_{c}) = (\Delta H^{\circ}_{c}) - (\Delta G^{\circ}_{c})/T \tag{3}$$

Thus, the thermodynamic parameters (ΔG°_{c}, ΔH°_{c} and ΔS°_{c}) are computed using CP values. Tables 5and 6 contain compiled thermodynamic data (ΔG°_{c}, ΔH°_{c} and ΔS°_{c}) for TBA^{+} surfactants surfactants (TBADS, TBADBS, TBAMES) and TBP^{+} surfactants (TBPDS and TBPDBS) respectively. The ΔG°_{c} data for all TBA^{+} surfactants show close agreement with the literature values. [102]. The thermodynamic parameters presented in

Tables 5 and 6 show that clouding process is spontaneous and mechanism of clouding seems similar with all the surfactants. The endothermic process is associated with a positive value of change in enthalpy. Similar endothermic process was reported for non-ionic amphiphiles [157,158] associated with +ve ΔH°_{c} values. By using the values of ΔG°_{c} and, ΔH°_{c}, ΔS°_{c} are obtained using equation 3 (*supravide*). Figure 7 shows the representative plot of $\Delta G^{\circ}_{c}/T$ vs $1/T$, for TBADS, to calculate ΔH°_{c} from the slope. In the present clouding process, dehydration of the head group region takes place initially with the absorption of heat followed by linking (bridging) of the dehydrated micelles which involves release of heat. For the quaternary surfactants, dehydration process contributes more than the linking process, responsible for positive ΔH°_{c}. The solvation and micellar linking are augmenting the process of clouding. Increasing concentration should favour increasing molecular association. The higher positive ΔH°_{c} value for TBADBS than TBADS shows that dehydration process is more favourable with TBADBS. This is expected from molecular structure of TBADBS (**scheme, chapter 2**) as it contains an extra phenyl ring in the chain which can contribute towards hydrophobic interactions with TBA^{+}. These factors will favour dehydration process and are responsible for more positive ΔH°_{c} . However; TBAMES has less ΔH°_{c} value (92 $kJ.mol^{-1}$, Table 5) which can be explained on the basis of similar structural arguments. The TBAMES contains an ester group together with extra methylene groups which can affect the dehydration process due to hydrophilic nature of the ester group (that can form H-bonding with water). This is also evident from the higher CP values obtained for TBAMES (Table 3). TBPDS and TBPDBS contain the same non polar tail but different counter ions than TBADS and TBADBS. Thus, distinct roles of counterion and alkyl head group could be observed. The ΔH°_{c} for the surfactants show that the nature of counterion (TBP^{+}/ TBA^{+}) has a role to play in dehydration process. The size of TBP^{+} is expected more than TBA^{+} *(supravide)* which can assist in dehydration process resulting in more positive ΔH°_{c} values. However, the process is weakly dependent on ΔS°_{c} values as they are nearly same for all the surfactants. This indicates that micelles are fairly independent entity though they are part of a loose cluster.

Table 5: Comparision of Thermodynamic Parameters for Clouding in TBADS, TBADBS and TBAMES at different concentrations

[surfactant]	**TBADS**			**TBADBS**			**TBAMES**		
	ΔG°_c	ΔH°_c	ΔS°_c	ΔG°_c	ΔH°_c	ΔS°_c	ΔG°_c	ΔH°_c	ΔS°_c
	kJ.mol^{-1}	**kJ.mol^{-1}**	**J.K^{-1}mol^{-1}**	**kJ.mol^{-1}**	**kJ.mol^{-1}**	**J.K^{-1}mol^{-1}**	**kJ.mol^{-1}**	**kJ.mol^{-1}**	**J.K^{-1}mol^{-1}**
15.1	-21.9	116.7	432	-	122.5	-	-	92.3	-
15.9	-		-	-21.6		452	-		-
20.0	-21.1		432	-		-	-		-
20.6	-		-	-20.9		451	-		-
25.2	-		-	-20.2		452	-		-
25.8	-20.2		433	-		-	-23.4		316
27.8	-		-	-19.9		451	-		-
29.5	-		-	-		-	-22.8		316
30.0	-		-	-19.6		453	-		-
32.2	-19.5		432	-		-	-		-
34.4	-		-	-		-	-22.2		316
35.3	-		-	-19.2		452	-		-
36.9	-19.1		432	-		-	-		-
41.3	-		-	-		-	-21.6		316
43.0	-18.6		432	-		-	-		-
51.6	-18.1		432	-		-	-		-
78.3	-		-	-		-	-19.2		317
263.0	-		-	-		-	-15.1		316

Table 6: Thermodynamic Parameters for Clouding in TBPDS and TBPDBS at different Concentrations

[surfactant]	TBPDS			TBPDBS		
	ΔG°_{c}	ΔH°_{c}	ΔS°_{c}	ΔG°_{c}	ΔH°_{c}	ΔS°_{c}
	$kJ.mol^{-1}$	$kJ.mol^{-1}$	$J.K^{-1}mol^{-1}$	$kJ.mol^{-1}$	$kJ.mol^{-1}$	$J.K^{-1}mol^{-1}$
1.0	-	-	-	-28.2	139.1	538
1.4	-	-	-	-27.1	-	540
1.9	-26.6	155.8	585	-26.2	-	539
2.6	-25.7	-	585	-	-	-
2.8	-	-	-	-25.1	-	539
3.7	-24.6	-	586	-	-	-
3.8	-	-	-	-24.2	-	538
4.1	-	-	-	-24.0	-	538
5.0	-	-	-	-23.3	-	540
5.2	-23.6	-	585	-	-	-
6.5	-22.9	-	586	-	-	-

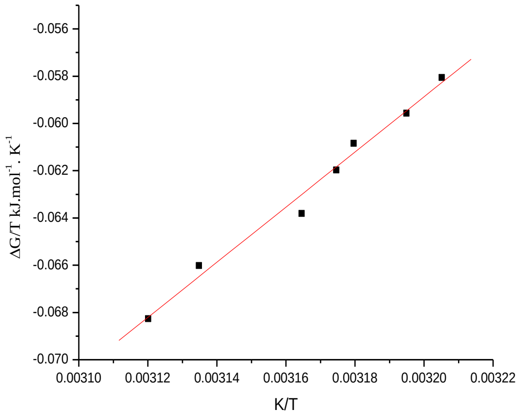


Figure 7: ΔG°_{c} /T vs 1/T plot of TBADS to derive the enthalpy change of clouding

The thermodynamic data (Tables 7-10) were also collected with two TBA surfactants (TBADS and TBADBS) in presence of $Ca(NO_3)_2$ and $Al(NO_3)_3$. The data reveal that for both the salts ΔG°_{c} is negative. However, ΔH°_{c} and ΔS°_{c} are found to be negative or positive depending upon [salt]. At lower [salt] all thermodynamic parameters are found negative. While at higher [salt], only ΔG°_{c} is negative. Figure 8 shows the representative plot of $\Delta G^{\circ}_{c}/T$ vs $1/T$, for TBADS, to calculate ΔH°_{c} from the slope. This indicates that at lower [salt], the micellar structures are more ordered and ΔH°_{c} values are in similar range as were found for non ionic amphiphiles [155,156]. This also suggests that clouding phenomenon in presence of salts is an exothermic process which changes to endothermic at higher [salt]. Moreover, ΔS°_{c} value suggests that micelles are more ordered initially in presence of Al^{+3}. This may be due to the presence of higher charge on Al^{+3} which may replace three TBA^{+} ions from the micelle-water interface. However, it seems that disordering increases at higher [salt], as more TBA^{+} ions are available to form loose bridges of the micelles. This indeed reflects from data given in Tables 7 and 8. Tables 9 and 10 contain thermodynamic data of TBADBS in presence of $Ca\ (NO_3)_2$ and $Al\ (NO_3)_3$. The behaviour of $Ca\ (NO_3)_2$ and $Al\ (NO_3)_3$ are similar with a difference that, with $Ca\ (NO_3)_2$ system is also showing negative ΔH°_{c} and ΔS°_{c} at higher [salt]. The similar behaviour could have been observed with $Al\ (NO_3)_3$. But poor solubility of $Al(NO_3)_3$ in TBADBS micellar solution hampered the CP determination at higher $[Al(NO_3)_3]$.

However, ΔH°_{c} and ΔS°_{c} are higher for $Al(NO_3)_3$ than the $Ca(NO_3)_2$ case till $Al(NO_3)_3$ was added. This shows that with $Al(NO_3)_3$ the process is mainly endothermic.

Table 7: Thermodynamic Parameters for Clouding in 0.03M TBADS Aqueous Solution in Presence of different [$Ca(NO_3)_2$]

$[Ca^{+2}]$ 10^3.M	ΔG°_{c} kJ.mol^{-1}	ΔH°_{c} kJ.mol^{-1}	ΔS°_{c} kJ.K^{-}
4.50	-24.7	-333.2	-0.978
7.20	-23.6		-0.977
10.20	-22.7		-0.977
15.30	-21.7	113.8	0.423
20.40	-20.8		0.423
24.48	-20.2		0.424
30.60	-19.5		0.424
40.80	-18.7		0.423
50.00	-18.1		0.423

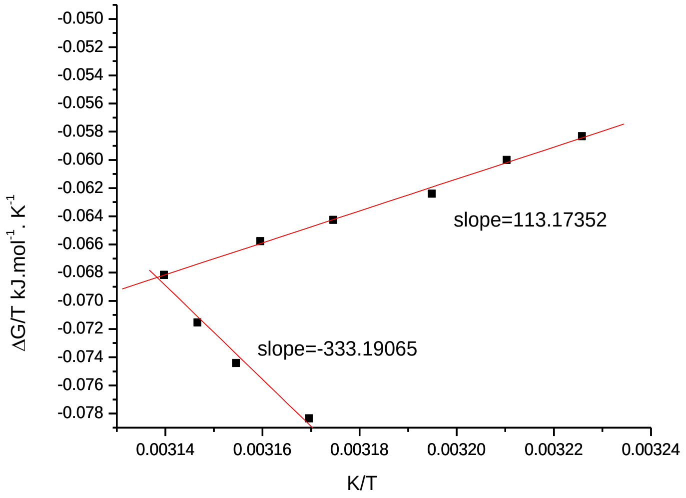


Figure 8: ΔG°_{c} /T vs 1/T plot of TBADS+$CaNO_3$ to derive the enthalpy change of clouding

Table 8: Thermodynamic Parameters for Clouding in 0.03M TBADS Aqueous Solution in Presence of different [$Al(NO_3)_3$]

$[Al^{+3}]$ 10^3.M	ΔG°_{c} kJ.mol^{-1}	ΔH°_{c} kJ.mol^{-1}	ΔS°_{c} kJ.K^{-1}mol^{-}
1.33	-27.3	-367.3	-1.10
1.45	-27.2		-1.10
2.00	-26.4		-1.10
2.66	-25.5	59.6	0.28
3.20	-24.9		0.28
4.00	-23.9		0.28

Table 9: Thermodynamic Parameters for Clouding in 0.03M TBADBS Aqueous Solution in Presence of different [Ca(NO$_3$)$_2$]

[Ca^{+2}] 10^3.M	ΔG°_c kJ.mol^{-1}	ΔH°_c kJ.mol^{-1}	ΔS°_c kJ.K^{-1}mol^{-1}
0.30	-31.6	-432.3	-1.28
0.33	-31.3		-1.28
0.47	-30.4		-1.28
0.52	-30.1		-1.29
1.00	-27.9	59.4	0.28
1.50	-26.6		0.28
2.00	-25.3		0.28
2.40	-24.6		0.29

Table 10: Thermodynamic Parameters for Clouding in 0.03M TBADBS Aqueous Solution in Presence of different [Al(NO$_3$)$_3$]

[Al^{+3}] 10^3.M	ΔG°_c kJ.mol^{-1}	ΔH°_c kJ.mol^{-1}	ΔS°_c kJ.K^{-1}mol^{-1}
0.05	-36.3	464.0	1.59
0.10	-34.5		1.59
0.21	-32.4		1.59
0.31	-31.3		1.59
0.42	-30.5		1.59
0.50	-30.0		1.60

The thermodynamic parameters of TBADBS (0.5 M) and TBPDS (0.4M) in presence of AHC are given in Table 11. The data revealed that for both the surfactants ΔG°_{c} is negative. However, ΔH°_{c} and ΔS°_{c} are both positive in the concentration range of AHC studied. This suggests that clouding phenomenon in the presence of AHC is an exothermic process. Moreover, the ΔS°_{c} values suggest that micelles are disordered in presence of above intermediate. This dis-ordering is expected more at higher concentration of additive. This interpretation may find support from the fact that both butyl chains (of the counterions) and AHC may compete for the similar solubilisation site in the micellar interior. Therefore, it is expected that a few above counterion butyl chains could be excluded from the micellar interior towards the micellar surface. Therefore, such chains are also available for linking micelles (loose bridges) and facilitating cluster formation. If this is correct, CP should be observed at lower temperature with the AHC. This indeed was observed in Figure 6. However, the thermodynamic parameters in the presence of intermediate are different for two surfactants considered here (TBADBS and TBPDS). As mentioned earlier (scheme, Chapter 2), these two surfactants are having different counter ions and alkyl head groups and, therefore, will interact in a different ways to AHC and will influence the CP and thermodynamic parameters.

Table 11: Thermodynamic Parameters for Clouding in 0.5M TBADBS and 0.4M TBPDS at different Drug concentration

	0.5M TBADBS			0.4M TBPDS		
[AHC]	ΔG°_c	ΔH°_c	ΔS°_c	ΔG°_c	ΔH°_c	ΔS°_c
mM	kJ.mol^{-1}	kJ.mol^{-1}	J.K^{-1}mol^{-1}	kJ.mol^{-1}	kJ.mol^{-1}	J.K^{-1}mol^{-1}
0.25	-	-	-	-31.1	142.2	570
0.4	-31.5	66.5	306	-	-	-
0.5	-30.9	-	305	-	-	-
0.6	-	-	-	-28.8	-	565
0.63	-30.2	-	304	-	-	-
0.7	-29.7	-	303	-	-	-
0.75	-	-	-	-28.2	-	564
0.83	-29.1	-	303	-	-	-
1.0	-28.5	-	302	-27.2	-	566
1.25	-27.8	-	302	-	-	-
1.43	-27.3	-	302	-	-	-
1.5	-	-	-	-25.9	-	567
1.66	-26.5	-	304	-	-	-
2.0	-25.8	-	304	-	-	-
2.5	-25.1		304	-	-	-
3.0	-	-	-	-23.9	-	567

3.3. Conclusions

Micellization process of quaternary surfactants facilitate initially with heating followed by usual temperature effect reported for conventional anionic surfactants. Conductivity variation with temperature shows [TBADS] dependence. CP can be tuned with [surfactant], nature of salt and [salt]. Clouding phenomenon in the present anionic surfactants is a spontaneous process both in presence or absence of inorganic salts. When a particular temperature is achieved, phase-separation involves a distinct change in the interaction forces between the micelles and water with temperature. As the temperature increases, the repulsive forces resulting from the hydrated micelles decrease due to loss of H-bonding whereas the attractive forces (van der Waals and hydrophobic interactions) become increasingly important. This increase in micellar interactions derives the removal of a more hydrophobic entity from water resulting in the clouding and the phase separation. Both $\Delta H^{\circ}_{\mathrm{c}}$ and $\Delta S^{\circ}_{\mathrm{c}}$ are positive and negative depending upon the added [salt] contributing to the net interaction between micelles. The clouding behaviour of these surfactants, in binary aqueous solution (surfactant + water), is an endothermic process. However, presence of salt makes the process endo- or exothermic depending upon the [salt] as well as the charge on the salt counter ion. It is also observed that at lower [salt], the micellar structures are more ordered (-ve $\Delta S^{\circ}_{\mathrm{c}}$) whereas the entropy cost of ordering water around the bulk counterion becomes untenable on increasing [salt] tending towards the disordered (+ve $\Delta S^{\circ}_{\mathrm{c}}$) system.