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Research Article

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Influence of PVP and PEO on Cloud Point of Poly (oxyethylene) 10 Oleyl Ether (Brij-97): A Thermodynamic Approach

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ABSTRACT

The cloud point (CP) temperature was investigated for aqueous solutions of poly(oxyethylene) 10-oleyl ether (Brij-97) and it's mixture with polymer, poly vinyl pyrolidone (PVP) and poly ethylene oxide (PEO) at different concentrations. The cloud point of pure Brij-97 was found to be decreased with increasing concentration. At fixed concentration of surfactant, the CP of mixed system shows decreasing trends with increasing concentration of PVP and increases with increasing concentration of PEO. Considering the cloud point as threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG0Cl, ΔH0Cl and ΔS0Cl) has been evaluated using "Phase Separation Model". The phase separation results from micelle-micelle interaction. It was found that the overall clouding process was endothermic and ΔS0Cl>ΔH0Cl, indicating that the process of clouding was guided by both enthalpy and entropy.

Keywords: Brij-97; PVP; PEO; Cloud point; Phase separation model

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INTRODUCTION

Surfactants are amphipilic molecules which have two distinct regions in their chemical structure, one of which is hydrophilic or "water-liking" and the other is hydrophobic or "water-hating". The interaction between nonionic and ionic surfactants with water soluble polymers have been studied by several research workers [1-13], this is mainly due to their wide range of applications in the field of cosmetics, paints, coatings, food, pharmaceuticals products, photographic films, lubricants etc. The physicochemical studies of polymer surfactant solutions have created much interest regarding their industrial importance. The CP is an important property of nonionic surfactants, below CP a single phase of molecular solution or micellar solution exists, above CP the solubility of surfactant in water is reduced and results into cloudy dispersion. This temperature at which the surfactant solution becomes turbid on heating is called cloud point (CP) temperature. When surfactants are added to water at low concentration, they are dispersed as discrete molecules. However at a particular concentration, surfactant molecules associate to form aggregates called micelles. This is known as critical micellar concentration (CMC). Micelles have particular importance in pharmacy and other industrial processes because of their ability to increase the solubility of sparingly soluble substances in water [14]. The occurrence of CMC results from a balance of intermolecular forces. The main attractive force results from the hydrophobic interaction among the nonpolar surfactant tails, whereas in case of ionic surfactants the main opposing repulsive force results from steric and electrostatic intertactions between the surfactant polar head groups [15]. The physicochemical properties of nonionic surfactants are different from those of the ionic surfactants. At CP, the micellar solutions seperates in to two phases, a surfactant rich phase and a surfactant poor phase [16]. Clouding of nonionic surfactant was attributed to a more or less sudden dehydration of polyoxyethylene chains occurring at the CP. This dehydration is due to a conformational change of polyoxyethylene chains with increase in temperature [17]. When two micelles approach each other, their hydration spheres are overlapped and some water molecules are freed, thereby increasing the entropy at CP and total free energy is much more negative [18]. The CP of nonionic surfactant depends on its molecular structure, i.e., the lipohilic nonpolar and the hydrophilic (PEO) parts. Increasing the hydrophobicity decreases the CP whereas increasing the hydrophilicty increases the CP for nonionic surfactants with nonpolar chains of different structures [19]. Increasing length of the polyoxyethylene moiety has increased the hydrophile-lipophile balance (HLB) and thus CP values increases for nonionic surfactants [20,21]. The CP of nonionic surfactants is highly sensitive to the presence of additives in the system even at very low concentration [22]. Many researchers have investigated the effect of additives on the CP of ionic and nonionic surfactants [23-26].

In this study the results for the clouding phenomenon of aqueous solution of Brij-97 alone and its mixture with water soluble polymer PVP and PEO at different concentrations have been reported. The thermodynamic parameters of clouding have been evaluated with respect to interaction between nonionic surfactant and polymer.

EXPERIMENTAL SECTION

Materials

Non-ionic surfactant Poly(oxyethylene) 10 olyel ether (Brij-97) C18H35(OCH2CH2)nOH. (n=10) and polymer, Poly vinyl pyrolidone (PVP) (Mole wt.40000) and Poly ethylene oxide (PEO) (Mole wt.100000) 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 (Figure 1).

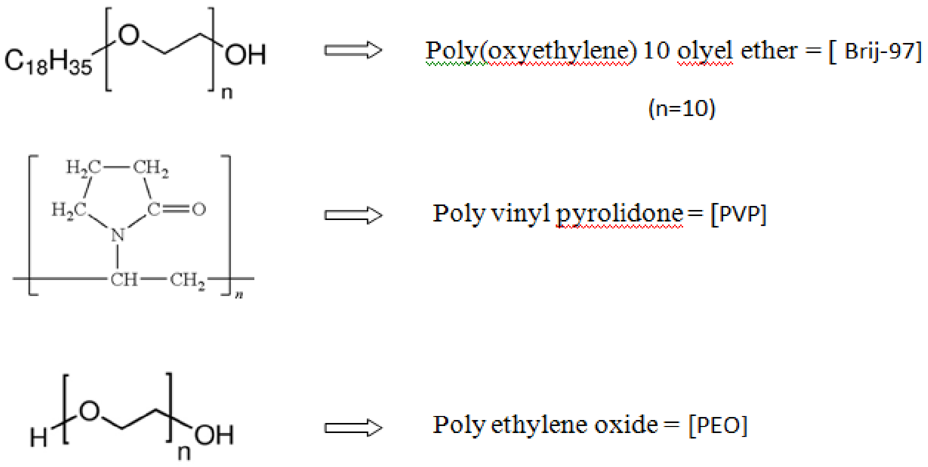

Figure 1. Molecular structure of non-ionic surfactant (a) Brij-97 and additives polymers (b) PVP and (c) PEO

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 thin glass tube immersed in beaker containing water, the sample solution was stirred while being heated. The heating rate of sample was <1°C/min. The reproducibility of the measurement was found to be within ± 0.2°C. The cloud point (CP) was determined by controlled heating in well stirred surfactant solution as well as surfactant - PVP and surfactant - PEO 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 was regulated to about 10°C/minute.

RESULTS 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 essentially constant over a wide range of concentration. The values of CP decreases from 56.2°C to 54.5°C with increase in 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 micelle increases, hydrophobicity increases. When the solutions are heated sufficiently, the POE chains become dehydrated and the solubility of the surfactant decreases markedly and thus CP decreases (Figure 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

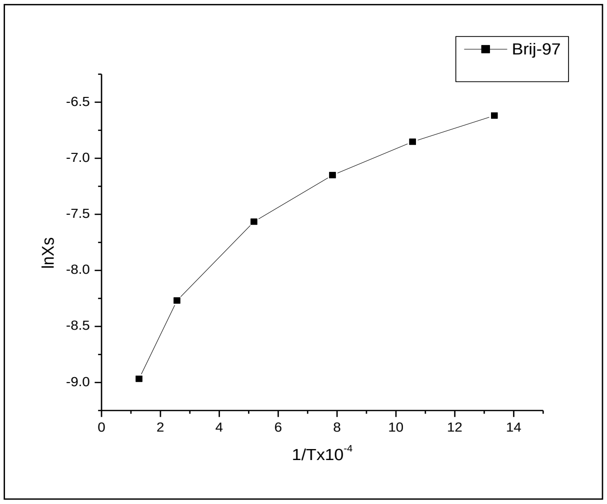

Figure 2. Variation of lnXs Vs. 1/Tx10-4 of Brij-97

Cloud Point (CP) of Brij-97 - PVP System

The influence of PVP (Mol.wt.40000) on the CP of Brij-97 at different concentration have been studied. The results are given in Table 2. These results indicating that the cloud point of surfactant polymer mixtures decreases with increasing concentration of surfactant. For 0.5 wt% of Brij-97 CP increases from 56.5 to 57.10C with increasing concentration of PVP from 0.005 to 0.05wt% of PVP. While for 1% to 5% of Brij-97 CP decreases considerably with increasing concentration of PVP 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. Due to increase in hydrophobicity of micelle with increase in concentration of surfactant in binary mixture of surfactant-polymer system, the cloud point of mixed system decreases. It has been observed that, with increase in concentration of PVP, 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, with the exception of 0.5wt% of surfactant in which the CP increases with increase in concentration of PVP.

Table 2. Influence of PVP (MW=40 000) on CP of Brij-97

Brij-97 wt%	**PVP (MW=40 000) wt%**						
	0.000	**0.005**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**
0.5	56.2	56.5	56.9	57.1	57.5	57.8	57.1
1	55.6	55.7	55.3	55.0	54.2	54.0	53.7
2	55.5	55.2	54.7	54.4	53.5	53.0	52.5
3	55.2	54.8	53.6	53.1	52.6	52.1	51.4
4	54.8	54.1	52.6	52.2	51.8	50.6	49.0
5	54.5	53.5	52.4	52.0	50.5	49.4	47.7

MW: Molecular Weight

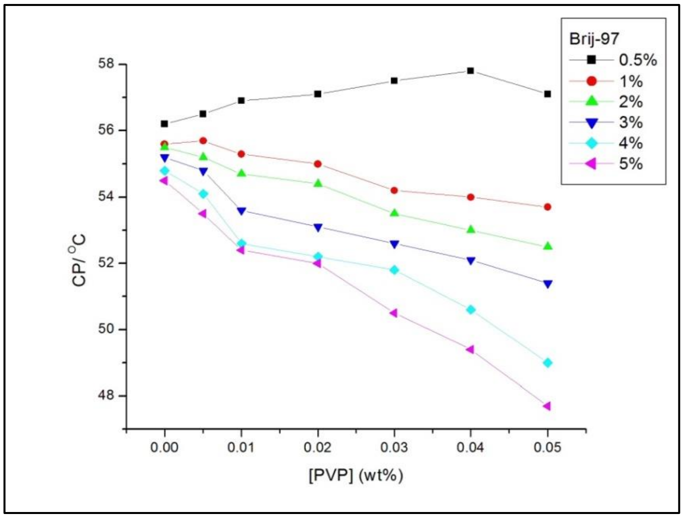

Figure 3. Effect of [PVP] on CP of Brij-97

It has been found that at low concentration of PVP below 0.005wt% did not have much effect on the CP of pure Brij-97 and it remain around 560C. The decrease in CP with addition of PVP in Brij-97 may be due to the formation of intra chain polymer-surfactant complex by incorporation of PVP in to Brij-97, which results in to the attraction of micelles and facilitates their collisions and thus lowering of CP. The influence of [PVP] on CP of Brij-97 is shown in Figure 3.

Cloud Point of Brij-97-PEO System

The influences of PEO (Mol.wt.100000) on the Cp of Brij-97 at different concentration have been a studied. The results are given in Table 3. These results indicating that the cloud point of surfactant polymer mixtures decreases with increasing concentration of surfactant and increases with increasing concentration of PEO at fixed concentration of surfactant. This decrease in CP is due to the fact that as the surfactant concentration increases in pure and mixed system with constant concentration of PEO, the hydrophobicity, molecular weight and aggregation number of the micelle formed increases which decreases the surface energy.

Table 3. Influence of PEO (MW=100 000) on CP of Brij-97

Brij-97 wt%	**PEO (MW=100 000) wt%**						
	0.0	**0.005**	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**
0.5	56.2	62.5	63.0	64.5	65.0	65.5	66.0
1	55.6	58.0	58.5	59.0	59.5	60.0	61.0
2	55.5	53.5	54.0	54.0	55.0	55.5	56.0
3	55.2	51.5	52.0	52.5	53.0	53.5	54.5
4	54.8	44.5	45.0	46.5	47.5	48.5	51.0
5	54.5	42.5	43.0	43.5	44.0	45.5	46.5

While increase in concentration of PEO with fixed concentration of surfactant, the CP of mixed system increases indicating that addition of PEO decreases the hydrophobicity of the solution, thereby aggregation takes place at higher temperature. The influence of [PEO] on CP of Brij-97 is shown in Figure 4.

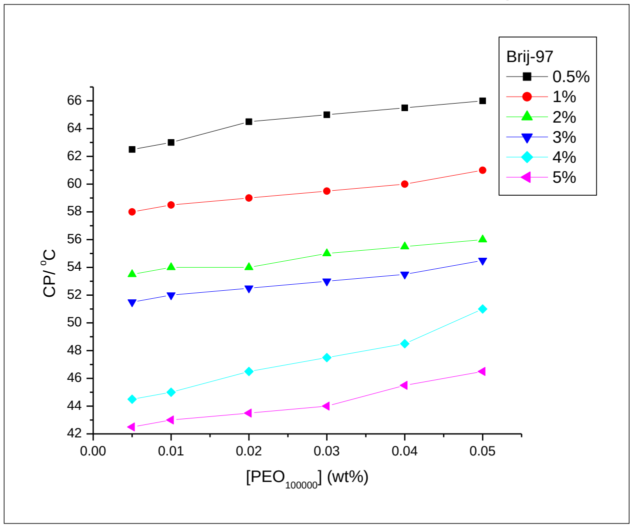

Figure 4. Effect of [PEO] on CP of Brij-97

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 as given below

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

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

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

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

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 Tables 5 and 6 respectively. ΔG^0_{Cl} of Brij-97 decreased with increase in additive polymer concentration, these positive values of ΔG^0_{Cl} indicates that the clouding process proceeds non-spontaneously. Also the positive values of ΔH^0_{Cl} indicates 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 [27,28]. The present work supports the probable interactions between Brij-97 with PVP and PEO.

Table 5. Thermodynamic parameters of Brij-97 in presence of PVP (MW=40 000)

[PVP] wt%	ΔG^o_{Cl} kJ.mol^{-1}	ΔH^o_{Cl} kJ.mol^{-1}	ΔS^o_{Cl} J.mol^{-}1.k^{-1}
0.005	48.3028	272.5967	681.3302
0.01	46.3984	191.1895	438.8939
0.02	44.5238	183.1390	419.9188

0.03	43.4635	162.5977	360.4665
0.04	42.7114	128.1937	258.4108
0.05	42.1358	93.8619	155.4914

Table 6. Thermodynamic parameters of Brij-97 in presence of PEO (MW=100 000)

[PEO] wt%	**ΔG^o_{Cl} kJ.mol^{-1}**	**ΔH^o_{Cl} kJ.mol^{-1}**	**ΔS^o_{Cl} J.mol$^{-1\cdot}$k^{-1}**
0.005	51.6754	36.3895	- 45.5615
0.01	49.8160	36.4978	- 39.6375
0.02	48.0930	37.9780	- 29.9704
0.03	47.0247	38.6999	- 24.6296
0.04	46.2844	42.0574	- 12.4874
0.05	45.7236	44.3317	- 04.0589

CONCLUSION

The separation of 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 increase in temperature [29]. The CP of pure Brij-97 as well as mixed system of Brij-97-PVP and Brij-97- PEO was found to decrease with increase in concentration of Brij-97 at fixed concentration of polymers, probably due to increasing aggregation number, molecular weight of micelle and hence hydrophobicity with increase in concentration of surfactant.

For mixed system of Brij-97-PVP, keeping the concentration of surfactant constant, it was observed that CP decreases with increasing concentration of polymer, this is probably due to the fact that as polymer PVP concentration increases the solubility of surfactant in water decreases, hydrophobicity increases due to association of water molecule. Also PVP can incorporate Brij-97 monomers and form intra-chain polymer-surfactant complex. This results in the attraction of micelles and facilitates their collision and lowering the CP.

However, in case of Brij-97-PEO mixed system, the CP increases with increase in concentration of polymer PEO, keeping the surfactant concentration constant. Additional PEO breaks the structure of water and enhances the solvation power of water, thus increasing 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 inter micellar interactions.

The interactions in between Brij-97 with PVP indicate thermodynamic parameters of clouding process ∆H0Cl, ∆S0Cl and ∆G0Cl are positive; the process becomes spontaneous at high temperature. But in case of Brij-97 with PEO indicates thermodynamic parameters in clouding process ∆H0Cl and ∆G0Cl are positive and ∆S0Cl is negative indicates that clouding process non-spontaneous. The overall clouding process was found to be endothermic i.e. ∆S0Cl > ∆H0Cl.

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