Effect of molecular weight of PEG on the cloud point of Polyoxyethylene (10) oleyl ether (Brij-97). - A Thermodynamic approach

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ABSTRACT

The cloud point (CP), temperature for aqueous solution of Polyoxyethylene (10) oleyl ether (Brij-97) and in the presence of added polymer PEG_{4000} and PEG_{6000} at various concentrations was investigated. It is observed that CP of Brij-97 decreases with increasing concentration. At fixed concentration of surfactant the cloud point of Brij-97-PEG_{4000} mixed system shows decreasing order/trend with increasing concentration of PEG_{4000}, while the cloud point of Brij-97-PEG_{6000} mixed system shows increasing trend with increasing concentration of PEG_{6000}.

The thermodynamic parameters of these pure and mixed systems are determined at different additive concentrations. The standard Gibb's free energy, enthalpy and entropy were found to be positive for both PEG_{4000} and PEG_{6000}. The overall clouding process was endothermic and non-spontaneous. The CP of pure Brij-97 was found to be decreased from 56.2 to 54.5 with increasing concentration of Brij-97 from 0.5% to5%. The cloud point of mixed system shows decreasing trends with increasing concentration of Brij-97.

Key Words:- Cloud point, nonionic surfactant, phase separation model thermodynamic parameters.

INTRODUCTION:-

The interactions between water-soluble polymers and surfactants have long been a subject of intensive research, mainly due to their wide applications in various fields such as cosmetics, paints and coatings, adhesives and glues, lubricants, photographic films, food and pharmaceutical products [1]. Study of nature of polymer surfactant interaction both in bulk aqueous solution and at air water interface will helpful in the manufacture of such products. Several research workers have been studied the interaction between surfactant and water soluble polymer [2-17]. These interactions can be either associative, due to an attraction between the surfactant and polymer, or segregative, due to an repulsion between surfactant and polymer. Any of this type of interaction can affect several physicochemical properties of both species. One of the most important ways to study the interaction in nonionic surfactant aqueous solutions is to find out the changes of cloud point of aqueous solutions, because the CP is a indication of the association of surfactant with water and can be affected by the addition of a third species like polymer in to the system[18].

Surfactants and water-soluble polymers are used together in order to boost the properties of the surfactant by the added polymer, and vice versa, or in order to produce properties that none of the surfactant or polymer possesses when used alone [19]. Amphiphiles are the molecules consisting of one water attracting moiety, i.e., hydrophilic, and other water repelling or oil attracting moiety, called as hydrophobic or lipophilic. Non ionic surfactants are wiely use in the textile, detergent and cosmetic industries. Due to high hydration of oxyethylene chains non ionic surfactant are soluble in water [20]. Since hydrogen bonding is temperature sensitive phenomenon, heating of aqueous surfactant solutions to a particular temperature results in appearance of turbidity due to incomplete solubility. This temperature is called 'Cloud Point' temperature at which phase separation occurs [4,5]. The phase separation is reversible and is due to the sharp increase in the aggregate number of micelles and surfactant loss all or some of its functions above cloud point. [7,8] . Cloud point is very sensitive to the presence of additives at very low concentration. The additives modify the surfactant solvent interaction and change the critical micelle concentration (cmc), the size of the micelles and the phase behavior in the surfactant solutions [12, 21].

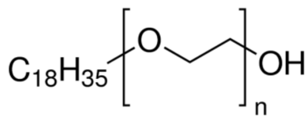
Clouding behavior, also known as lower consulate behavior or coacervate phase behavior is a typical physical change in which homogenous solutions of amphiphilic substances, due to which the solution separates' in to a surfactant rich and surfactant poor phase at a definite temperature at which phase separation occurs. Aqueous solutions of several nonionic and zwitterionic surfactants when heated or cooled exhibit clouding phenomena, which depend on the nature and concentration of the amphiphile [22]. Surfactants are often added to polymer solutions to alter the rheological properties and to enhance the stability of dispersions [23]. In general, polymers are added to the systems to control rheology, stability, and to manipulate surface adsorption. Interactions within the mixture are driven by hydrophobic, dipolar, and electrostatic forces [24].

In this paper we have investigated the effect of water soluble polymer PEG_{4000} and PEG_{6000} on the cloud point (CP) of the non ionic surfactant Brij-97 in aqueous solution. The thermodynamic parameters of these mixtures were calculated at different surfactant and polymer concentrations.

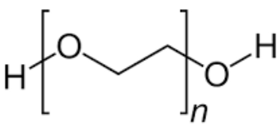
EXPERIMENTAL SECTION

Materials

The structures of non-ionic surfactant Poly(oxyethylene) 10 olyel ether (Brij-97) $C_{18}H_{35}(OCH_2CH_2)_nOH$. (n=10) and polymer, Poly ethylene glycol (PEG_{4000}) and Poly ethylene glycol (PEG_{6000}) are shown in fig. 1(a) and fig. 1 (b) respectively, was obtained from Sigma-Aldrich, USA (purity>99%) was used without further purification. Doubly distilled water with specific conductance 2.4µScm^{-1} at 303.15K was used in the preparation of all solutions of different concentrations.



⟹ Poly(oxyethylene) 10 olyel ether = [Brij-97]



⟹ Poly Ethylene Glycol [PEG]

$H-(O-CH_2-CH_2)_n-OH$

Figure 1: Molecular structure of non-ionic surfactant
(a) Brij-97 and additives polymers (b) PEG

Methods

Cloud point temperatures of surfactant solution were determined by visual observation and the abrupt change in the appearance of the surfactant solution, which occurs during the heating of the sample solutions. The cloud point (CP) was determined by controlled heating of the sample solutions in a thin glass tube immersed in a beaker containing water; the sample solution was stirred while being heated. The heating rate of the sample was < 1^0C/min. The reproducibility of the measurement was found to be within ± 0.2^{0}C.The cloud point (CP) was determined by controlled heating in well-stirred surfactant solution as well as the surfactant – PEG_{4000} and surfactant – PEG_{6000} mixture until it clouded or got turbid. 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 test solution. Heating and cooling were regulated to about 1^{0}C/minute.

RESULT AND DISCUSSION

Cloud points (CP) of Brij-97

The cloud point of Brij-97 pure nonionic surfactant at different concentrations in (wt %) are given in table 1. The CP of Brij-97 is mostly constant over a wide range of concentration. When the solutions are heated sufficiently, the POE chains become dehydrated, and the solubility of the surfactant decreases markedly, and thus CP decreases from 56.2^{0}C to 54.5^{0}C with increase in the concentration of surfactant from 0.5 to 5 wt.%.

As the concentration of surfactant solution increases the micellar molecular weight increases, as a result, the aggregation number of micelles increases, hydrophobicity increases and thus cloud point decreases. The variation of lnXs Vs. 1/Tx10^{-4} of Brij-97 is shown in fig.2.

Table 1 Cloud point of Brij-97 at different concentration (wt.%)

Brij-97 wt.%	Molarity x10^{-2}	Mole fraction x10^{-4}	-lnXs	CP / ^{0}C
0.5	0.7052	1.2756	8.9669	56.2
1	1.4104	2.5643	8.2688	55.6
2	2.8209	5.1789	7.5657	55.5
3	4.2313	7.8459	7.1503	55.2
4	5.6417	10.567	6.8526	54.8
5	7.0522	13.344	6.6192	54.5

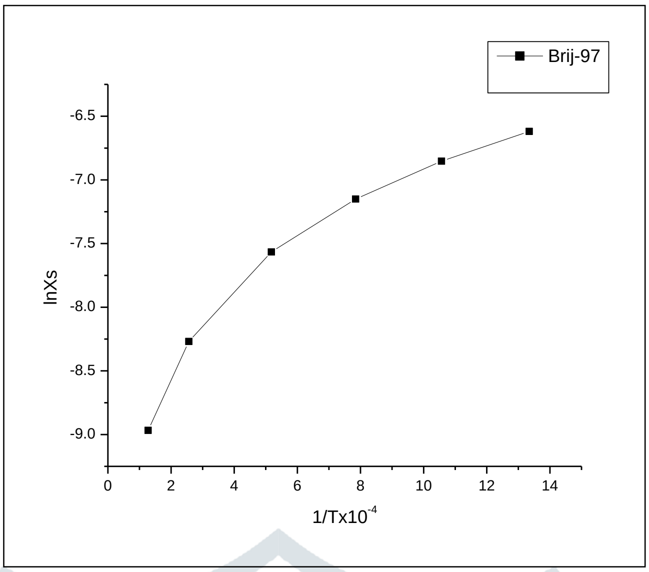


Figure 2: Variation of lnXs Vs. $1/Tx10^{-4}$ of Brij-97.

Cloud point (CP) of Brij-97–PEG_{4000} system

The influence of PEG (Mol.wt.4,000) on the CP of Brij-97 at different concentration have been studied. The results are given in table 2. These results were indicating that the cloud point of surfactant polymer mixtures decreases with increasing concentration of surfactant. For 0.5 wt% of Brij-97 CP decreases from 56.2 to 52.2^0C with increasing concentration of PEG_{4000} from 0.005 to 0.05 wt% of PEG_{4000}. While for 1% to 5% of Brij-97 CP decreases considerably with increasing concentration of PEG_{4000} from 0.005 to 0.5wt%. As the surfactant concentration increases in surfactant–polymer mixture, the size and hence molecular weight of micelle increases which increases the aggregation number and hydrophobicity of micelle, and thus the cloud point of the mixed system decreases. It has been observed that, with increase in concentration of $PEG_{4,000}$, at fixed concentration of surfactant the CP decreases, this is probably due to the increase in chain length of polyoxyethyle chain by the addition of polymer. Addition of PEG to the binary mixture develops attractive interactions between micelles (depletion interaction). These interactions dominates and decreases the phase separation temperature (CP) of aqueous solution of polymer-surfactant as compared with the aqueous solution of surfactant alone.

Table 2: Influence of PEG (MW=40 00) on CP of Brij-97

Brij-97 (wt%)	PEG_{4000} (wt%)						
	0.000	0.005	0.01	0.02	0.03	0.04	0.05
0.5%	56.2	56.2	55.4	54.5	53.6	53.0	52.2
1%	55.6	55.3	53.6	52.4	52.0	51.7	51.1
2%	55.5	53.8	51.8	50.5	49.6	48.5	48.0
3%	55.2	52.6	50.4	49.0	48.3	47.6	47.1
4%	54.8	51.5	49.2	48.1	47.4	46.6	45.2
5%	54.5	49.4	48.6	47.1	46.0	45.5	44.0

*MW = Molecular Weight

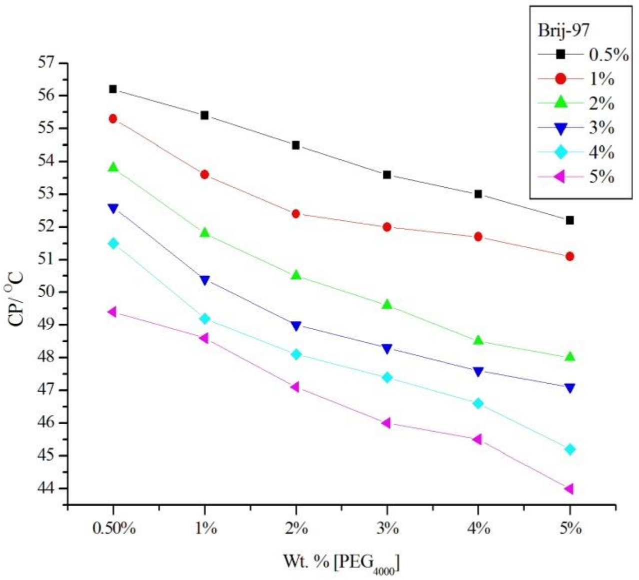


Figure 3: Effect of [PEG4000] on CP of Brij-97.

It has been found that at low concentration of PEG below 0.005wt% did not have much effect on the CP of pure Brij-97 and it remains around 56^0C. The decrease in CP with the addition of PEG_{4000} in Brij-97 may be due to the formation of intra chain polymer-surfactant complex by incorporation of PEG into Brij-97, which results into the attraction of micelles and facilitates their collisions and thus lowering of CP[18]. The influence of [PEG_{4000}] on CP of Brij-97 is shown in fig 3.

The cloud point of the Brij-97-PEG_{6000} system

The influences of PEG (Mol.wt.6000) on the Cp of Brij-97 at different concentration have been a studied. The results are given in table 3. These results were indicating that the cloud point of surfactant polymer mixtures decreases with increasing concentration of surfactant and increases with increasing concentration of PEG_{6000} at a fixed concentration of surfactant. This decrease in CP is because as the surfactant concentration increases in a pure and mixed system with the constant concentration of PEG_{6000}, the hydrophobicity, molecular weight and aggregation number of the micelle formed increases which decrease the surface energy [13,19].

Table 3: Influence of PEG (MW=6000) on CP of Brij-97

Brij-97 (wt%)	PEG $_{6000}$ (wt%)						
	0.000	0.005	0.01	0.02	0.03	0.04	0.05
0.5%	56.2	64.5	66.5	67.5	68.0	68.5	69.5
1%	55.6	58.5	59.0	59.5	60.0	60.5	62.0
2%	55.5	54.5	55.0	55.5	56.0	56.5	57.5
3%	55.2	52.5	53.5	54.0	55.0	55.5	56.0
4%	54.8	49.5	50.5	51.5	52.5	53.5	54.5
5%	54.5	48.0	48.5	49.0	50.5	51.0	52.0

While the increase in the concentration of PEG_{6000} with a fixed concentration of surfactant, the CP of a mixed system increases indicating that addition of PEG decreases the hydrophobicity of the solution, thereby aggregation takes place at higher temperature [19, 25]. The influence of [PEG_{6000}] on CP of Brij-97 is shown in figure 4.

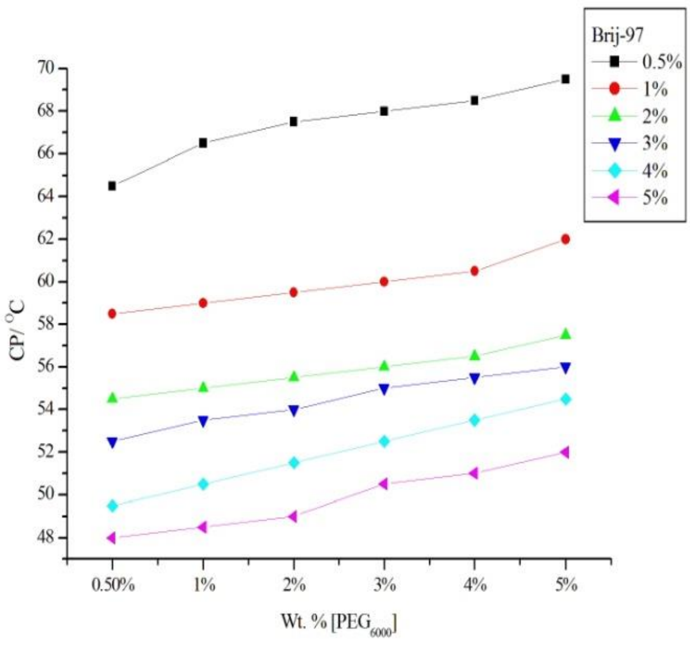


Figure 4: Effect of [PEG6000] on CP of Brij-97.

Thermodynamics of clouding

All physicochemical processes are controlled energetically, and the micelle formation of the surfactant molecules is guided by the thermodynamic principles. Considering CP as the phase separation point, hence limit of solubility, the thermodynamic parameters of clouding process such as standard free energy change (ΔG^0_{Cl}), standard enthalpy change (ΔH^0_{Cl}) and standard entropy change (ΔS^0_{Cl}) were calculated using the phase separation model [25] as given below

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

Where 'Cl' stands for clouding process and lnXs is the mole fraction of the solute. R is the gas content ($J.K^{-1}.M^{-1}.$), and T is the temperature in Kelvin.

From the slope of the linear plot of lnXs Vs. $1/T \times 10^{-4}$, the standard enthalpy change (ΔH^0_{Cl}) for the clouding process have been calculated.

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

The standard entropy of micellization, 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 of Brij-97 and the mixed system are given in table 4 and table 5,6 respectively. ΔG^0_{Cl} of Brij-97 decreased with an increase in additive polymer concentration, these positive values of ΔG^0_{Cl} indicate that the clouding process proceeds non-spontaneously. Also, the positive values of ΔH^0_{Cl} indicate that disruption of water structure around the hydrophobic alkyl tails of Brij-97.

Table 4: Thermodynamic parameter of cloud point of Pure Brij-97

[Brij-97] wt.%	**ΔG^O_{cl} kJ. mol^{-1}**	**ΔH^o_{Cl} kJ.mol^{-1}**	**ΔS^o_{Cl} J.mol^{-1}.k^{-1}**
0.5	24.5421	55.5229	94.0936
1	22.5902		100.2212
2	20.6631		106.1181
3	19.5107		109.7264
4	18.6585		112.4600
5	18.0230		114.5035

The study showed that $\Delta H^0_{Cl} > \Delta G^0_{Cl}$ indicating that overall clouding process is endothermic and also $\Delta S^0_{Cl} > \Delta H^0_{Cl}$ indicates that the process of clouding is guided by both enthalpy and entropy [26]. The present work supports the probable interactions between Brij-97 with PVP and PEO.

Table 5: Thermodynamic parameters of Brij-97 in the presence of PEG (MW=4,000)

[PEG_{4000}] wt.%	**ΔG^o_{Cl} kJ.mol^{-1}**	**ΔH^o_{Cl} kJ.mol^{-1}**	**ΔS^o_{Cl} J.mol^{-}1.k^{-1}**
0.005	41.8951	105.9918	194.7044
0.01	39.9006	121.5151	248.5216
0.02	37.9038	117.1830	242.0739
0.03	37.6983	106.2084	212.8295
0.04	35.8508	102.2733	197.6150
0.05	35.1594	87.3277	160.4191

Table 6: Thermodynamic parameters of Brij-97 in the presence of PEG (MW=6,000)

[PEG_{6000}] wt.%	**ΔG^o_{Cl} kJ.mol^{-1}**	**ΔH^o_{Cl} kJ.mol^{-1}**	**ΔS^o_{Cl} J.mol^{-1}·k^{-1}**
0.005	44.0892	59.6023	45.9647
0.01	42.3938	60.7214	53.9840
0.02	40.5560	62.0572	63.1459
0.03	39.4659	68.9524	86.4707
0.04	38.7067	70.3603	92.6899
0.05	38.1842	71.5156	97.3179

CONCLUSIONS

The separation of the two phases is due to the sharp increase in the number of the micelles aggregate and the decrease in intermicellar repulsion. This decrease results from the decreased hydration of the oxyethylene oxygen in the POE hydrophilic group with the increase in temperature [27]. The CP of pure Brij-97 as well as a mixed system of Brij-97- PEG_{4000} and Brij-97- PEG_{6000} was found to decrease with increase in the concentration of Brij-97 at a fixed concentration of polymers, probably due to increasing aggregation number, the molecular weight of micelle and hence hydrophobicity.

For a mixed system of Brij-97-PEG_{4000}, keeping the concentration of surfactant constant, it was observed that CP decreases with increasing concentration of polymer. As the concentration of PEG_{4000} increases the solubility of the surfactant in water decreases, hydrophobicity increases due to the association of water molecule. Also, PEG_{4000}can incorporate Brij-97 monomers and form an intra-chain polymer-surfactant complex. This results in the attraction of micelles and facilitates their collision and lowering the CP[19].

However, in the case of Brij-97- PEG_{6000} mixed system, the CP increases with increase in the concentration of polymer PEG_{6000}, keeping the surfactant concentration constant. Additional PEG_{6000} breaks the structure of water and enhances the solvation power of water, thus increasing the solubility of surfactant. This increases the micelle-micelle repulsion and makes the micelle more hydrophilic (i.e., decreases the hydrophobicity). This indicates that the influence of an additive on the clod point depends on how it affects the intermicellar interactions[19].

The interactions in between Brij-97 with PEG indicate that thermodynamic parameters of clouding process ΔH^0_{Cl}, ΔS^0_{Cl} and ΔG^0_{Cl} are positive, the process becomes spontaneous at high temperature. But in the case of Brij-97 with PEG_{6000} indicates thermodynamic parameters in clouding process ΔH^0_{Cl} and ΔG^0_{Cl} are positive, and ΔS^0_{Cl} is negative indicates that the clouding process non-spontaneous[26]. The overall clouding process was found to be endothermic, i.e., $\Delta S^0_{Cl} > \Delta H^0_{Cl}$.

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