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## Nonelectrolyte-Induced CP Variation of TX-114+TBAB System

KABIR-UD-DIN\* KHATOON Suraiya# NAQVI Andleeb Z.

(Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India)

**Abstract:** The effects of nonelectrolytes (ureas, amino acids, sugars) on the cloud point (CP) of nonionic surfactant Triton X-114 (TX-114) and tetra-*n*-butylammonium bromide (TBAB) system were studied. Ureas as well as thioureas increased the CP. Behaviors of amino acids depended upon their nature. Nonpolar and uncharged polar amino acids were less effective in changing the CP. However, tryptophan and phenylalanine increased the CP sharply. Acidic amino acid (aspartic acid) and sugars decreased the CP. The results were explained in terms of their effect on water structure. Amino acids got solubilized either in the micellar interior or in the bulk phase.

**Key Words:** Cloud point; Triton X-114; Urea; Thiourea; Sugar; Amino acid

The self association of surfactant molecules in aqueous solutions leads to many unusual properties<sup>[1–3]</sup>. Understanding the science that controls this self association is important with respect to their wide range of applications in nanoscience including synthesis of optical sensors<sup>[4]</sup>, electronic devices<sup>[5]</sup>, enhancement of chemical reactions<sup>[6]</sup>, etc. Despite their importance and applications, temperature dependence of self assembly of surfactants in aqueous solutions is still not very clear.

Nonionic surfactants are widely used as solubilizers and emulsifiers. Some of the more important and practical applications of these surfactants seem to lie in the area of separation science, for example, in separation of biological materials, removal of toxic solutes from polluted water, etc<sup>[7,8]</sup>. The commercial products of these surfactants are in general polydispersed<sup>[9]</sup> containing a distribution of chain lengths of the polyoxyethylene chain as the hydrophilic moiety.

The solubility of a surfactant in water is from simple thermodynamic arguments predicted to increase on heating. However, for almost all nonionic surfactants, an opposite behavior is observed: the solubility decreases as the temperature increases. At some point it becomes more favorable for the system to demix<sup>[10]</sup>. This temperature is referred to as the lower consolute temperature or simply the ‘cloud point’ (CP). At CP a single isotropic micellar phase separates into two isotropic phases, both of which contain surfactant and water but differ in total amphiphile concentration. This liquid-liquid phase separation can be induced in a system by changing the temperature, salt concentration, pressure, and other solution conditions<sup>[11–13]</sup>. The additives affect the CP by modifying the surfactant–solvent interactions and by bringing change in the size of the micelles. Many efforts have been

made to study the effect of additives (e.g., salts<sup>[12,14,15]</sup>, organics<sup>[16,17]</sup>, and surfactants<sup>[9,12,18–20]</sup>) on the CP of surfactants.

The mechanism of CP has not been exactly known and has been discussed from two view points. One is that the aggregation number of the micelles increases and intermicellar repulsions decrease with the increase in temperature<sup>[21,22]</sup>. As the temperature increases, micellar growth and increased intermicellar attraction cause the formation of particles, e.g., rodlike micelles, that are so large that the solution becomes visibly turbid<sup>[23]</sup>. However, Corti *et al.*<sup>[24]</sup> explained the behavior as critical fluctuation. The interpretation is that as the CP is approached the micelles come together, and above the CP they separate out as second phase.

Detailed accounts of clouding behavior of nonionic surfactants can be found in the published work<sup>[12,13,16,17]</sup>. However, in those studies additives were present singly or as a combination of two electrolytes. This is the first report where CP of Triton X-114 (TX-114) is studied simultaneously in the presence of a quaternary salt and nonelectrolytes. In contrast to inorganic ions, symmetrical quaternary ions are essentially nonhydrated and show ambivalent nature in aqueous solutions. In these ions the single positive charge is buried in a paraffin shell.

TX-114 is a nonionic surfactant that is easily available. Its chemical name is polyethylene glycol *tert*-octylphenyl ether with an average chain length of 7–8 oxyethylene units. The critical micelle concentration (cmc) of TX-114 is 0.20 mmol·L<sup>-1</sup><sup>[25]</sup>. In the absence of any additive, its CP is strongly dependent on [TX-114]<sup>[12,19,26]</sup>. However, CP of 0.8 mmol·L<sup>-1</sup> TX-114+80 mmol·L<sup>-1</sup> TBAB system is 41 °C<sup>[26]</sup> (whereas the CP of 0.8 mmol·L<sup>-1</sup> TX-114 solution is 23 °C), which provides a broad temperature range to see the effect of additives on CP. The results are expected to

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\*Corresponding author. Email: kabir7@rediffmail.com.

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broaden the spectrum of CP extraction methodologies<sup>[27]</sup>.

## 1 Experimental

### 1.1 Chemicals

TX-114 ( $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ ,  $x=7-8$ , (Fluka, Switzerland, product No. 93422) was used without any further purification. The quaternary salt, TBAB, was also from Fluka, Switzerland. The amino acids used included  $\beta$ -alanine, 99% (SISCO, India); L-leucine, L-proline, 99% (BDH, England); L(-)-phenylalanine, 99% (Merck, Germany); L-methionine, 99% (SISCO, India); L-tryptophan, 99% (Merck, Germany); L-isoleucine, 99% (s.d. fine, India); L-histidine, 99% (LOBA chemie, India); glycine, 99.5% (SISCO, India); L-asparagine, 98.5% (BDH, England); DL-aspartic acid, 98.5% (BDH, England); L-glutamine, 99%, DL-serine, 99% (SISCO, India); and L-threonine, 99.5% (Sarabhai M. Chemicals, India). All the additives of urea family (urea, 99.5% (Sigma, USA); monomethylurea, 97% (Merck-Schuchardt, Germany); dimethylurea, 97% (Fluka, Switzerland); tetramethylurea, 99% (Fluka, Switzerland); thiourea, 99% (Sigma, USA); dimethylthiourea, 98% (Lancaster, England)); and sugar family (xylose, 99% (s.d. fine, India); fructose, 99% (Merck, India); arabinose, 98% (Sigma, USA); dextrose, 99% (E. Merck, India); mannose, 99% (s.d. fine, India); sorbose, 98% (Fluka, Switzerland)) were used as received.

### 1.2 Preparation of solution

All solutions were prepared in doubly distilled water (first time over alkaline  $\text{KMnO}_4$ ). Freshly prepared stock solutions of TX-114 were used to obtain sample solutions containing salt (TBAB) without or with additives.

### 1.3 Determination of CP

CP was obtained by placing graduated Pyrex glass tube containing solution into a temperature controlled bath with a stability of  $\pm 0.5^\circ\text{C}$ . The tubes were kept properly stoppered to avoid evaporation. The temperature at the first sign of turbidity was taken as the CP<sup>[26,28]</sup>. On cooling, the phase-separated surfactant redissolved immediately. The temperature was again increased to obtain CP. The temperature was cycled twice to confirm the result. The quoted values of CP are the mean of two such sets of determinations of temperatures of appearance and disappearance of turbidity.

After determining CP of a particular system, it was diluted successively to low [additive] by adding required amount of the stock solution (TX-114+TBAB) using pipette. The above procedure was then repeated to get CPs of solutions containing varying amounts of the additives.

## 2 Results and discussion

### 2.1 Variation of CP

CP of TX-114 in low concentration range is highly sensitive to the surfactant concentration, showing a minimum at  $0.4\text{ mmol}\cdot\text{L}^{-1}$  TX-114 (CP ca  $19^\circ\text{C}$ )<sup>[26]</sup>. However, at high concentrations CP remains more or less constant. Addition of  $80\text{ mmol}\cdot\text{L}^{-1}$  TBAB to  $0.8\text{ mmol}\cdot\text{L}^{-1}$  TX-114 solution increases the CP from

23 to  $41^\circ\text{C}$ <sup>[26]</sup>.

Clouding is the expression of the solvation/desolvation equilibrium in micellar solutions. Therefore, the effect of additives depends on how they change this equilibrium. Effect of water-soluble compounds can be explained by taking into consideration their influence on water-structure. However, effect of additives less soluble in water can be explained by considering their effect on packing properties of the micelles.

Fig.1 depicts the CP variation of the  $0.8\text{ mmol}\cdot\text{L}^{-1}$  TX-114+ $80\text{ mmol}\cdot\text{L}^{-1}$  TBAB system in presence of various ureas and thioureas. To understand the microscopic basis of urea action, two different mechanisms have been proposed<sup>[29-31]</sup>, (i) urea affects the solvent (indirect mechanism): urea alters the water structure and facilitates the solvation of the hydrophobic species; (ii) urea replaces the solvent (direct mechanism): urea participates in the solvation of the hydrophobic species by replacing some water molecules in the hydration shell. The indirect mechanism is widely accepted, and many experimental results seem to support the hypothesis that urea acts as a "water-structure breaker"<sup>[32]</sup>. In particular, the urea addition to micellar solutions leads to an increase in cmc<sup>[33]</sup> or decrease in aggregation number<sup>[34]</sup>. This is attributed to the breaking of water structure favoring the dissolution of hydrophobic solutes<sup>[35]</sup>.

Results presented in Fig.1 also support the indirect mechanism. Urea acts as a water-structure breaker and increases the CP. The CP increasing effect becomes more pronounced with the addition of methyl groups to urea and the order being urea<methylurea<dimethylurea<tetramethylurea. In earlier studies, these alkylureas were also found as micelle destabilizing agents<sup>[36,37]</sup>. Fig.1 also depicts the effect of thioureas on the CP of the said system. The same CP increasing effect is observed with both thiourea and dimethylthiourea, but the effect is more than that of ureas. The structure of thiourea closely resembles that of urea with less aqueous solubility and better thermal stability. Studies on thiourea-surfactant systems show that thiourea is a better water-structure breaker compared with urea at similar concentrations<sup>[34,38]</sup>. Water-structure breakers increase the CP by making more water molecules available to the micelles.

Results of CP variation with added sugars are presented in

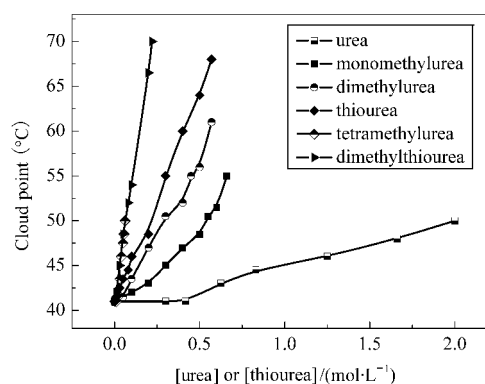
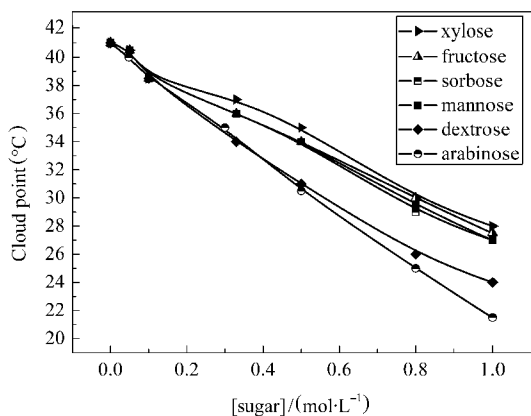


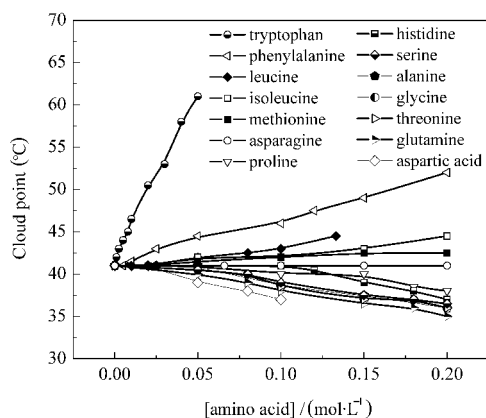
Fig.1 Effect of ureas/thioureas on the CP of  $0.8\text{ mmol}\cdot\text{L}^{-1}$  TX-114+ $80\text{ mmol}\cdot\text{L}^{-1}$  TBAB solutions



**Fig.2** Effect of sugars on the CP of 0.8 mmol·L<sup>-1</sup> TX-114+80 mmol·L<sup>-1</sup> TBAB solutions

Fig.2. Sugars decrease the CP of TX-114+TBAB system. Sugars, well known water-structure makers, increase the hydrophobic interactions and decrease the cmc of surfactants<sup>[39]</sup>. These observations are similar to the decrease in aqueous solubility of hydrophobic compounds by sugars. The sugars decrease the water of hydration of the micelles by competing for water molecules associated with the micelles and hence, CP decreases in presence of sugars. The results of Fig.2 indeed support the explanation.

Fig.3 shows the variation of CP of TX-114+TBAB system with the addition of amino acids. We can see that aspartic acid decreases the CP, whereas nonpolar and uncharged polar amino acids are less effective. The effect of amino acids on the CP might be explained on the basis of taking cognizance of polarity and hydrophobicity. Because of its acidic nature, aspartic acid interacts with TX-114+TBAB mixed micelles. This will decrease the head-head repulsions causing intermicellar compactness. As a result, CP decreases. Nonpolar and uncharged polar amino acids would prefer either the micelle interior or bulk water and in doing so would not affect the micellar hydration. Therefore, CP shows mild changes. Surprisingly, tryptophan and phenylalanine, although nonpolar, increase the CP of the system



**Fig.3** Effect of amino acids on the CP of 0.8 mmol·L<sup>-1</sup> TX-114+80 mmol·L<sup>-1</sup> TBAB solutions

sharply. These amino acids possess larger hydrophobic portion compared to the other nonpolar amino acids used in this study and hence, would sit deeper inside the micelles. This will decrease the compactness of the micelles and micelle hydration increases.

## 2.2 Energetics of Clouding

Recently, attempts have been made to explain the process of phase separation in terms of thermodynamics based on the mole-fractional solubility of the clouding species in presence of additives<sup>[40,41]</sup>. The clouding is considered as the formation of a separate phase in the solution where the clouding species become dehydrated and separate out in the solution. The CPs (Figs.1-3) can therefore, be taken as the solubility limit of the clouding species at that temperature. The standard Gibbs free energy ( $\Delta G^0$ ) of solution (here called clouding) of the species is then given by the relation

$$\Delta G^0 = -RT \ln X \quad (1)$$

where  $X$ ,  $R$ , and  $T$  are mole fractional solubility at CP, the gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ), and absolute temperature ((CP+273.15) K), respectively.

The standard enthalpy and entropy of the process can be calculated by the relations

$$\delta(\Delta G^0/T)/\delta(1/T) = \Delta H^0 \quad (2)$$

and

$$T\Delta S^0 = \Delta H^0 - \Delta G^0 \quad (3)$$

The values of energetic parameters for some selected additives are given in Table 1.  $\Delta H^0$  values are negative for fructose, dextrose, xylose, arabinose, aspartic acid, glutamine, and proline, whereas it is positive for ureas/thioureas, phenylalanine, and tryptophan. For the transfer of monomers into the micelles the net heat change is because of the two processes: (i) disruption of the water structure around the nonpolar tails of the surfactant molecules, and (ii) incorporation of the monomers into the micelles. The first process is endothermic and increases the entropy, whereas the second one is exothermic and decreases the entropy. The energetic parameters reveal that the solubilization process is controlled by both enthalpy and entropy. For tryptophan, there are three stages in  $\Delta G^0/T$  vs  $1/T$  curves, but for the other additives, there are only two stages. The first stage is controlled by both enthalpy as well as entropy, i.e.,  $\Delta H^0 - T\Delta S^0$ . For the second stage  $\Delta H^0 > T\Delta S^0$  (for the third stage of tryptophan  $\Delta H^0 > T\Delta S^0$  and thus this stage too is enthalpy controlled). For sugars, aspartic acid, glutamine, and proline,  $\Delta H^0$  and  $T\Delta S^0$  values are negative, whereas for other additives both are positive.

No doubt, the exothermicity of the clouding phenomenon is because of the aggregation of weakly solvated amphiphile molecules and their phasing out into the condensed phase. This is a simplified explanation, otherwise, various environmental and structural factors and their combinations (like desolvation, solvent modification, micellar growth, morphological transition, intermicellar interactions, etc.) have their due share on the energetics of clouding.

**Table 1 Energetic parameters for clouding in 0.8 mmol·L<sup>-1</sup> TX-114+80 mmol·L<sup>-1</sup> TBAB+additive systems**

Additive	$\Delta G^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$T\Delta S^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	Additive	$\Delta G^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$T\Delta S^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	
urea	0.1	23.6	23.5	dextrose	0.2	-145.0	-145.2	
	0.1		23.5		0.2		-145.2	
	0.2		23.4		0.4		-145.4	
	0.3	5.0	4.7		0.5		-7.4	-7.9
	0.3		4.7		1.5		-8.9	
	0.4		4.6		2.5		-9.9	
	0.7		4.3		arabinose		0.2	-103.3
tetramethylurea	2.2	92.6	90.4	0.2		-103.5		
	2.4		90.2	0.4		-103.7		
	2.5		90.1	0.6	-6.7	-7.3		
	2.9		89.7	1.6		-8.3		
	3.4		89.2	2.6		-9.3		
	4.3		88.3	L-proline	0.9	-414.3	-415.2	
thiourea	0.3	150.0	149.7	1.0		-415.3		
	0.4		149.6	1.1	-33.3	-34.4		
	0.5		149.5	1.5		-34.8		
	0.7		149.3	2.5		-35.9		
	0.9		149.1	DL-aspartic acid	1.5	-571.4	-572.9	
	1.6		12.0	10.4	1.8		-573.2	
	1.8			10.2	2.5	-100.0	-102.5	
	2.5			9.5	4.3		-104.3	
	3.4			8.6	5.8		-105.8	
	5.8		6.2	L-glutamine	0.8	-222.2	-223.0	
dimethylthiourea	0.9	187.5	186.6	0.9		-223.1		
	1.0		186.5	1.1	-75.0	-76.1		
	1.6		16.2	14.6	1.5		-76.5	
	1.8			14.4	1.8		-76.8	
	2.5			13.7	2.5		-77.5	
	3.4			12.8	L(-)-phenylalanine	1.0	333.3	332.3
	5.7			10.5	1.2		332.1	
	7.4			8.8	1.4		331.9	
xylose	0.2	-155.6	-155.8	1.6		331.7		
	0.3		-155.9	2.5	33.0	30.5		
	0.4		-156.0	3.8		29.2		
	0.6		-15.4	-16.0	7.4		25.6	
	1.5			-16.9	L-tryptophan	2.7	33.3	30.6
	2.5			-17.9	3.1		30.2	
2.5	-17.9	3.6			29.7			
fructose	0.2	-120.0	-120.2	4.4	118.7	114.3		
	0.3		-120.3	5.8		112.9		
	0.4		-120.4	6.4	375.0	368.6		
	0.6		-6.0	-6.6	7.5		367.5	
	1.5			-7.5	9.2		365.8	
	2.5			-8.5	11.6		363.4	
	2.5			-8.5	11.6		363.4	

### 3 Conclusions

The effect of additives studied on the CP of TX-114+TBAB system can be explained in terms of their influence on several factors, like solubility, water structure, polarity, hydrophobicity, etc. CP decreased in presence of sugars, whereas it increased with ureas, as sugars were water structure makers and ureas were wa-

ter structure breakers. Amino acids solubilized in bulk phase or micellar interior, and hence, CP changed slowly with nonpolar and uncharged polar amino acids. With tryptophan and phenylalanine, however, CP increased because of their deeper micelle penetration. Aspartic acid interacted with TX-114+TBAB micelles resulting in compact micelles: this increased dehydration

and decreased the CP.

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