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Research Article

Thermodynamic of Clouding Behavior of Non-ionic Surfactant, Polyoxyethylene (10) Cetyl Ether (Brij-56) With and Without Non-polar Additives

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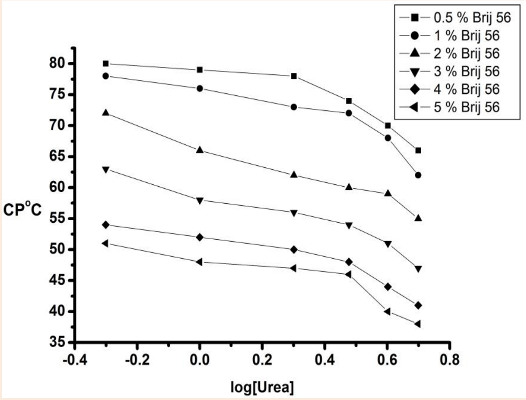
Abstract

Cloud point (CP) data have been acquired for non-ionic surfactant, Poly oxyethylene (10) Cetyl Ether (Brij-56) with and without additives urea and acetamide. The energetics of clouding process, standard Gibbs free energy change (ΔG^0_{C1}), standard enthalpy change (ΔH^0_{C1}) and standard entropy change (ΔS^0_{C1}) were evaluated. The release of solvated water from the clouding component causes the phase separation. Hence CP was taken as the limit of its solubility. The phase separation results from micelle-micelle interaction. Considering cloud point as threshold temperature of the solubility. The energetic of clouding process ΔG^0_{C1}, ΔH^0_{C1} and ΔS^0_{C1} have been evaluated using "Phase Separation Model". The ΔH^0_{C1} of pure Brij-56 was -38.285kJ mol^{-1} and ΔS^0_{C1} was decreases from -182.36 to -170.408 J mol^{-1}K^{-1}with increases in concentration of Brij-56 from 0.5 to 5wt%. The addition of urea and acetamide results in decrease of ΔG^0_{C1}, ΔH^0_{C1} and ΔS^0_{C1} than pure Brij-56. It is found that the overall clouding is exothermic and $\Delta H^0_{C1} > \Delta S^0_{C1}$ indicating that the process of clouding is guided by both enthalpy and entropy. This work supports the conjecture that the CP is critical phenomenon rather the growth of micelles.



Keywords: Thermodynamics of clouding, Cloud point, Non-ionic surfactant, Brij 56, Urea, Acetamide, Phase separation model

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Introduction

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids or that between a liquid and a solid. There is a broad range of different surfactant types, each having unique properties and characteristics, Depending on the type of charge of the head, surfactants belong to be anionic, cationic, non ionic, amphoteric or Zwitterionic family. Surfactant or detergents are amphiphilic materials having potential application in the solubilization of insoluble substrate in aqueous or non aqueous solvents. Non-ionic surfactant solutions have the property to undergo clouding on heating, followed by phase separation into two isotropic phases [1]. This separation is reversible when the system is cooled. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloud by appearance.

The cloud point is an important characteristic property of non-ionic surfactants. Anionic surfactants are more water soluble than non-ionic surfactants due to the presence of negatively charged head and typically exhibits higher cloud points. The presence of additives in the formulation of surfactant can affect the cloud point of the mixture. Nonionic surfactant is a different class of surfactant that about 45% of the total surfactant production worldwide. They do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ester, ether or amide. A large proportion these non-ionic surfactants are made hydrophilic by the presence of a polyethleneglycol chain, obtained by the poly condensation of ethylene oxide. They are called polyethoxylated non-ionic. Some common non-ionic surfactants are Triton-X-100 cetyl alcohol, lauryl glucoside, Brij-56, Brij-57, Brij 58, Brij-35 etc.

Cloud points (CP) are the characteristics of non-ionic surfactant systems. Cloud points are the manifestation of the solvation or desolvation phenomenon in non-ionic surfactant solutions [2-3]. The desolvation of the hydrophilic groups of the surfactant leads to the formation of cloud in the surfactant solution. Kjellander et al [2] stated that the appearance of cloud point is entropy dominated. At the cloud point, the water molecules get totally detached from the micelles. The overall entropy is very high and hence the free energy change is relatively more negative [4] and the appearance of the cloud point is facile. The effects of different additives on the CP behavior of polymers [5] and non-ionic surfactants have been investigated [6]

In this present communication, we are reporting the CP and thermodynamic data of clouding phenomenon in non-ionic surfactant, Brij solutions in the presence and absence of additives Urea and Acetamide at various concentrations. 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 $\Delta G^0_{C1,}$ ΔH^0_{C1}, ΔS^0_{C1} have been evaluated using a "Phase Separation Model".

Experimental

Materials and Methods

Non-ionic surfactant Brij-56 was obtained from Sigma Aldrich, USA, having M.Wt. 682 g/mol and it was used as received. The additives urea and acetamide was the product of Sigma Aldrich, USA, (Urea Mol.wt. 60.60 and Acetamide Mol. Wt. 59.07 g/mol). Both the additives are dialyzed to remove low molecular weight fractions and other associated electrolytic impurities before use. Deionized doubly distilled water having a specific conductivity in the range 1-2x10^{-6} S cm^{-1}, at 303.15 K was used in the preparations of all solutions of different concentrations.
The CP was measured by visual observations and of the abrupt change in the appearance of the surfactant solution from being clear to the first turbidity [7]. Pure Brij-56 solutions of different concentrations containing the mixed additives were equilibrated at room temperature for one hour before measuring the cloud point temperature.

The cloud point of a micellar solution of pure Brij-56 non-ionic surfactant and with mixed systems was determined by visual observation of the temperature at which the clear solution turns turbid upon being heated up and vice versa on cooling. The samples were heated at a rate of 1^0C min^{-1}. After the temperature exceeded the CP, the solution was cooled below the CP temperature and then it was heated again to check the reproducibility of the measurement. The maximum uncertainty in the CP measurement was ± 0.5^0C [8].

Clouding Species

Non-ionic Surfactant –

$C_{16}H_{33}(-OCH_2-CH_2)_n$ OH
n = 10
Polyoxyethylene (10) Cetyl Ether (Brij-56) Mol : wt. 682 g/mol

Additives

a) Urea :- Mol. Wt. 60.60 g/mol.
Molecular formula CH_4N_2O $NH_2–CO–NH_2$

b) Acetamide – Mol. Wt. 59.07 g/mol
Molecular formula C_2H_5NO CH_3-CO–NH_2

Result and Discussion

Cloud Points (CP) of Pure Brij-56

The cloud points of pure Brij-56, non-ionic surfactants at different concentrations 0.5 to 5wt% are given in Table 1. The CP of the surfactant was found to be decreased from 81 to 52^{0}Cwith increase in concentration of Bj-56 from 0.5 to 5wt%. This is due to increase in micelle concentration. The phase separation occurs due to micelle-micelle interaction. It is also observed that below 0.5 wt% there is mild decreased in cloud point. This is mainly due to lower concentration of surfactant moiety required to from agglomerate of visible micelle. The results are shown in Table 1.

Table 1 CP of Brij 56 pure Non-ionic surfactant at different concentration (wt %)

[Brij 56] wt %	Molarity $x10^{-3}$	Mole fraction X_s $x10^{-4}$	lnX_s	CP /^{0}C
0.5	0.733	1.318	-8.933	81
1	1.466	2.636	-8.241	79
2	2.932	5.271	-7.548	74
3	4.398	7.905	-7.142	70
4	5.865	10.538	-6.855	56
5	7.331	13.168	-6.632	52

Cloud points (CP) Brij-56 - Urea system:

The influence of urea (Mol. wt. 60.60) on the, cloud point of Brij-56 from 0.5 to 5wt% has been studied. The results are given in Table 2 and Figure 1. These results indicating that the cloud point of Brij-56 declined considerable with increase in concentrations of urea from 0.5 to 5wt%. CP of 0.5 wt% Brij-56 decreases from 80^{0}C to 66^{0}C with an increase in the concentration of urea from 0.5 to 5wt%. Similarly CP of 5 wt% Bj-56 decreases from 51 to 38^{0}C with increase in concentrations of urea from 0.5 to 5wt% (Figure 1). This is mainly due to increase micelle concentrations. The influence of Urea on the cloud point of Brij-56 is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing [9, 10]

Table 2 Influence of [Urea] on CP °C of Brij 56

[Brij 56] wt %	[Urea] wt %					
	0.5	1	2	3	4	5
0.5	80	79	78	74	70	66
1	78	76	73	72	68	62
2	72	66	62	60	59	55
3	63	58	56	54	51	47
4	54	52	50	48	44	41
5	51	48	47	46	40	38

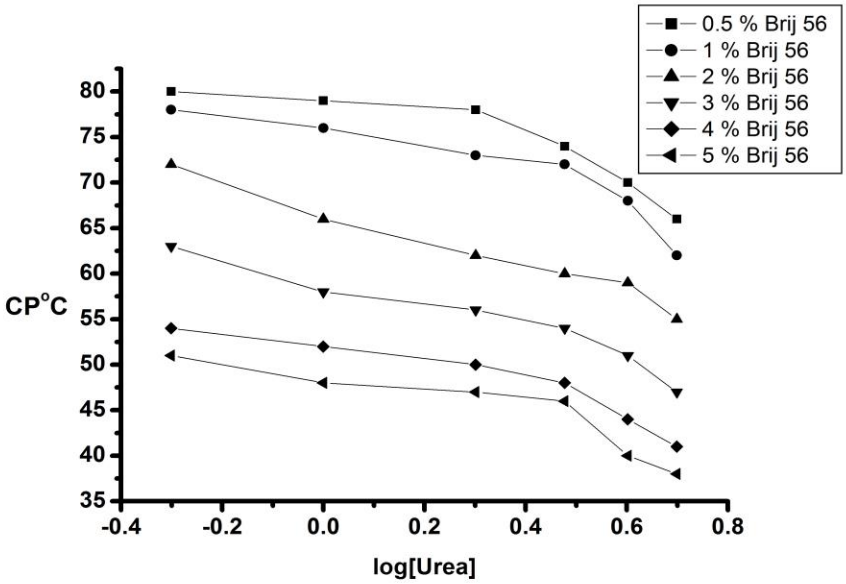

Figure 1 CP Vs log [Urea] at different Brij 56 [0.5 to 5 wt %]

Cloud points (CP) Brij-56 - Acetamide system

The influence of Acemide (Mol.wt. 59.07) on the CP of Brij-56 from 0.5 to 5wt% has been shown in Figure 2. The results are given in Table 3. These results indicating that the cloud point of Brij-56 declined considerable with increase in concentrations of Acetamide from 0.5 to 5wt% for all the concentrations of Brij-56 studied. The CP of 0.5 wt% of Brij-56 decreases from 76^{0}C to 61^{0}C with an increase in the concentration of acetamide from 0.5 to 5wt%. Similarly CP of 5wt% Bj-56 decreases from 51 to 34^{0}C with increase in concentrations of acetamide from 0.5 to 5wt% (Figure 2) which is in conformity with earlier findings [9]. This is mainly due to increase micelle concentrations. The influence of urea and acetamide on the cloud point of Brij-56 is a clear indication the phenomenon of clouding is associated with the different micelles coalescing [10]. The decrease in CP of 0.5 to 5 wt% of Brij-56 was more with addition of acetamide than urea of same concentration.

Table 3 Influence of [Acetamide] on CP °C of Brij 56

[Brij 56]	**[Acetamide] wt %**					
wt %	**0.5**	**1**	**2**	**3**	**4**	**5**
0.5	79	76	74	69	66	61
1	76	73	71	65	64	60
2	64	61	60	58	54	50
3	59	56	52	47	42	40
4	54	51	45	43	41	35
5	51	47	44	37	36	34

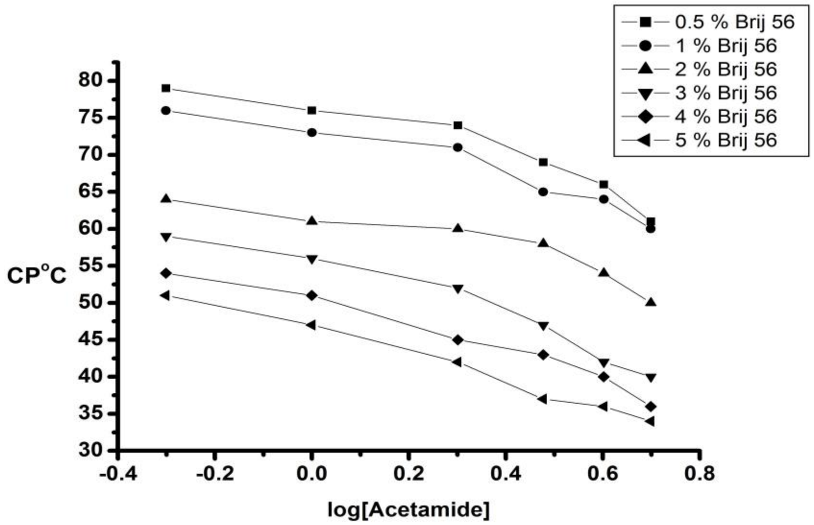

Figure 2 CP Vs log [Acetamide] at different Brij 56 [0.5 to 5 Wt %]

Thermodynamics of Clouding

Table 4 Thermodynamic parameters of solubilization of pure Brij 56

[Brij 56] wt %	ΔG^0_{cl} kJmole^{-1}	$-\Delta H^0_{cl}$ kJmole^{-1}	$-\Delta S^0_{cl}$ Jmole^{-1}K^{-1}
0.5	26.30		182.36
1	24.13		177.240
2	21.78	38.285	173.038
3	20.37		170.954
4	19.04		171.566
5	18.31		170.408

Table 5 Thermodynamic parameters of [Brij 56] in presence of [Urea]

[Urea] wt %	ΔG^0_{cl} kJmole^{-1}	$-\Delta H^0_{cl}$ kJmole^{-1}	$-\Delta S^0_{cl}$ Jmole^{-1}K^{-1}
0.5	19.12	27.72	24.34
1	17.04	27.58	29.90
2	14.98	28.30	37.92
3	13.65	28.84	83.09
4	12.68	26.42	40.05
5	11.91	28.66	49.39

All physicochemical processes are energetically controlled. The spontaneous formations of micelle are obviously guided by thermodynamic principles. Cloud points are the characteristics of non-ionic surfactants. Thermodynamic parameters of solubilization of pure Brij-56 are given in Table 4 and Brij-56 -Urea, Brij-56 -Acetamide mixed systems are given in Table 5 and 6 respectively.

Table 6 Thermodynamic parameters of [Brij 56] in presence of [Acetamide]

[Acetamide] wt %	**ΔG^0_{cl} kJmole^{-1}**	**$-\Delta H^0_{cl}$ kJmole^{-1}**	**$-\Delta S^0_{cl}$ Jmole^{-1}K^{-1}**
0.5	18.99	31.08	34.31
1	16.83	29.78	37.09
2	14.74	26.35	33.45
3	13.38	25.41	35.16
4	12.46	25.37	38.09
5	11.66	25.84	42.41

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" The following relation can be written as –

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

Where "cl" stands for clouding process and $\ln X_s$ is the mole fraction 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 $\ln X_s$ Vs1/T of all the concentrations in (Figure 3, 4, and 5)

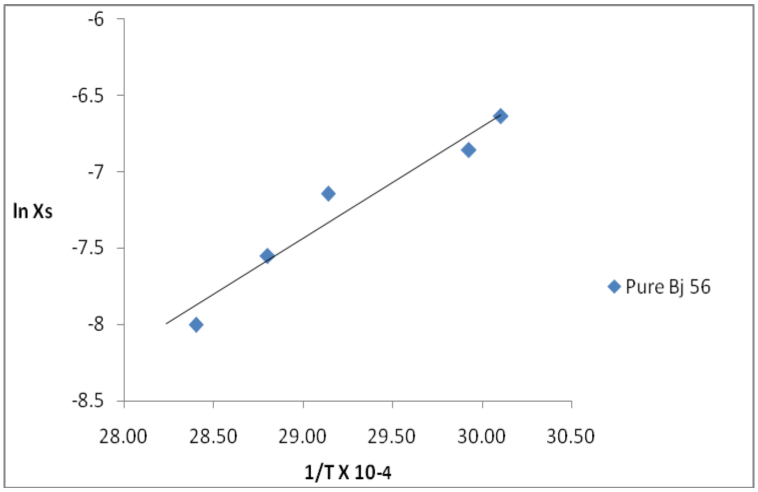

Figure 3 ln Xs Vs 1/T X 10^{-4} for pure Brij 56

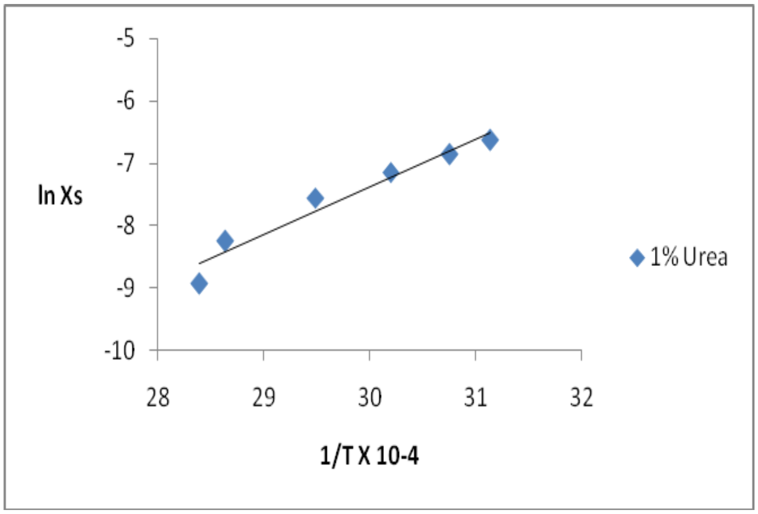

Figure 4 ln Xs Vs 1/T X 10^{-4} for 1% Urea

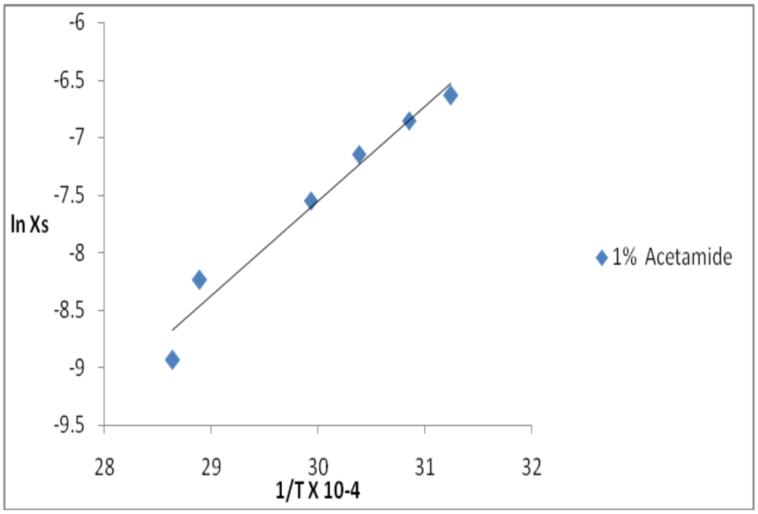

Figure 5 ln Xs Vs 1/T X 10^{-4} for 1% Acetamide

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

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

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

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table 4 and Table 5, 6 respectively. The ΔH^0_{C1} of pure Brij-56 was -38.285 kJ mol^{-1}, ΔS^0_{C1} and ΔG^0_{cl} was decreases from -182.36 to -170.408 J mol^{-1}K^{-1} and 26.30 to 18.31 kJ mol^{-1} respectively with increases in concentration of Brij-56 from 0.5 to 5wt%. The addition of urea results in to decrease in ΔG^0_{C1} from 19.12 to 11.91 kJ mol^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt% The increase in ΔH^0_{C1} from -27.72 to -28.84 kJ mol^{-1} with increases in concentration of Brij-56 from 0.5 to 3 wt%, while ΔS^0_{cl} increase from -24.34 to -49.39 J mol^{-1}K^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt%. The addition of acetamide results in to decrease in ΔG^0_{C1} from 18.99 to 11.66 kJ mol^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt% The decrease in ΔH^0_{C1} from -31.08 to -

25.84 kJ mol^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt%, while ΔS^0_{cl} increase from -34.31 to -42.41 J mol^{-1}K^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt%. $\Delta H^0_{cl} < \Delta G^0_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H^0_{cl} > T\Delta S_{cl}$ 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 non ionic surfactants and additive molecules, organic compounds leading to the phase separation at the cloud point. The effect of urea and acetamide on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing.

Conclusions

It was observed that cloud point of Brij-56 was decreases with increases in concentration from 0.5 to 5 wt% this may be due to increased micelle concentration. The CP of Brij-56 decreases with addition of urea and acetamide from 0.5 to 5 wt%. The decrease in CP of Brij-56 was more with addition of acetamide than that of urea of same concentration. The energetic of clouding process found to be exothermic and $\Delta H^0_{cl} > \Delta S^0_{cl}$ indicating that the process of clouding is guided by both enthalpy and entropy. The ΔH^0_{C1} of pure Brij-56 was -38.285 kJ mol^{-1}, The standard free energy change of clouding ΔG^0_{cl} decreases from 26.30 to 18.31 kJmole^{-1} with increase in concentration of Brij-56 from 0.5 to 5wt%. Also ΔS^0_{C1} was decreases from -182.36 to -170.408 J mol^{-1}K^{-1} with increases in concentration of Brij-56 from 0.5 to 5wt%.

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