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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 $NaCl$,$CaCl_2$,$AlCl_3$ 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 ($NaCl$,$CaCl_2$,$AlCl_3$) 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 ($NaCl$, $CaCl_2$, $AlCl_3$) 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.

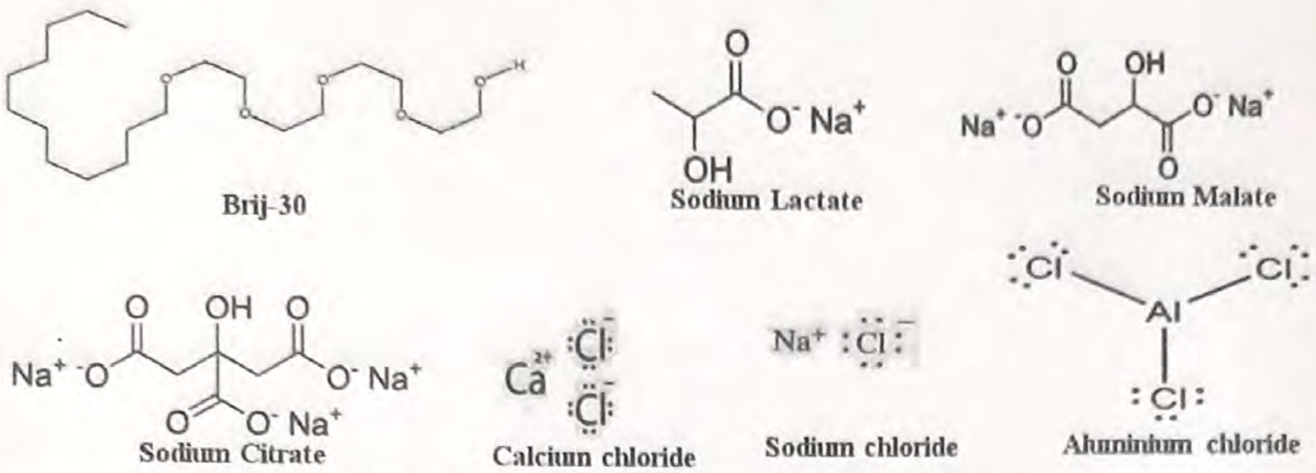


**Figure 1** Molecular structures of surfactant Brij-30, Organic additives and Inorganic additives

*Methods*

Brij-30 has very low cloud point (CP= 7$^0$C) 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$^0$C per minute around the CP. The reproducibility of the measurement was found to be within ± 0.2$^0$C. 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) + | CP $^0$C at Molar Concentration of Organic Additives | | | | | | |
|---|---|---|---|---|---|---|---|
| **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) + | CP $^0$C at Molar Concentration of Inorganic Aditives | | | | | | |
|---|---|---|---|---|---|---|---|
| **Inorganic Additives** | **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.

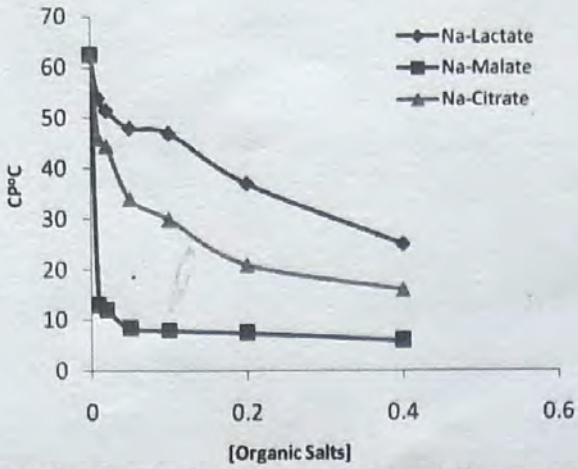


**Figure 2** Cloud Points of Brij-30 in presence of Organic Additives

***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 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 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.

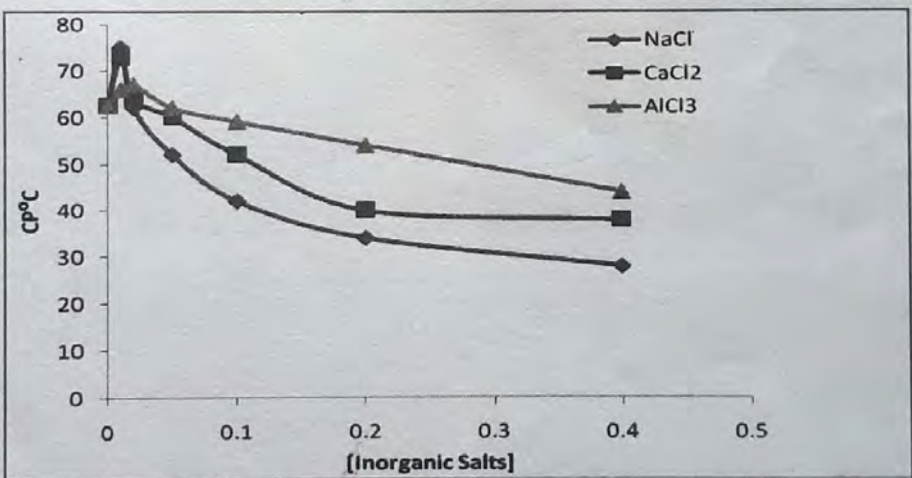


**Figure 3** Cloud Points of Brij-30 in presence of Inorganic Additives

***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 ($\Delta G^0_{cl}$), enthalpy change ($\Delta H^0_{cl}$) and entropy change ($\Delta S^0_{cl}$) for the clouding process have been calculated using the phase separation model [17]. The

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standard free energy change ($\Delta G^0_{cl}$) is given by the equation.

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

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

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

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

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

The thermodynamic parameters for pure surfactant and in mixed systems are given in **Tables 3-8** 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.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) | $\Delta G^0_{Cl}$ kJmol$^{-1}$ | $\Delta H^0_{Cl}$ kJmol$^{-1}$ | $\Delta S^0_{Cl}$ 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) | $\Delta G^0_{Cl}$ kJmol$^{-1}$ | $\Delta H^0_{Cl}$ kJmol$^{-1}$ | $\Delta S^0_{Cl}$ 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) | $\Delta G^0_{Cl}$ kJmol$^{-1}$ | $\Delta H^0_{Cl}$ kJmol$^{-1}$ | $\Delta S^0_{Cl}$ 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) | $\Delta G^0_{Cl}$ kJmol$^{-1}$ | $\Delta H^0_{Cl}$ kJmol$^{-1}$ | $\Delta S^0_{Cl}$ 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 $CaCl_2$

| Brij-30 1% (w/v) + $CaCl_2$ (Moles) | $\Delta G^0_{cl}$ $kJmol^{-1}$ | $\Delta H^0_{cl}$ $kJmol^{-1}$ | $\Delta S^0_{cl}$ $Jmol^{-1}K^{-1}$ |
|---|---|---|---|
| 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 $AlCl_3$

| Brij-30 1% (w/v) + $AlCl_3$ (Moles) | $\Delta G^0_{cl}$ $kJmol^{-1}$ | $\Delta H^0_{cl}$ $kJmol^{-1}$ | $\Delta S^0_{cl}$ $Jmol^{-1}K^{-1}$ |
|---|---|---|---|
| 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 $\Delta G^0_{cl}$ values decreases and $\Delta S^0_{cl}$ 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. If we see the valency of electrolyte, in case of

Organic electrolyte $\Delta H^0_{cl}$ and $\Delta S^0_{cl}$ 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 $\Delta H^0_{cl}$ and $\Delta S^0_{cl}$ 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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