3.1 Introduction

Unusual properties of surfactants continue to attract the interest of scientists/technologists and have inspired them to design new surfactant systems with intriguing solution behavior [1-3]. Amphiphilicity of surfactants has extensively been exploited in the pre-concentration of metal ions, solvent extraction, mobility of drugs in aqueous media, probing of biological systems, templating of nanomaterials etc. The relation between solution behavior and heating observed in ionic surfactants is found different than their nonionic counterparts. The clouding phenomenon occurs in ionic surfactant solutions is not common, which may be due to the presence of coulombic repulsions between ionic micelles. Recently, research activities have been directed towards studying this, relatively, uncommon phenomenon with ionic surfactant solutions [4-9]. Most of the work on clouding in aqueous anionic surfactant systems has been made when tetra-*n*-alkylammonium counter ion (TAA^+) was added or was a counter ion of the surface active species [6,7,9-12].

Various phenomena in surface and colloid science that involve counterions show pronounced ion specificity. More than a century back, Franz Hofmeister concluded that the effectiveness of the salts in denaturing proteins increases with their water structuring ability [13]. Since the report of Hofmeister, it is now common to discuss about ion series instead of series of salts. In a recent report [14], a comprehensive attempt has been made to establish a Hofmeister like series for surfactant headgroups. The proposed series was based on numerous experimental observations. A simple “law of matching water affinities" has been proposed by Collins et al. [15]. This law correlates the tendency of association of oppositely charged ions in aqueous solution. As mentioned above, the clouding phenomenon in ionic surfactant solutions is also the consequence of the interactions of oppositely charged counterions and amphiphilic species [4-12, 16-18].

Some aqueous surfactant systems are spontaneously converted from micelles to a lamellar array in the presence of higher salt content. On a molecular level, this change in morphology is facilitated by an increased counterion binding and dehydration of

the headgroups and counterions. The dehydration of the headgroup is also important for the occurrence of clouding phenomenon in aqueous surfactant solutions *(vide supra)* [1].

Present study is designed to test the applicability of Hofmeister like series proposed for the headgroups [14] in the context of clouding in ionic surfactant solutions. Hence we have added TBAB to various surfactant solutions and CP measurements have been carried out. Few cmc and micelle size measurements are also performed using conductometry, surface tensiometry and DLS, respectively. The surfactants chosen for the purpose are: SDS, SDBS, MES and PES. This study may provide an insight regarding the headgroup specificity of clouding phenomenon.

3.2 Results and Discussion

3.2.1 Clouding in an Anionic surfactant + TBAB system

All the surfactant solutions studied here do not show clouding phenomenon in aqueous solution without TBAB. The presence of TBAB in the solution is found responsible for the clouding phenomenon. The TBA^+ counterion consists of four butyl chains in addition to the positive charge on the nitrogen atom. TBA^+ ions are essentially less hydrated and amphiphilic in nature. In these ions the positive charge is buried in a paraffin shell. As a rule of thumb, counterions having less affinity to water lead to higher binding to the anionic micelles. Hence, the TBA^+ can interact with anionic micellar surface electrostatically as well as hydrophobically resulting in mixed micelles. Based on polarizable continuum solvent model and molecular dynamics simulations relative cation-anion association free energies ($\Delta\Delta G$) were reported in the past [14]. The values of $\Delta\Delta G$ connected with replacing K^+ by Na^+ in a contact ion pair with acetate (-2.50 kcal / mol) or methyl sulfate (+ 0.37 kcal / mol) or methyl sulfonate (~ 4-5 kcal / mol) anion. These values suggest that acetate would prefer Na^+ over K^+ while methyl sulfonate will prefer K^+ over Na^+. It is known that K^+ is less hydrated than Na^+. The same analogy can be extended for TBA^+ (less hydrated than K^+). Therefore, TBA^+ is expected to form close ion-pair with alkyl sulfonate than alkyl carboxylate. Hence, organic counterion should strongly interact

with the soft sulfate/sulfonate headgroup resulting in an ion-pair close to an uncharged dipolar headgroup [14]. These propositions are used to interpret CP and DLS data. The formation of hydrophobic aggregates is then expected, which can have poor solubility in the bulk solution. Formation of two morphologies in the aqueous anionic surfactant systems seems the root cause of clouding and phase separation. For emulsions, Jansson et al. [21] argued that attractive hydrophobic interactions between the droplets are facilitated with the adsorption of such hydrophobic counterions. With the increase of temperature the entropy cost of ordering water around butyl chains of TBA^+ becomes untenable (dehydration of TBA^+). Then TBA^+ will interact more strongly with anionic headgroup attached to an alkyl chain at higher temperature. Such ion-pairs (hydrophobic entity) will be much less hydrated than separate ions and headgroups. The hydration of each ion-pair will depend upon the nature of headgroup to which the TBA^+ is attached (carboxylate or sulfonate). The resulting energetic effect (at higher temperature) due to the loss of hydrogen bonding drives the removal of a more hydrophobic entity from water [22]. The discussion may find support from the fact that clouding in anionic surfactant solution appears mostly where TBA^+(less hydrated) was added or was part of the surfactant molecule. It was noted that less TPeAB is required to show clouding phenomenon than TBAB when present with SDS [10]. However, clouding phenomenon is also reported with unsymmetrical organic counterions [23]. Hence, hydophobicity of the counterion seems more important than the symmetrical / unsymmetrical characteristic of counterion to show clouding. In contrast, inorganic counterion addition such as Na^+ or K^+ (more hydrated counterion) does not show clouding with SDS which confirms the proposition that the interaction of counterion and headgroup depends on the matching of water affinities [14,17].

3.2.2 CP Phenomenon for SDS/SDBS + TBAB system

The CP data of surfactant-TBAB combinations at different surfactant concentrations (henceforth will be used as [surfactant]) and TBAB concentrations (used as [TBAB]) are summarized in Table 1. The perusal of data demonstrates that for SDS+TBAB and SDBS+TBAB, CP values are lower for latter combination though the same

concentrations of SDS or SDBS (*e.g.* 15 mM) and TBAB (*e.g.* 35 mM) are considered. This is true even for other concentration combinations. The lower CP with SDBS may be due to combined effect of the presence of benzene ring (increased chain length) and nature of headgroup (sulfonate group). It is known that substituents on aromatic rings may modify the charge density in the ring and the interaction with counterion. Therefore, the softness (less hydrated) of sulfonate headgroup may partly be due to the presence of phenyl ring in SDBS.

Table 1 CP data on SDS/SDBS + TBAB aqueous system

[surfactant] mM	[TBAB] mM	CP ($^{\circ}$C)			
		SDS	SDBS	MES	PES
5.0	10.5	46.2	43.8	No CP	No CP
	17.5	40.0	38.2	No CP	No CP
	35.0	34.0	24.0	76.8	75.0
	52.6	31.8	14.0	70.2	69.2
10.0	10.5	54.2	49.8	No CP	No CP
	17.5	43.0	39.0	No CP	No CP
	35.0	35.8	25.0	78.0	75.0
	52.6	33.0	14.0	71.0	69.2
15.0	10.5	70.2	62.2	No CP	No CP
	17.5	46.0	41.8	No CP	No CP
	35.0	36.0	25.0	82.2	79.0
	52.6	32.0	15.0	72.0	70.0
	100.0	28.0	-	60.0	59.6

The *cmc* data (Table 2) for the two surfactants (SDS and SDBS) also show similar trend as for CP. The CP behavior could be understood in view of ordering of surfactant headgroups regarding their capabilities to form close ion pairs with counterions [14]. It has been mentioned here that alkyl sulfonate is a stronger chaotrope (less hydrated) than alkylsulfate (more hydrated). Therefore, sulfonate headgroup may interact strongly (electrostatically) with TBA^+ than sulfate. Hence, sulfonate group will form close ion-pair with TBA^+ counterions with a simultaneous increased dehydration of SDBS micellar surface and a lower CP than in case of SDS. It was indeed observed (Table 1).

Table 2*cmc* and α for different surfactant systems at 30 $^{\circ}$C.

Surfactant system	*cmc* (mM)		α
	Conductometry	Tensiometry	
SDS	7.9	8.32 [a]	0.36
SDBS	2.30	2.00 ± 0.2 [b]	0.80
MES	3.4	3.17 [c]	0.48
PES	0.65	0.59 [d]	0.62
SDS+15 mM TBAB	0.16	0.165	0.42
SDBS+15 mM TBAB	0.24	-	0.69
MES+15 mM TBAB	0.146	0.14	0.55
PES+15 mM TBAB	0.018	0.017	0.56

[a] ref. [11], [b]Colloids Surf. A, 2006, 274, 91-99, [c] Langmuir, 2000, 16, 3777, [d] ref.[20]

It has also been reported that presence of TBA^+ counterion fails to produce clouding with carboxylate headgroup [24]. This could be understood in the light of the fact that carboxylate headgroup is hard (cosmotrope or highly hydrated) while TBA^+ is soft (chaotrope or less hydrated) and a mismatch of water affinities with a concomitant effect on phase behavior (no clouding). These observations fit into the ordering of

headgroups: carboxylate, sulfate, sulfonate [14]. Therefore, clouding phenomenon also follows Hofmeister like series of surfactant headgroups and broadens the spectrum of the prediction for other phenomena of surface and colloid science. However, the above ordering is purely arbitrary and needs further experimentation. Similar to ionic surfactants, various amphiphilic drugs show clouding phenomenon [25]. Therefore, conditions leading to clouding from ionic supramolecular systems are of interest both theoretical and practical point of view [26,27]. The extraction of the organic pollutants from environmental solid samples was reported using the acid induced coacervation (phase separation) of alkyl sulfates, sulfonates and sulfosuccinates [28].

3.2.3 CP Phenomenon in MES/PES + TBAB System

Table 1 also summarizes the CP data of other two surfactants (MES and PES) with TBAB. Perusal of CP data indicates that higher [TBAB] is required to observe CP with MES or PES. Further, CP values are higher for MES and PES than observed with SDS or SDBS. It has been discussed in previous paragraph that sulfonate headgroup is softer than sulfate headgroup. However, the same sulfonate is also present in MES or PES. But CP data are not satisfying the earlier proposition (Figure 1). The key lies in the structure of surfactant (MES or PES) which contains ester group near the alkyl sulfonate headgroup. Presence of this ester group can change the water affinity characteristics of alkyl sulfonate headgroup with a simultaneous change in its characteristics from chaotrope to cosmotrope. It is clearly seen from the CP data given in Table 1. The observation suggests that a softer headgroup can also be changed to harder one owing to the structure of chemical species present near it. If we compare the behavior of MES and PES (both have same headgroup), it is seen that CP values are lower for PES than MES. PES has two methylene groups extra than MES. Due to the additional hydrophobicity of alkyl chain part, the PES has lower CP than MES for the same surfactant and TBAB concentrations. However, it has been reported that no clouding was observed in TBA dodecanoate (harder headgroup) or in TBAB + NaOA [29,30]. Furthermore, a gel phase and phase separation was observed with TBA carboxylate with higher alkyl tail length [24,31]. These observations are

parallel to what we observed in the present study. This could be a good example of structure-property relationship [32,33].

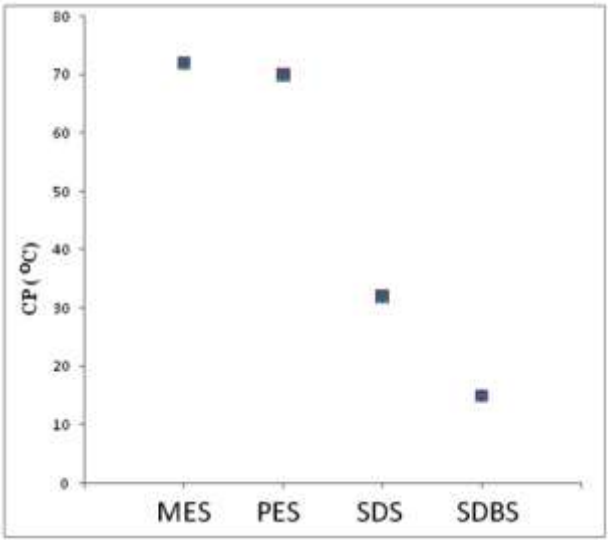

Figure 1: Cloud point (°C) values for 15 mM Surfactant + 52.6 mM TBAB.

When we compared CP data of all the surfactants and their CMCs it can be seen that CMC is lower for PES (Table 2), while CP was lower in the case of SDBS (+TBAB). This is due to the fact that *cmc* values are determined by hydrophobic alkyl chain (present in PES) while CP is decided both by the hydration (water affinity) of the headgroup and the alkyl chain. Data allow to propose that influence of the nature of headgroup contributes predominantly in deciding the final CP. However, the role of adjacent group (benzene ring or ester) near the headgroup has a role to play.

3.2.4 Morphology of Surfactant + TBAB Aqueous System

Compared to inorganic counterions, TBA^+ counterion has been reported to be more efficient in promoting micellar growth and morphological transitions [34,35]. However, the most anionic surfactant systems containing such counterions show precipitation or CP behavior [10]. Micellar growth in anionic surfactant solutions is relatively less documented, though it is believed to be more useful in enhanced oil recovery [36]. The morphological changes, accompanying the clouding phenomenon,

are investigated by determining aggregate size using DLS measurements. For this purpose, aqueous systems containing 15 mM surfactant + 100 mM TBAB have been chosen. 15 mM SDBS + 100 mM TBAB system has CP about 15 $^{\circ}$C and hence not been considered for the study. The study was restricted to the temperature below the CP or at CP. DLS data (Figure 2 a-f) indicate that micellar size increases with increase in temperature. In Figure 2a micelle diameters ~ 2 nm to 9 – 13 nm (bimodal distribution) were generally found at 25 $^{\circ}$C. However, Figure 2c shows a grown micellar distribution at about 40 nm appeared apart from 9 – 13 nm distribution (as in Figure 2a) at higher temperature (27 $^{\circ}$C). The similar trend is observed at further higher temperature (27.8 $^{\circ}$C, Figure 2e) where 40 nm distributions shown a remarkable growth (230 – 454 nm distribution) while 9 – 13 nm distribution shown a insignificant change (9 – 15 nm). This indicates that two populations are present in the sample out of which one of the populations (larger one) shown significant size change (increase in diameter) with increase in temperature. However, at CP (Figure 2f) a single population of comparatively very large size is obtained. It may be mentioned here that the sample composition kept constant throughout the temperature change. This shows that sample components (SDS and TBAB) redistribute with increase in temperature. One may expect that the amount of SDS in the larger aggregates increases with increase in temperature. Further, a similar bimodal distribution has been observed with other surfactant-TBAB combinations (Figures 3 and 4). In a separate study, by using NMR, it has been confirmed that two types of micellar aggregates are present when anionic micellar solution was heated towards CP. A detailed discussion on formation of two morphologies can be found in a recent study [9]. Micellar growth can be understood in the light of the fact that the TBA^{+} possesses four short hydrocarbon chain with a symmetrical structure. The geometric restriction makes it infeasible for all four chains to penetrate into the micellar core. Generally, two directions may be chosen for bending the butyl chains: one is toward the water phase and the other two penetrate the micellar core [37]. The bending of the butyl chains will decrease the trans conformation and increase the gauche conformations of higher energy. We call this enhanced energy, due to the bending of hydrophobic chains at the micellar surface conformation energy of the micellar

surface layer. The endothermic nature of the micellar growth of our system may be interpreted as due to the fact that the contribution of the conformation energy of the micellar surface layer is larger than the contribution of hydrophobic enthalpy brought about from the shrinking of the micellar core-water interface (on heating).When the micellar surface layer is more crowded with TBA^+ the degree of bending of the butyl chains in the core process should be larger, leading to a higher conformation energy of the micellar surface layer. Consequently, the micellar size should grow more rapidly (Figures 2 – 4) at or near the CP (Table 1). The idea of larger morphology in the presence of TBA^+ counterion may find support from the fact that R_p [38] increases in the presence of various counterions due to a decrease in the value of a_0. The formation of various surfactant microstructures in aqueous salt solutions has been observed and explained in the light of an increase in R_p [17, 39, 40]. The temperature increase causes loss of hydrogen bonding [22] which drives the growth of micelle. In the past, various structures (uni- and multilamellar vesicles, flat aggregates, or bilayer fragment) were assigned for the bigger morphology [17, 40, 41]. With increase in temperature the data (Figures 2-4) clearly demonstrate that softness of headgroup works well even for micellar growth (SDS ~ PES > MES) in presence of softer counterion (TBA^+).

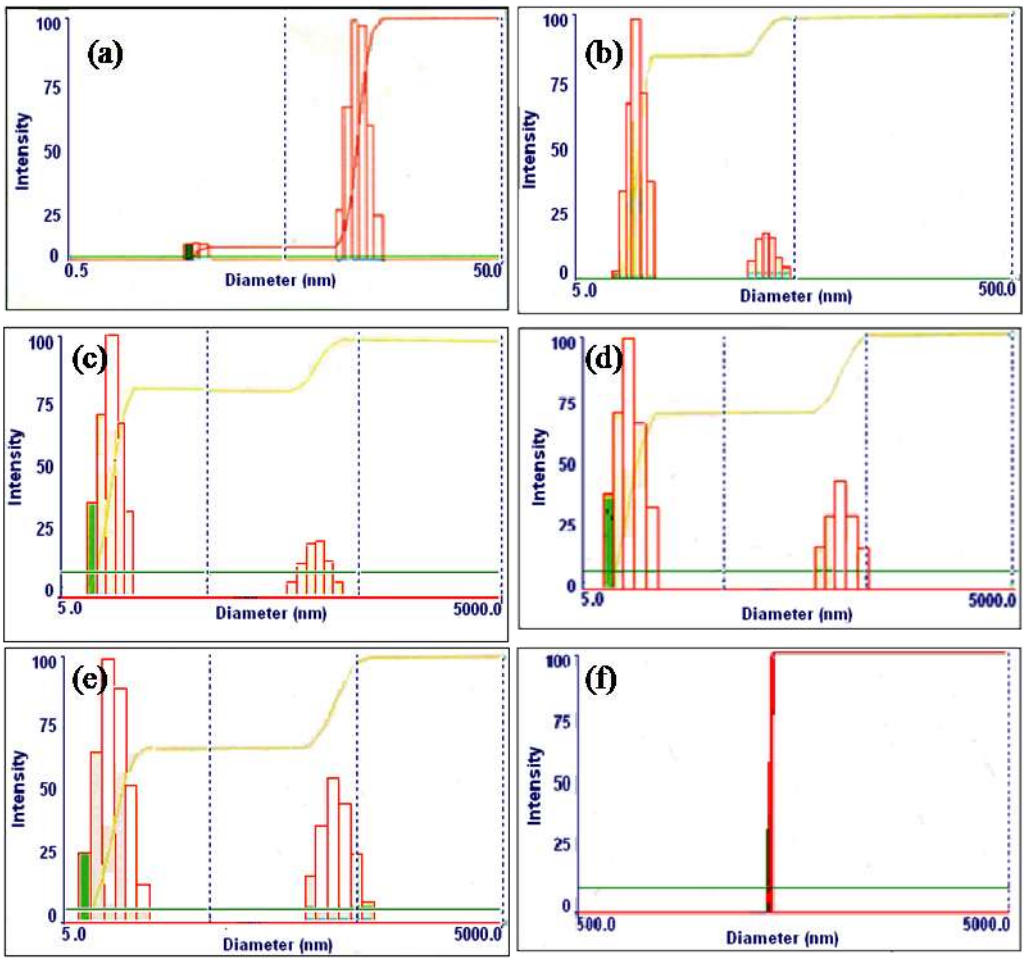

Figure 2: Intensity *vs.* aggregate diameter distribution obtained with the NNLS correlation analysis of DLS data for aqueous 15 mM SDS +100 mM TBAB (CP = 28 °C) at different temperatures:(a) 25 °C (b) 26 °C (c) 27 °C (d) 27.5 °C (e) 27.8 °C (f) 28 °C.

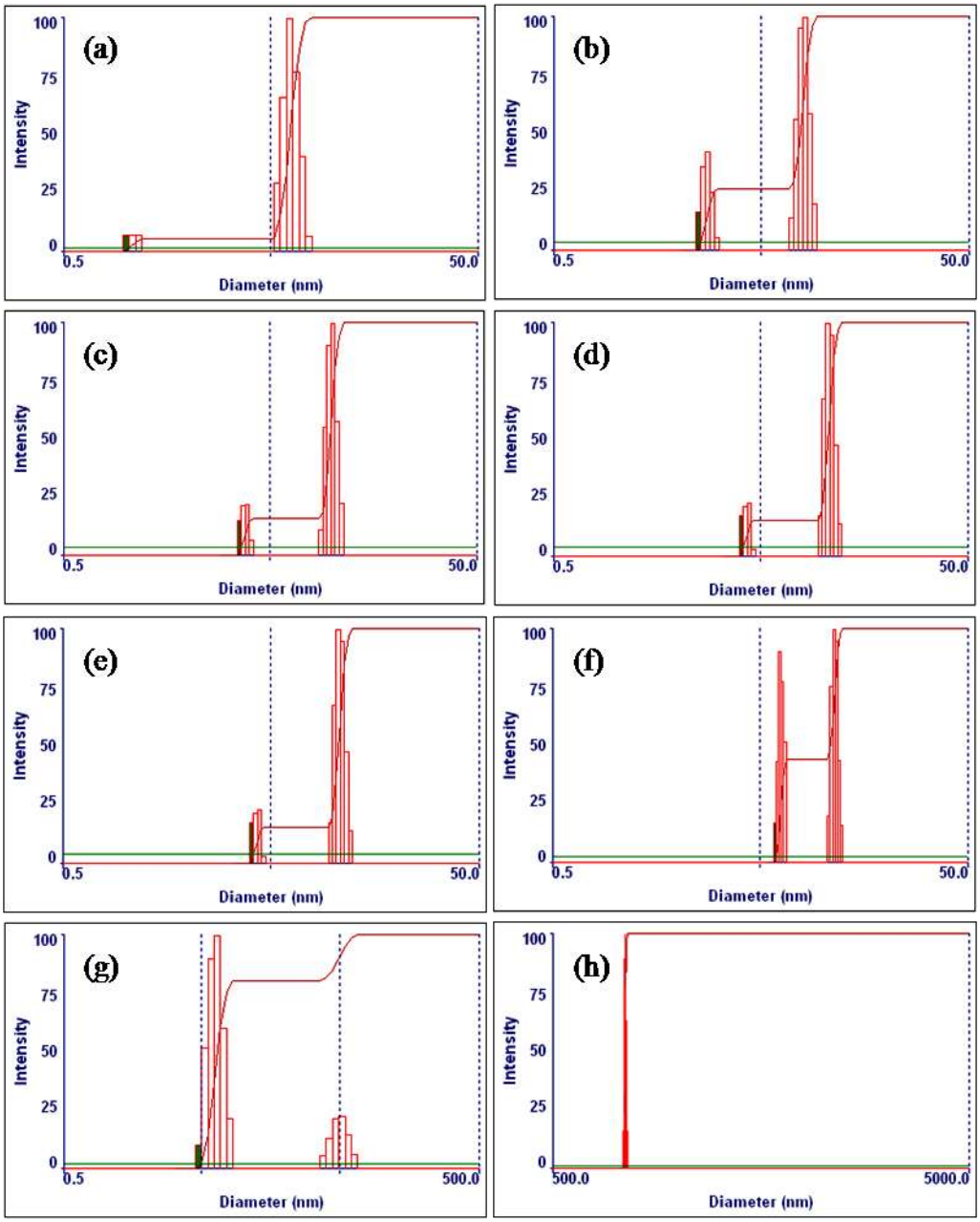

Figure 3: Intensity *vs.* aggregate diameter distribution obtained with the NNLS correlation analysis of DLS data for aqueous 15 mM MES +100 mM TBAB (CP = 60 °C) at different temperatures: (a) 25 °C (b) 45 °C (c)56 °C (d) 58 °C (e) 59 °C (f) 59.2 °C (g) 59.9 °C (h) 60 °C

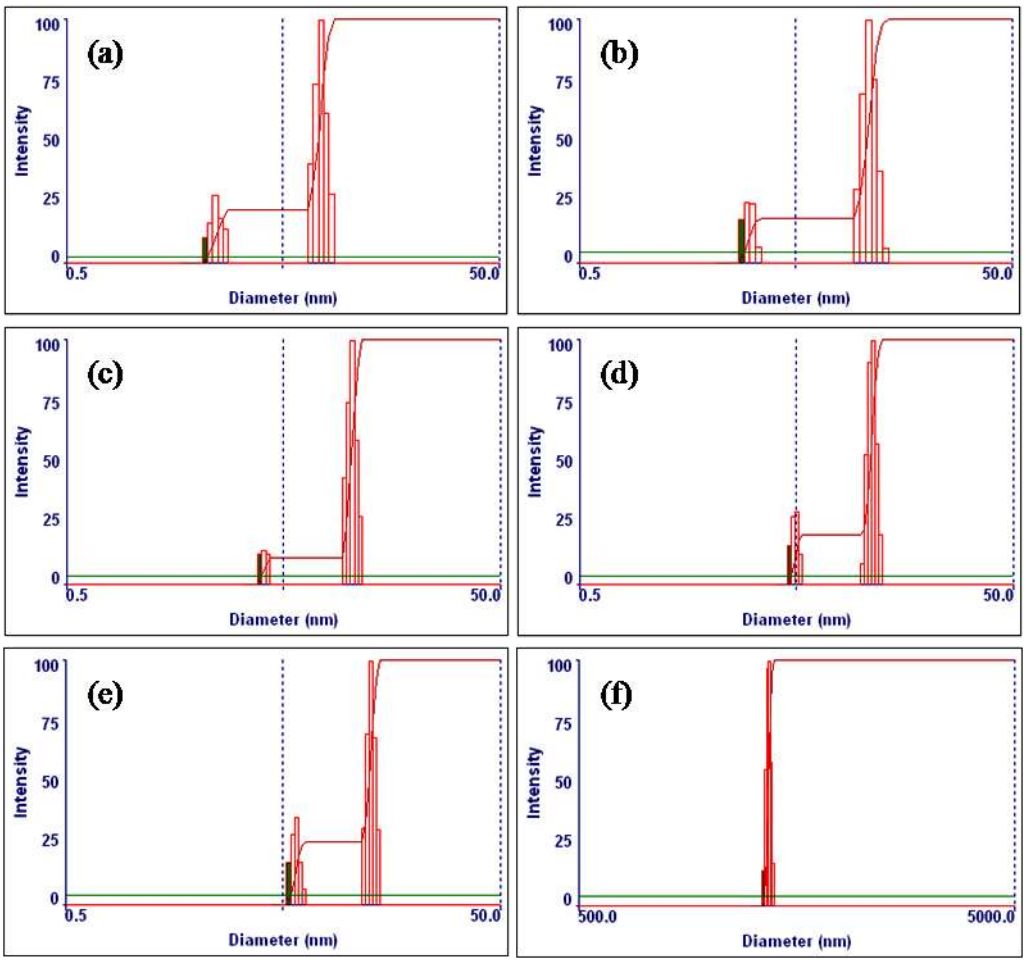

Figure 4: Intensity *vs.* aggregate diameter distribution obtained with the NNLS correlation analysis of DLS data for aqueous 15 mM PES +100 mM TBAB (CP = 59.5 °C) at different temperatures: (a) 25 °C (b) 57 °C (c) 58 °C (d) 59 °C (e) 59.3 °C (f) 59.5 °C.

On the basis of the data presented on clouding and micellar morphology, it is shown that Hofmeister- like series for surfactant headgroups can be established (Figure 5). The data fit well in the generalization proposed by Vlachy et al. for ordering of headgroups to form close pairs with counterions (carboxylate < phosphate < sulfate < sulfonate) [14]. Nevertheless, it should be kept in mind that headgroup effects do not depend only on the individual properties (*i.e.*, charge, size, charge distribution and polarizability) but also on nature and overall charge of the counterion, as well as on the possible cooperating binding sites (surfactant headgroup in a micelle).

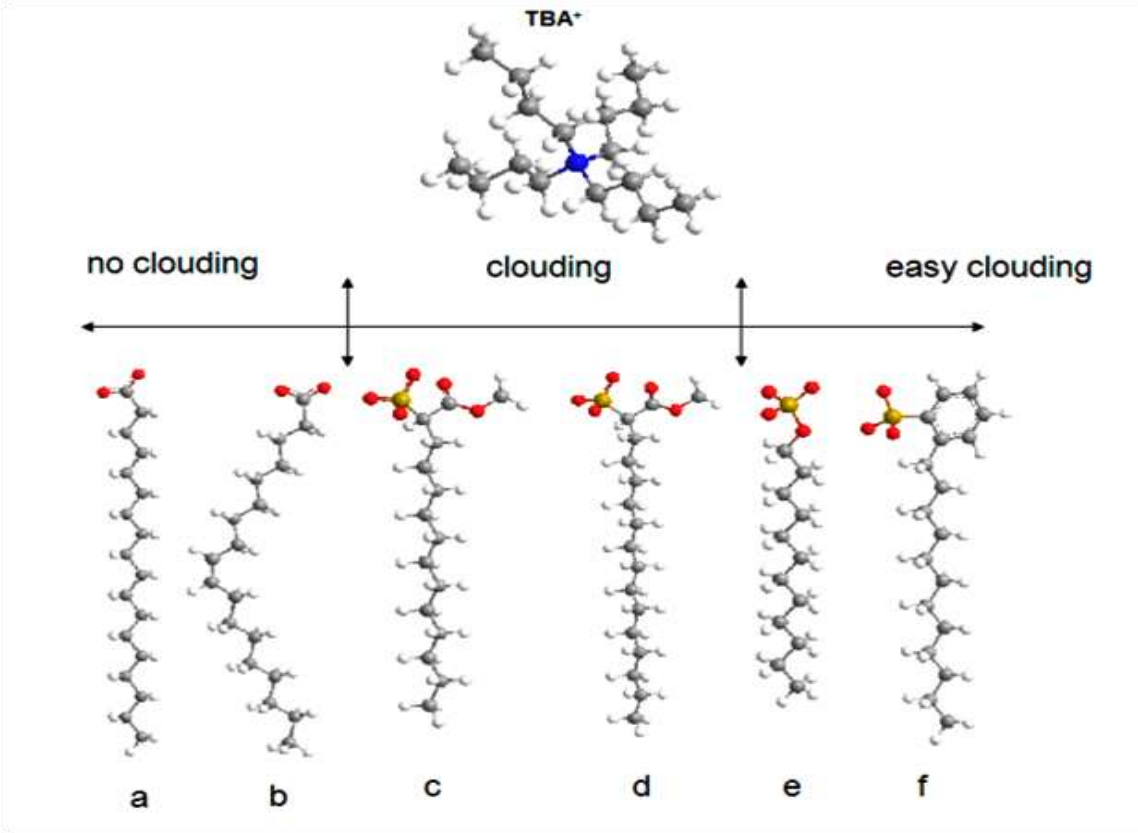

Figure 5: Ordering of anionic surfactant head groups with respect to TBA^+ counter-ion regarding their capacity to produce clouding phenomenon: (a) sodium octadecanoate (ref.29); (b) sodium oleate (ref.28); (c) α-sulfonato myristic acid methyl ester; (d) α-sulfonato palmitic acid methyl ester; (e) sodium dodecyl sulfate; (f) sodium dodecyl benzene sulfonate.

3.3 Conclusions

In this chapter, effect of nature of the headgroup on the CP of various anionic surfactant + TBAB systems has been studied and explained by considering interactions of TBA^+ with surfactant head or with water. The study supports the general proposition based on water affinities of headgroup and counterions. The proposition works well even for temperature induced micellar growth. This is an attempt to establish a Hofmeister-like series for surfactant headgroups in context of important phenomenon of surface and colloid science *i.e.* clouding and growth of association colloids (*i.e.* micelle). Two types of micellar aggregates near CP can have promising applications as a smart nanocontainer for loading amphiphilic compounds (*e.g.* drugs, dyes or proteins). These aggregates also have thermo responsive surface that is useful for physical affinity control [42]. The charged micellar systems may find applications in metal extraction and can be used in pollution abatement [43].

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