

Research Article

Influence of Various Electrolytes on Clouding Behavior of A Non-Ionic Surfactant Brij-30

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Abstract

Cloud point (CP) of non-ionic surfactant Brij-30 was studied in the presence of inorganic electrolytes contain multivalent cations and monovalent anions such as NaCl, CaCl₂, AlCl₃ and organic electrolytes contain multivalent anions and monovalent cations such as Sodium-Lactate, Sodium-Malate and Sodium Citrate. The CP of Brij-30 was found to be decrease with increase in concentration of organic additives such as Sodium-Lactate, Sodium-Malate and Sodium Citrate. The extent of decrease in CP value was more significant at divalent anionic radicals than trivalent and monovalent anionic radicals. In presence of inorganic electrolytes the CP of Brij-30 was found to be increases at 0.01 M concentration and then further decreases with increase in concentration of inorganic electrolytes. The CP same trend was found was observed for all three additives. The decrease in CP with increase in concentration of radicals is entropy driven process.

Keywords: Surfactants, Non-ionic surfactants, Thermodynamic parameters, Cloud point, Additives, Brij-30

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Introduction

The non ionic surfactants are well known to their characteristic property, cloud point (CP).The cloud point is the temperature at which solvation and desolvation equilibrium are affected and surfactant solution separates into two phases, one which is surfactant rich phase and the other one the aqueous phase. The non ionic surfactant remains soluble below CP and above CP surfactant phase remain separated from aqueous phase, because of this, non ionic surfactants are useful in cloud point extractions of metal ions, organic compounds, biomolecules like amino acids, proteins and removal of higher aromatic compounds and oil from soil substrate. Cloud point extraction is also useful for extraction of bi-product from fermentation process [1, 2]. The CP of nonionic surfactants is very sensitive to the additives in the system even at very low concentration [3-5].The nonionic surfactants are useful as detergents, solubilisers and emulsifiers [6-8]. Solution properties of mixed surfactant systems have importance in industrial preparation, pharmaceutical and medicinal formulation, enhanced oil recovery process, etc [9-11]. Brij-30 is widely used in biological works, such as separation of proteins from cell membranes, [12]. 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, [13-16].Recently we have reported that, water soluble polymers such as PAA and PAM acts as cloud point modifier at very low concentration for Brij-30 and Triton-X-100 [17, 18].

In this study we have undertaken a systematic study on clouding phenomenon of nonionic surfactants Brij-30 in the presence of varying concentration of valency of ionic radicals such as cations from inorganic salts (NaCl, CaCl₂, AlCl₃) and anions from organic salts (Sodium-Lactate, Sodium-Malate, Sodium Citrate). The structure of surfactant and additives under investigation as shown in **Figure 1**.

Experimental

Materials

Nonionic surfactant Brij-30 was obtained from Loba Chemie (India).The inorganic salts (NaCl, CaCl₂, AlCl₃) was

obtained from SD fine chemicals (India) and organic salts (Sodium-Lactate, Sodium-Malate, Sodium Citrate) obtained from Sigma Aldrich (UK). Double distilled water was used for preparation of solutions.

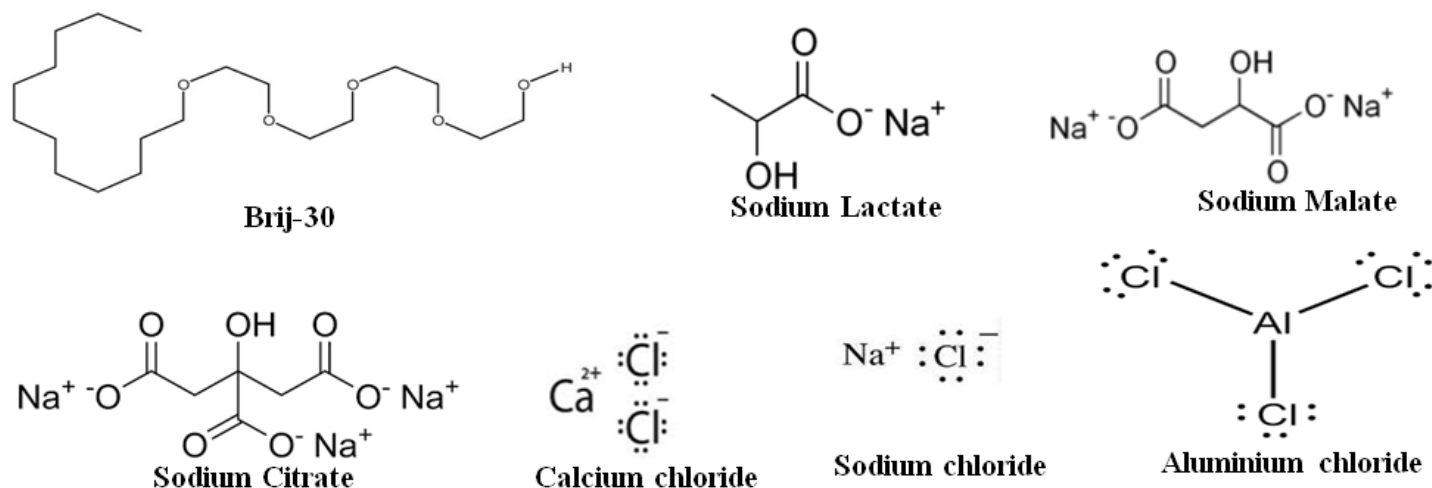


Figure 1 Molecular structures of surfactant Brij-30, Organic additives and Inorganic additives

Methods

Brij-30 has very low cloud point (CP= 7^oC) hence it is difficult to prepared its aqueous solution at room temperature. Therefore all surfactant solutions under study are prepared in 30% alcoholic solvent. The CP for all solutions of Surfactant and different additive mixture were determined by heating-cooling 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^oC per minute around the CP. The reproducibility of the measurement was found to be within ± 0.2^oC. 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**.

Table 1 CP of Brij-30 in presence of Organic electrolytes

Brij-30 1% (w/v) + Organic Additives	CP ^o 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	54	51.5	48	47	37	25
Na-Malate	62.5	13	12	8.5	8	7.5	6
Na-Citrate	62.5	46	44.5	34	30	21	16

Table 2 CP of Brij-30 in presence of Inorganic electrolytes.

Brij-30 1% (w/v) + Inorganic Additives	CP ^o C at Molar Concentration of Inorganic Aditives						
	0.00	0.01	0.02	0.05	0.1	0.2	0.4
NaCl	62.5	75	62	52	42	34	28
CaCl ₂	62.5	73	64	60	52	40	38
AlCl ₃	62.5	66	67	62	59	54	44

Result and Discussion

Cloud point and organic electrolytes

The effect of monovalent, bivalent and trivalent anionic radicals from organic electrolytes on CP of Brij-30 (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 decreases with increasing concentration of electrolyte, The CP value of Brij-30 for bivalent anion shows significant decrease than the monovalent anion and trivalent anion for all concentrations (**Figure 2**).This may be due to the higher binding or the complex formation capacity of bivalent ions. Trivalent citrate anion shows less complex formation, this may be due to the steric interaction.

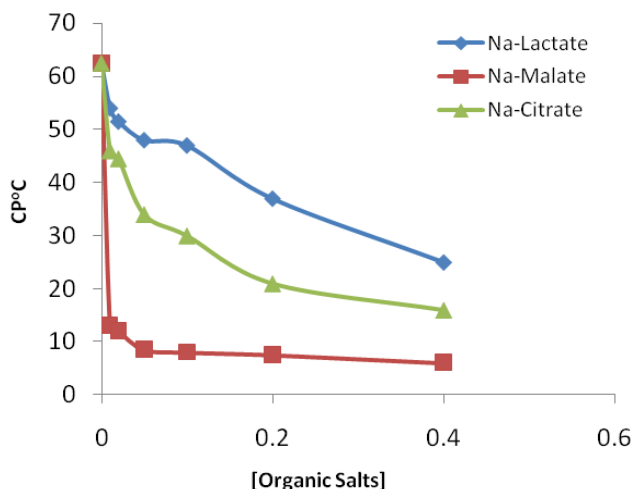


Figure 2 Cloud Points of Brij-30 in presence of Organic Additives

Cloud point and Inorganic electrolytes

The effect of monovalent (NaCl), bivalent (CaCl_2) and trivalent (AlCl_3) basic radicals from inorganic electrolytes on CP of Brij-30 (1% w/v) surfactant was studied at different 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 monovalent and divalent cation than trivalent cation. This may be due to the fact that at low concentration of electrolyte facilitates the complex formation and increase the stability of complex and hence increase in CP value of surfactant system. However at higher concentration of electrolytes facilitates 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 monovalent, then divalent than trivalent anions (**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.

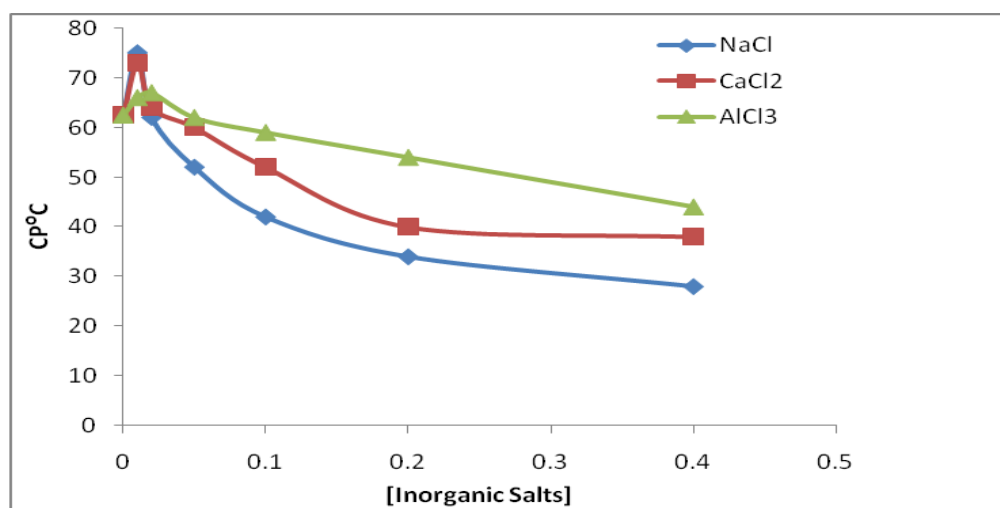


Figure 3 Cloud Points of Brij-30 in presence of Inorganic Additives

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. Brij-30 and Organic electrolyte, Brij-30 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_{cl}^0), enthalpy change (ΔH_{cl}^0) and entropy change (ΔS_{cl}^0) for the clouding process have been calculated using the phase separation model [17]. The

standard free energy change (ΔG_{cl}^0) is given by the equation.

$$\Delta G_{cl}^0 = -RT \ln X_s \quad (1)$$

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

$$d \ln X_s / dT = \Delta H_{cl}^0 / RT^2 \quad (2)$$

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

$$\Delta S_{cl}^0 = (\Delta H_{cl}^0 - \Delta G_{cl}^0) / T \quad (3)$$

The thermodynamic parameters for pure surfactant and in mixed systems are given in **Tables 3-8** respectively. $\Delta H_{cl}^0 > \Delta G_{cl}^0$ indicating that overall clouding process is endothermic and also $\Delta H_{cl}^0 > T\Delta S_{cl}^0$ indicate that the process of clouding is guided by both enthalpy and entropy. 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.

Table 3 Thermodynamic parameters of Brij-30 in presence of Na Lactate

Brij-30 1% (w/v) + Na-Lactate (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	22.5375		58.37
0.02	20.4916		65.12
0.05	17.8147	41.62	74.17
0.1	15.8975		80.40
0.2	13.5851		90.45
0.4	11.2690		101.86

Table 4 Thermodynamic parameters of Brij-30 in presence of Na Malate

Brij-30 1% (w/v) + di-Na-Malate (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	20.4996		435.37
0.02	18.7809		442.93
0.05	16.3953		456.91
0.1	14.7279	145.02	463.66
0.2	13.0470		470.48
0.4	11.2834		479.33

Table 5 Thermodynamic Parameters of Brij-30 in presence of Na Citrate

Brij-30 1% (w/v) + Tri - Na-Citrate (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	22.8620		50.44
0.02	20.8845		56.91
0.05	17.8656	38.95	68.69
0.1	15.8512		76.24
0.2	13.6156		86.18
0.4	11.5817		94.71

Table 6 Thermodynamic parameters of Brij-30 in presence of NaCl

Brij-30 1% (w/v) + NaCl (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	18.1687		36.38
0.02	15.6493		45.32
0.05	12.6735	30.83	55.87
0.1	10.4142		64.81
0.2	8.2720		73.48
0.4	6.1484		82.00

Table 7 Thermodynamic parameters of Brij-30 in presence of CaCl₂

Brij-30 1% (w/v) + CaCl ₂ (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	24.8269		40.07
0.02	22.2115		48.90
0.05	19.3983		57.94
0.1	17.0516		66.58
0.2	14.5936	38.69	76.99
0.4	12.6587		83.71

Table 8 Thermodynamic parameters of Brij-30 in presence of AlCl₃

Brij-30 1% (w/v) + AlCl ₃ (Moles)	ΔG_{cl}^0 kJmol ⁻¹	ΔH_{cl}^0 kJmol ⁻¹	ΔS_{cl}^0 Jmol ⁻¹ K ⁻¹
0.01	24.2990		103.31
0.02	22.4079		108.56
0.05	19.5167		118.81
0.1	17.4125	59.31	126.23
0.2	15.2337		134.82
0.4	12.8777		146.49

The ΔG_{cl}^0 values decreases and ΔS_{cl}^0 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. If we see the valency of electrolyte, in case of

Organic electrolyte ΔH_{cl}^0 and ΔS_{cl}^0 value of bivalent anion i.e. malate shows higher value than monovalent and trivalent anions, hence lower the CP value in presence of bivalent malate. In case of inorganic electrolyte ΔH_{cl}^0 and ΔS_{cl}^0 value increase with increase in valences of cationic radicals, hence CP value decreases with valences of cationic radicals.

Conclusion

The present studies are exploring the influence of valency of cationic and anionic radicals on CP of nonionic surfactant Brij-30.

The CP value of surfactant was easily tuned by changing the type, valencies and concentration of electrolytes. The CP values observed to decreases with increase in concentration for both organic and inorganic electrolytes except 0.01 M concentration for inorganic electrolyte. The change in CP value with valency of electrolyte radicals were observed in reverse trend, for organic electrolytes CP values decreases with increase in valencies of anionic radicals except bivalent anions shows significant decrease in CP value. While in inorganic electrolytes CP values was observed to increase with increase in valency of electrolytes. The overall clouding phenomenon of surfactant in presence of electrolyte are endothermic and entropy driven process.

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