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Influence of Chloramine-T on the Thermodynamics of Clouding Behaviour of Non-Ionic Surfactant Triton X-100

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The phenomenon of solubilization of nonionic surfactant Triton X-100 has been studied through the influence of additive chloramine-T in aqueous medium by measuring the cloud points of the pure surfactant and with chloramine-T. The cloud points of pure surfactant found to be declined with increased concentration of Triton X-100. The cloud points of mixed system show increasing trends with increased chloramine-T. This is mainly due to increased micelle concentrations. The influence of chloramine-T on the cloud point of Triton X-100 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^o_{cl}, ΔH^o_{cl} and ΔS^o_{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 $\Delta H^o_{cl} > T\Delta S^o_{cl}$ 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, Triton X-100, Chloramine-T, 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 are 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 critical micellar concentration, the surfactants exist as aggregates or micelles. Critical micellar concentration of a surfactant is determined by several methods such as conductance, surface tension, solubilization, light scattering, diffusion, ultrasonic velocity measurement *etc*.

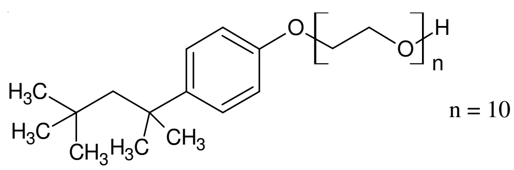
Nonionic surfactants and electrolytes in aqueous solution cannot withstand at elevated temperatures and become separated which can be seen even with naked eye known as clouding. The cloud point is an important property of non-ionic surfactants. Below cloud points a single phase of molecular solution or micellar solution exists and above cloud points, 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]. Triton X-100 is widely used as detergent in molecular biology[13]. It has been shown earlier that by the addition of electrolyte, cloud points of Triton X-100 is affected by the additives[14]. Some inorganic and organic compounds are added to detergents in order to make detergent cheap, user friendly and to boost it's power[15], these compounds are called "builders". Chloramine-T is used as an disinfectant, algaecide, bactericide, germicide, for parasite control and for drinking water disinfection. Due to these properties chloramine-T is used as a "builder" in detergents.

In this study, the results on the clouding phenomenon of pure Triton X-100 and in presence chloramine-T at various concentrations has 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^o_{cl}, ΔH^o_{cl} and ΔS^o_{cl}) have been evaluated using "phase separation model".

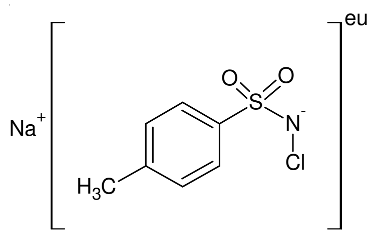
EXPERIMENTAL

The nonionic surfactant Triton X-100 (m.w. 646) and chloramine-T trihydrate (m.w. 281.69) were the products of Sigma-Aldrich, USA and these were used as received. Doubly distilled water with specific conductance 2-4 μS cm^{-1} at 303.15 K is used in the preparation of all solutions of different concentrations.

The cloud point was determined by controlled heating of the sample solutions in thin glass tube immersed in a beaker containing water, the sample solution is stirred while being heated. The heating rate of sample is controlled by less than 1 ºC/min. The detailed procedure is given in previous publication[16]. The reproducibility of the measurement was found to be within ± 0.2 ºC. As the cloud points values are not small, the observed values have been rounded off to the nearest degree and presented in the tables.



Triton X-100



Chloramine-T

Molecular structures of clouding species (Triton X-100) and additive (chloramine-T)

RESULTS AND DISCUSSION

Cloud points of pure Triton X-100: The cloud points of pure surfactant, Triton X-100 at various concentrations in weight percentage are given in Table-1. The cloud points of the surfactant Triton X-100 was found to be decreased with increased concentration of Triton X-100. This is due to increase in micelle concentration. The phase separation occurs due to micelle-micelle interaction.

TABLE-1
CLOUD POINTS OF PURE TRITON X-100

Weight (%)	Molarity × 10^{-3}	Mole fraction × 10^{-4}	CP/ºC
0.08	1.238	0.223	65.8
0.10	1.548	0.279	65.5
0.20	3.096	0.557	65.0
0.40	6.192	1.114	64.5
0.60	9.288	1.672	64.1
0.80	12.384	2.229	63.8
1.00	15.480	2.786	63.5

Triton X-100/chloramine-T systems: The influence of chloramine-T on the cloud points of Triton X-100 at different concentration of chloramine-T has been given in Table-2. These results indicate that the cloud point of surfactant increased considerably with increased [chloramine-T]. 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 cloud points. The additive surfactant complex is stronger due to solute solvent interaction. Some of the water molecules remain attached to this complex and hence higher temperature is required to breakdown this strong complex system. The dependence of cloud points on [chloramine-T] is depicted in Fig. 1.

TABLE-2
INFLUENCE OF CHLORAMINE-T ON CLOUD POINT OF TRITON X-100

[Triton X-100] Weight (%)	Weight % of chloramine-T				
	0.2	0.4	0.6	0.8	1.0
0.08	68.8	69.6	71.0	73.0	74.7
0.10	69.1	70.1	71.7	73.9	75.6
0.20	69.7	71.4	73.3	75.3	76.6
0.40	70.2	72.0	74.1	75.7	77.3
0.60	70.6	72.5	74.6	76.1	77.6

Thermodynamics of clouding: All physico-chemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. The energetics of such processes are required for formulation, uses and basic understanding. Thermodynamic parameters of pure Triton X-100 is given in Table-3 and for Triton X-100 + chloramine-T mixed system is given in

Table-4. 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^o_{cl}), enthalpy (ΔH^o_{cl}) and entropy (ΔS^o_{cl}) for the clouding process have been calculated using the phase separation model[17].

TABLE-3
THERMODYNAMIC PARAMETERS OF TRITON X-100

[Triton X-100] weight (%)	ΔG^o_{cl} (KJ mol^{-1})	$-\Delta H^o_{cl}$ (KJ mol^{-1})	$-\Delta S^o_{cl}$ (J mol^{-1} K^{-1})
0.08	30.17		1492.2
0.10	29.52		1491.6
0.20	27.53		1487.9
0.40	25.54	475.4	1484.2
0.60	24.37		1482.5
0.80	23.55		1481.4
1.00	22.90		1480.8

TABLE-4
THERMODYNAMIC PARAMETERS OF TRITON X-100/CHLORAMINE-T SYSTEM

[Chloramine-T] weight %	ΔG^o_{cl} (KJ mol^{-1})	$-\Delta H^o_{cl}$ (KJ mol^{-1})	$-\Delta S^o_{cl}$ (J mol^{-1} K^{-1})
0.2	25.48	490.8	1510.4
0.4	23.53	295.5	932.5
0.6	22.41	238.3	760.7
0.8	21.63	277.2	870.6
1.0	21.01	307.4	955.8

$$\Delta G^o_{cl} = -RT \ln Xs \quad (1)$$

where "cl" stands for clouding process and ln Xs = mole fractional solubility of the solute. The standard enthalpy (ΔH^o_{cl}) for the clouding process have been calculated from the slope of the linear plot (Fig. 2) of ln Xs *versus* 1/T.

$$d \ln Xs/dT = \Delta H^o cl/RT^2 \quad (2)$$

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

$$\Delta S^o_{cl} = (\Delta H^o_{cl} - \Delta G^o_{cl})/T \quad (3)$$

$\Delta H^o_{cl} < \Delta G^o_{cl}$ indicating that overall clouding process is exothermic, also $\Delta H^o_{cl} > T\Delta S^o_{cl}$ indicate that the process of clouding is governed by both enthalpy and entropy[18].

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 chloramine-T 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.

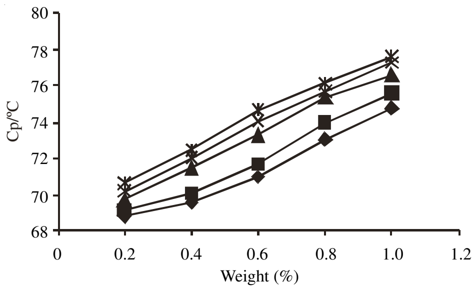


Fig. 1. Cloud points of Triton X-100 at different concentration

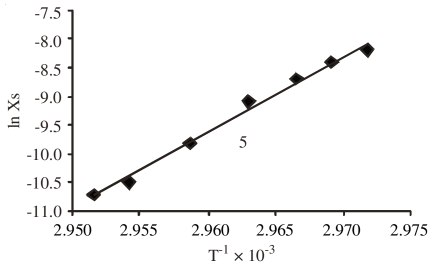


Fig. 2. Cloud points of Triton X-100 + chloramine-T

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