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Research Article

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Cloud point and thermodynamic properties of a non-ionic surfactant Triton-X-100 in presence of various organic and inorganic Salts

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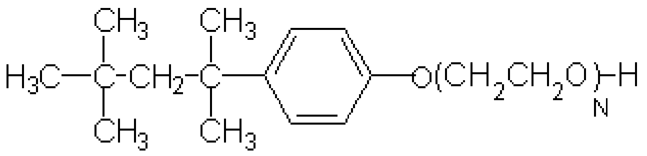
ABSTRACT

Cloud points (CPs) of non-ionic surfactants Triton-X-100 was studied in the presence of monovalent, divalent and trivalent cations (Basic radicals) from inorganic salts such asNa^+Cl*,*$Ca^{+2}Cl_2$*,* $Al^{+3}Cl_3$ *and anions (Acidic radicals) from organic salts such as Sodium-Lactate*$^-$*, Sodium-Malate*$^{-2}$*, Sodium Citrate*$^{-3}$ *respectively. Initially the CP of Triton-X-100 was found to be increase up to 0.01M but at higher concentration, the CP was found to decrease continuously. The extent of decrease in CP value was more significant at trivalent radical than divalent and monovalent radicals. The thermodynamic parameters of these systems was also evaluated and discussed. The decrease in CP with increase in concentration of radicals is entropy driven process.*

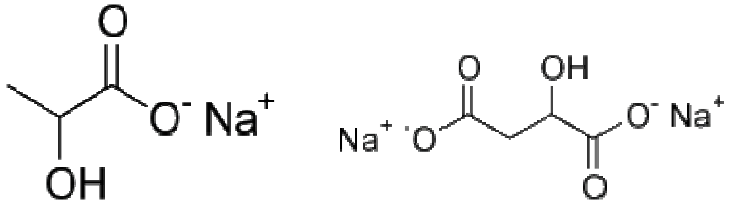
Keywords: Surfactants, Non-ionic surfactants, Thermodynamic parameters, Cloud point, Additives, Triton-X-100.

INTRODUCTION

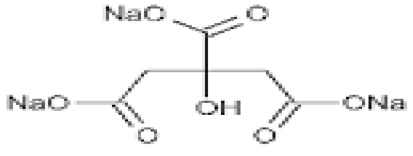
The non ionic surfactants containing polyoxyethylene chain show some unusual behavior at a certain temperature known as the cloud point (CP).At the cloud point, solvation and desolvation equilibrium are affected and surfactant solution separates into two parallel phases, one which is surfactant-rich phase and the other one the aqueous phase. Cloud point is a reversible process [1-3].The CP of non ionic surfactants is very sensitive to the presence of additives in the system even at very low concentration [4-12].The nonionic surfactants are useful as detergents, solubilisers and emulsifiers[13-14]. Solution properties of mixed surfactant systems have importance in industrial preparation, pharmaceutical and medicinal formulation, enhanced oil recovery process, etc [15]. Triton-X-100 is widely used in biological works, such as separation of proteins from cell membranes, [16, 17].In most of the practical applications, well chosen mixtures of surfactants can be made to perform better than the single components. In many cases, developments of such formulations have been achieved by trial and error methods. For practical applications such mixed micelles of ionic-ionic, ionic-nonionic and nonionic-nonionic combinations are possible and their physicochemical investigations and basic understanding for the system formulations, [18-25].
In this study we have undertaken a systematic study on clouding phenomenon of nonionic surfactants Triton-X-100 in the presence of varying concentration of ionic radicals such as cations from inorganic salts (Na^+Cl,$Ca^{+2}Cl_2$, $Al^{+3}Cl_3$) and anions from organic salts (Sodium-Lactate$^-$, Sodium-Malate^{-2}, Sodium Citrate^{-3}) as shown in **Figure 1.**



Iso-Octyl-phenoxy-polyethoxy-ethanol (Triton-X-100
(Where N is the number of ethoxy unit for Triton-X-100, N=10)



Sodium Lactate **Sodium Mallate**



Sodium Citrate

Figure 1 Molecular structures of surfactant, Iso-octyl-phenoxy-polyethoxy-ethanol (Triton-X- 100) and Additives - Sodium Lactate, Sodium Malate, Sodium Citrate

EXPERIMENTAL SECTION

2.1 Materials

Nonionic surfactant Triton-X-100 was obtained from Loba Chemie (India).The inorganic salts (Na^+Cl,$Ca^{+2}Cl_2$, $Al^{+3}Cl_3$) was obtained from SD fine chemicals (India) and organic salts (Sodium-Lactate, Sodium-Malate, Sodium Citrate) obtained from Sigma Aldrich (UK). Doubly distilled water was used for preparation of solutions.

2.2 Methods

The CP for all solutions of, Surfactant and variable additive mixture were determined by heating method using controlled heating plate with magnetic stirrer. The turbid solution was then allowed to cool slowly while being stirred and the temperature for the disappearance of turbidity was considered as the cloud point of the solution. Heating and cooling was regulated to about 1^0C per minute around the CP. The reproducibility of the measurement was found to be within ± 0.2^0C. As the CP value are not small, the observed values have been rounded off to the nearest degree and results are given in the **Tables 1 and 2.**

RESULT AND DISCUSSION

3.1 Cloud point and organic electrolytes **:-**The effect of monovalent (Sodium Lactate$^-$),divalent (Sodium Malate^{-2}) and trivalent (Sodium Citrate^{-3}) acidic radicals from organic electrolytes on CP of Triton-X-100 (1% w/v) surfactant was studied at variable concentration from 0.00,0.01,0.02,0.05,0.1,0.2 and 0.4M . The results are given in Table 1. The CP value initially increases at very low concentration of electrolyte, but on further increasing concentration of electrolyte CP value significantly decreases. The increase in CP value of surfactant at lower concentration is more for monovalent anion than divalent and trivalent anion. This may be due to at lower concentration of electrolyte facilate the complex formation and hence increase the CP value. The extent of decrease in CP value at higher concentration is significantly more for trivalent anion than divalent and monovalent anions (Figure 2). This may be due to charge density and more dehydration, decrease the stability and significantly decrease the CP value (Table-1)

Table 1 CP of Triton-X-100 in presence of Organic electrolytes

Triton-X-100 1% (w/v) + Organic Additives	CP ^{0}C at Molar Concentration of Organic Additives						
	0.00	**0.01**	**0.02**	**0.05**	**0.1**	**0.2**	**0.4**
Na-Lactate	62.5	62.5	66.6	66.0	65.0	61.0	52.0
Na-Malate	62.5	66.6	64.0	62.5	58.0	55.7	43.0
Na-Citrate	62.5	66.0	63.5	62.2	54.0	44.0	33.5

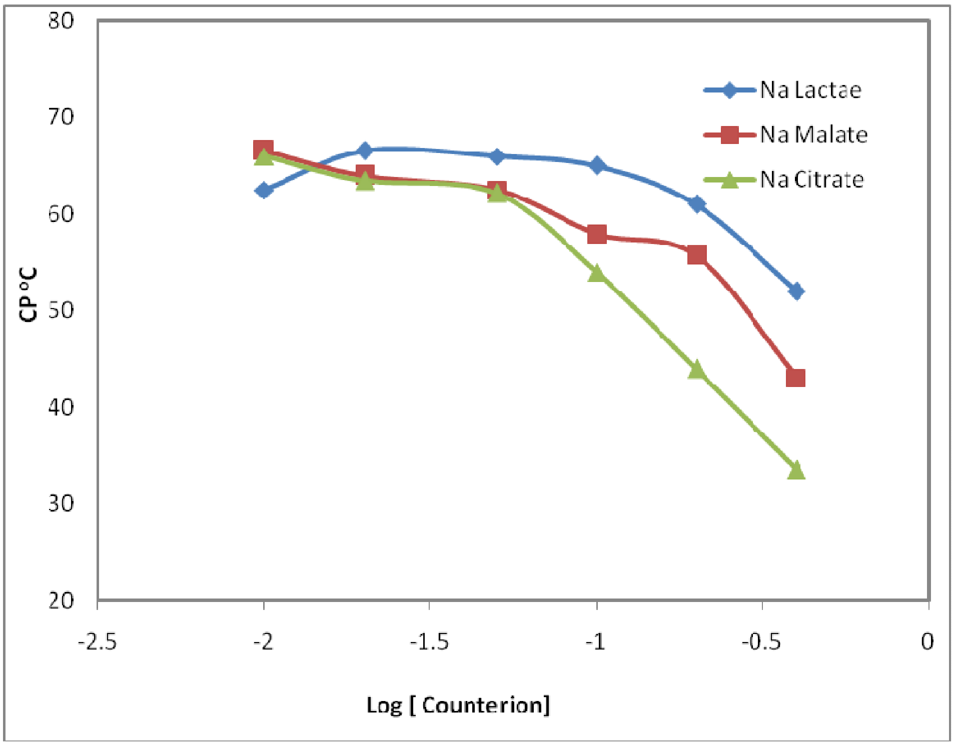


Figure 2 Cloud Points of Triton-X-100 in presence of Organic Additives

***3.2 Cloud point and Inorganic electrolytes* :-** The effect of monovalent (Na^+Cl),divalent ($Ca^{+2}Cl_2$) and trivalent ($Al^{+3}Cl_3$) basic radicals from inorganic electrolytes on CP of Triton-X-100 (1%w/v) surfactant was studied at variable concentration from 0.00,0.01,0.02,0.05,0.1,0.2 and 0.4 M . The results are given in Table 2. The CP value increases at very low concentration of electrolyte, but on further increasing concentration of electrolyte CP value decreases. The increase in CP value of surfactant at lower concentration (0.01M) is more for divalent cation than monovalent and trivalent cation. This may be due to the fact that at low concentration of electrolyte facilates the complex formation and increase the stability of complex and hence increase in CP value of surfactant system. However at higher concentration of electrolytes facilates the dehydration and decrease the stability and hence decrease in CP value of surfactant system. The extent of decrease in CP value of surfactant system at higher concentration is significantly more for trivalent, than mono and divalent anions. The decrease in CP value at higher concentration is more predominant for trivalent anions than trivalent cations (Figure 3). This may be due to charge density of anions and more dehydration, more hydrophobic interaction, decrease the stability and lowers the CP value.

Table 2 CP of Triton-X-100 in presence of Inorganic electrolytes

Triton-X-100 1% (w/v) + Inorganic Additives	CP ^{0}C at Molar Concentration of Inorganic Additives						
	0.00	**0.01**	**0.02**	**0.05**	**0.1**	**0.2**	**0.4**
NaCl	62.5	67.5	67.0	66.0	63.0	61.0	58.0
$CaCl_2$	62.5	68.5	65.5	64.0	62.5	58.5	57.0
$AlCl_3$	62.5	64.0	63.0	61.0	57.0	55.0	38.0

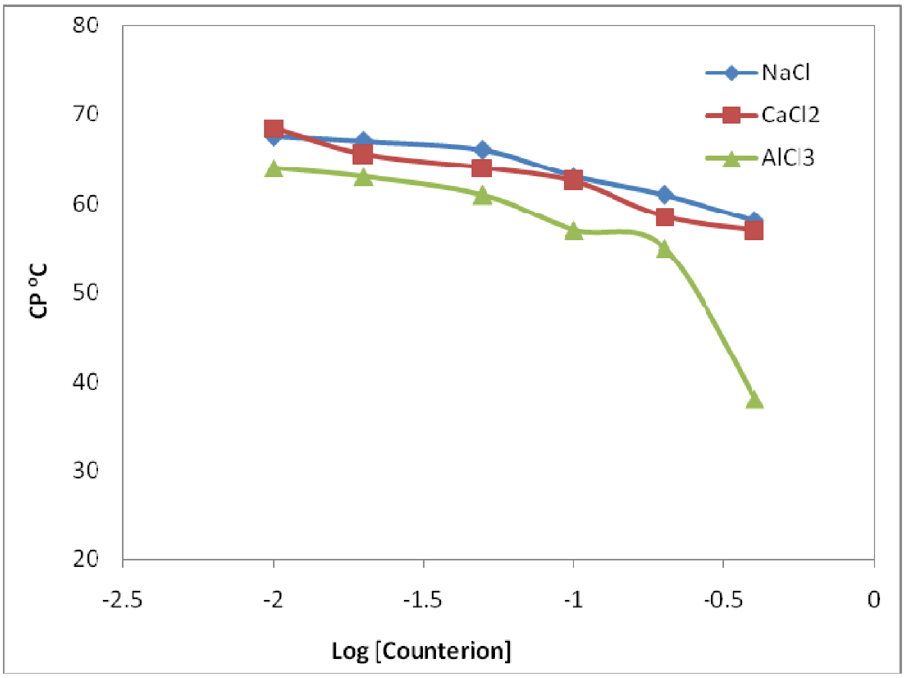


Figure 3 Cloud Points of Triton-X-100 in presence of Inorganic Additives

3.3 Thermodynamics of clouding

All physicochemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. CP is the characteristics of non-ionic surfactants. Triton-X-100 and Organic electrolyte, Triton-X-100 and Inorganic electrolytes mixed systems are given leads to the formation of cloud or turbidity at elevated temperature. In case of non-ionic surfactant the desolvation of hydrophilic groups of the surfactant 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 change (ΔG^0_{cl}), enthalpy change (ΔH^0_{cl}) and entropy change (ΔS^0_{cl}) for the clouding process have been calculated using the phase separation model [17]. The standard free energy change (ΔG^0_{cl}) is given by the equation.

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

Where “cl” stands for clouding process and $\ln X_s$ is the mole fractional solubility of the solute. The standard enthalpy change (ΔH^0_{cl}) for the clouding process is calculated from the slope of the linear plot of $\ln X_s$ vs. 1/T.

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

The standard entropy change of the clouding process ΔS^0_{cl} have been calculated from the following relationship

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

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table 3, 4,5,6,7 and 8 respectively. $\Delta H^0_{cl} > \Delta G^0_{cl}$ indicating that overall clouding process is endothermic and also $\Delta H^0_{cl} > T\Delta S^0_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy [18]. The present work would be supportive evidence regarding the probable interaction between nonionic surfactant and macromolecules, leading to the phase separation at the CP. The effect of Organic and Inorganic salts on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing.

The entropy ΔS^0_{cl} and enthalpyΔH^0_{cl} for inorganic additives are larger than organic additives. The ΔG^0_{cl} values decreases and ΔS^0_{cl} values increases with increase in the concentration of electrolytes help for the micellisation and hence decrease in CP with increase in concentration of both organic and inorganic electrolyte. This may be due to hydrophobic and ionic interaction between the surfactant and multivalent electrolyte.

Table 3 Thermodynamic parameters of Triton-X-100 in presence of Na Lactate

Triton-X-100 1% (w/v) + Na-Lactate (Molar)	**ΔG^0_{CI} kJmol^{-1}**	**ΔH^0_{CI} kJmol^{-1}**	**ΔS^0_{CI} Jmol^{-1} K^{-1}**
0.01	23.1089	67.76	133.09
0.02	21.4304		136.42
0.05	18.7990		144.43
0.1	16.7770		150.84
0.2	14.6163		159.11
0.4	12.2756		170.72

Table 4 Thermodynamic parameters of Triton-X-100 in presence of Na Malate^{-2}

Triton-X-100 1% (w/v)+di-Na-Malate (Molar)	**ΔG^0_{CI} kJmol^{-1}**	**ΔH^0_{CI} kJmol^{-1}**	**ΔS^0_{CI} Jmol^{-1} K^{-1}**
0.01	24.3411	59.49	103.50
0.02	22.2087		110.63
0.05	19.5403		119.08
0.1	17.3482		127.32
0.2	15.2890		134.47
0.4	12.7888		147.79

Table 5 Thermodynamic Parameters of Triton-X-100 in presence of Na Citrate^{-3}

Triton-X-100 1% (w/v) + Tri - Na-Citrate	**ΔG^0_{CI} kJmol^{-1}**	**ΔH^0_{CI} kJmol^{-1}**	**ΔS^0_{CI} Jmol^{-1} K^{-1}**
0.01	24.2952	41.12	49.96
0.02	22.1693		56.32
0.05	19.5060		64.48
0.1	17.1067		73.44
0.2	14.6810		83.40
0.4	11.8568		95.48

Table 6 Thermodynamic parameters of Triton-X-100 in presence of Na$^+$Cl

Triton-X-100 1% (w/v) + NaCl	**ΔG^0_{CI} kJmol^{-1}**	**ΔH^0_{CI} kJmol^{-1}**	**ΔS^0_{CI} Jmol^{-1} K^{-1}**
0.01	24.4084	201.3699	519.71
0.02	15.8830		545.55
0.05	13.2192		555.02
0.1	11.1084		566.25
0.2	8.9994		575.96
0.4	6.7610		587.94

Table 7 Thermodynamic parameters of Triton-X-100 in presence of Ca^{+2}Cl$_2$

Triton-X-100 1% (w/v) + CaCl$_2$	**ΔG^0_{CI} kJmol^{-1}**	**ΔH^0_{CI} kJmol^{-1}**	**ΔS^0_{CI} Jmol^{-1} K^{-1}**
0.01	24.4997	65.0174	118.65
0.02	22.3358		126.09
0.05	19.6619		134.59
0.1	17.6026		141.33
0.2	15.4562		149.51
0.4	13.0251		162.48

Table 8 Thermodynamic parameters of Triton-X-100 in presence of $Al^{+3}Cl_3$

Triton-X-100 1% (w/v) + $AlCl_3$	**ΔG^0_{Cl} $kJmol^{-1}$**	**ΔH^0_{Cl} $kJmol^{-1}$**	**ΔS^0_{Cl} $Jmol^{-1}K^{-1}$**
0.01	24.1555	110.5762	256.44
0.02	22.1445		263.19
0.05	19.4582		272.81
0.1	17.3075		282.63
0.2	15.2805		290.54
0.4	12.5149		315.30

CONCLUSION

The present studies are explore the influence of valency (mono, divalent, trivalent) of cations and anions on CP of nonionic surfactants Triton-X-100.

The CP value of surfactants was observed to increases up to 0.01M concentration, But CP values observed to decreases with increase in concentration of (cations and anions). The extent of decrease in CP was observed to be in order, Trivalent > divalent > Monovalent for both cations and anions from inorganic and organic electrolyte respectively. The clouding behavior of Triton-X-100 was more influenced by organic electrolytes than inorganic electrolytes. This may be due to more hydrophobic interaction between organic electrolytes and Triton-X-100.The $\Delta H^0_{cl} > \Delta G^0_{cl}$ indicating that overall clouding process is endothermic and also $\Delta H^0_{cl} > T\Delta S^0_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy.

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