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Influence of Chloramine-T on the thermodynamics of clouding behaviour of non ionic surfactant Triton X-114

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ABSTRACT

The phenomenon of solubilization of nonionic surfactant TritonX-114 has been studied through the influence of additive Chloramine-T in aqueous medium by measuring the cloud points (CP) of the pure surfactant and with Chloramine-T. The CP of pure surfactant found to be increased with increased concentration of TritonX-114. The CP of mixed system shows increasing trends with increased Chloramine-T. This is mainly due to increased micelle concentrations. The influence of Chloramine-T on the cloud point of TritonX-114 is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. Considering cloud point as threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG^0_{cl}, ΔH^0_{cl} and ΔS^0_{cl}) have been evaluated using "Phase Separation Model". The phase separation results from micelle-micelle interaction. It is found that the overall clouding process is exothermic and $\Delta H^0_{cl} > T\Delta S^0_{cl}$ indicating that the process of clouding is guided by both enthalpy and entropy. This work supports the conjecture that the clouding is critical phenomenon rather than the growth of micelles. Findings of the present work supports to made the probable evidence of electrolyte-surfactant interactions in aqueous medium.

Key words: Micellization, Cloud Point (CP), TritonX-114 (TX-114), Chloramine-T (CAT), Phase Separation Model

INTRODUCTION

Several research workers have studied the molecular interactions in surfactants in the presence of added electrolytes[1-4]. Surfactants contain two distinct grouping in their structure. Strongly polar or charged group at one end of surfactant molecule is the "head group" which is hydrophilic in nature and long chain of alkyl or aryl group is the "tail" which is hydrophobic in nature. When surfactants is added to water at low concentration, they are dispersed as discrete molecules. However at a particular concentration, surfactant molecules get associated to form aggregates or micelles[5-7]. This concentration is known as critical micellar concentration (CMC) which is an important property of surfactant. Above CMC, the surfactant molecules exist as aggregates or micelles. CMC of a surfactant was determined by several methods such as conductance, surface tension, solubilization, light scattering, diffusion, ultrasonic velocity measurement etc. Nonionic surfactants and electrolytes in aqueous solution cannot withstand at elevated temperatures and become seperated which can be seen even with naked eye known as clouding The cloud point is an important property of non ionic surfactants. Below CP a single phase of molecular solution or micellar solution exists and above CP, the solubility of surfactant in water is reduced and forms cloudy dispersion[8] by forming giant molecular aggregates in the state of separate phase[9-12]. TX-114 is used for pre-concentration in analytical chemistry[13]. The principle use of TX-114 surfactant is in industrial and household detergent applications and in emulsifying agents. It is used almost in every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents for fine fabrics. TX-114 is also important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers, stabilizers in latex polymers and emulsifiers for agricultural emulsion concentrates and wettable powders. It has been shown earlier that addition of electrolyte, CP of TX-114 get affected by the additives[14-15]. Some inorganic and organic compounds are added to detergents in order to make detergent cheap, user friendly and to boost it's power[16], these compounds are called "builders". Chloramine-T (CAT) is used as disinfectant, algaecide, bactericide, germicide, for parasite control and for drinking water disinfection. Due to these properties CAT is used as a "builder" in detergents.

In this paper, the results of present study on the clouding phenomenon of pure TX-114 and in the presence, CAT at various concentrations have been reported. These studies are important in the field of medicinal preparations, agrochemicals, detergents etc. Considering cloud point as threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG^0_{cl}, ΔH^0_{cl} and ΔS^0_{cl}) have been evaluated using "Phase Separation Model".

MATERIAL AND METHODS

The nonionic surfactant TritonX-114 (M.Wt. 537) and Chloramine-T.Trihydrate (M.Wt. 281.69) were the products of SIGMA-ALDRICH, USA. and these were used as received. Doubly distilled water with Specific Conductance 2 - 4 µ S cm^{-1} at 303.15 K was used in the preparation of all solutions of different concentrations.

The cloud point (CP) was determined by controlled heating of the sample solutions in thin glass tube immersed in beaker containing water, the sample solution was stirred while being heated. The heating rate of sample was controlled by less than 1^oC/min. The detailed procedure is in our previous publications[17]. The reproducibility of the measurement was found to be within $\pm 0.2^0C$. As the CP values are not small, the observed values have been rounded off to the nearest degree and presented in the tables.

RESULTS AND DISCUSSION

Cloud Points of Pure TritonX-114

The cloud points of pure surfactant, TritonX-114 at various concentrations in Wt% are given in Table: 1. The CP of the surfactant TX-114 was found to be increased with increased concentration of TX-114. Above certain concentration of surfactant in aqueous medium, increase in CP was observed which is mainly due to dehydration of oxy-ethylene (EO) group which required still high temperature to remove associated water resulting in to phase separation that is clouding.

TritonX-114/ CAT Systems

The influence of CAT on the CP of TritonX-114 at different concentration of CAT has been given as in Table:3. These results indicate that the cloud point of surfactant increased considerably with increased [CAT]. This is due to breakdown of structured additive-surfactant system. The removal of water from surfactant by added electrolyte helps the surfactant micelles to come closer with each other resulting in to increasing of CP. The additive surfactant complex is stronger due to solute solvent interaction. Some of the water molecules remain

Table 1: Cloud Points of Pure TritonX-114

Wt %	Molarity ^{3} x 10^-	Mole fraction x10^{-4}	CP/°C
1.0	18.622	3.351	24.5
3.0	55.866	10.046	25.6
5.0	93.110	16.732	26.2
7.0	130.354	23.409	27.8
9.0	167.598	30.077	28.4

Table 2: Thermodynamic Parameters of TritonX-114

[TritonX-114] Wt %	ΔG^0_{cl} KJ mol^{-1}	- ΔH^0_{cl} KJ mol^{-1}	-ΔS^0_{cl} J $mol^{-1}K^{-1}$
1.0	19.79		624.9
3.0	17.14		613.7
5.0	15.90		608.4
7.0	15.15	166.1	602.6
9.0	14.55		599.5

attached to this complex and hence higher temperature is required to breakdown this strong complex system. The dependence of CP on [CAT] is as depicted in Fig. 2.

Thermodynamics of Clouding

All physico-chemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. The energetic of such processes are required for formulation, uses and basic understanding. Thermodynamic parameters of pure TX-114 and TX-114+ CAT mixed system are given in Table 2 and 4 respectively. In case of non-ionic surfactant, the desolvation of hydrophilic groups of the surfactant leads to the formation of cloud or turbidity in the surfactant solution at elevated temperature. The appearance of cloud point is entropy dominated. At the cloud point, the water molecules get detached from the micelles. Considering cloud point as the phase separation point, the thermodynamic parameters such as standard free energy (ΔG^0_{cl}),enthalpy (ΔH^0_{cl}) and entropy (ΔS^0_{cl})for the clouding process have been calculated using the Phase separation Model[18].

$$\Delta G^0_{cl} = -RT \ln Xs \qquad ...(1)$$

Where "cl" stands for clouding process and ln Xs is the mole fractional solubility of the solute. The Standard enthalpy (ΔH^0_{cl}) for the clouding process have been calculated from the slope of the linear plot of ln Xs Vs 1/T in Fig.1

$$d \ln Xs / dT = \Delta H^0_{cl} / RT^2 \qquad ...(2)$$

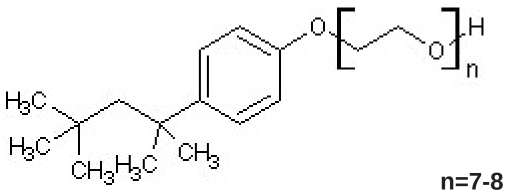
The Standard free energy (ΔS^0_{cl}) of the clouding process have been calculated from the following relationship

$$\Delta S^0_{cl} = (\Delta H^0_{cl} - \Delta G^0_{cl}) / T \qquad ...(3)$$

$\Delta H^0_{cl} < \Delta G^0_{cl}$ indicating that overall clouding process is exothermic and $\Delta H^0_{cl} > T\Delta S^0_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy[19].

Clouding species

TritonX-114



Additive: CAT

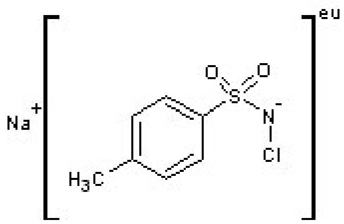


Fig. 1: Molecular structures of clouding species and additive

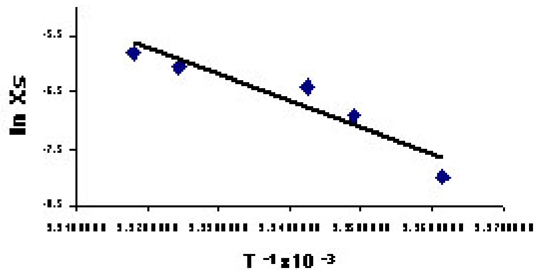


Fig. 1: CP of TritonX-114 at different concentration

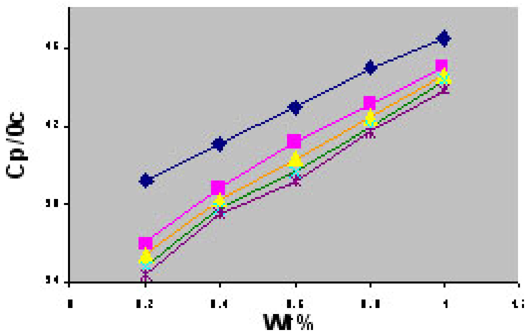


Fig. 2: CP of TritonX-114+CAT

Table 3: Influence of CAT on CP of TritonX-114

[TritonX-114]	Wt % of CAT				
Wt%	0.2	0.4	0.6	0.8	1.0
1.0	39.2	41.1	43.0	44.9	46.5
3.0	36.0	39.8	41.2	43.1	45.1
5.0	35.4	38.2	40.3	42.5	44.6
7.0	34.8	37.8	39.7	42.0	44.3
9.0	34.3	37.5	39.2	41.6	43.9

The present work would be supportive evidence regarding the probable interaction between non-ionic surfactant and macromolecules leading to the phase separation at the cloud point. The effect of CAT on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. This paper supports the conjecture that the cloud point is a critical phenomenon.

Table 4: Thermodynamic Parameters of TritonX-114/CAT System

[CAT] Wt %	ΔG^0_{cl} KJ mol^{-1}	$-\Delta H^0_{cl}$ KJ mol^{-1}	$-\Delta S^0_{cl}$ J mol^{-1}K^{-1}
0.2	23.27	153.9	567.6
0.4	21.25	197.1	706.5
0.6	20.17	206.7	735.8
0.8	19.40	242.6	851.3
1.0	18.79	315.0	1086.2

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