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Thermodynamics of Clouding Behaviour of Polyoxyethylene-(20)-cetyl Ether (Brij-58) with Glycine and Serine

B.S. BHADANE* and T.J. PATIL†
Department of Chemistry, Kisan A.C.S. College, Parola-425 111, India
E-mail: tjpatil123@rediffmail.com

The phenomenon of solubilization of non-ionic surfactant polyoxyethylene(20)cetyl ether (Brij-58) have been studied through the influence of additives such as amino acids *i.e.*, glycine and serine in aqueous medium by measuring the cloud points of the pure surfactant and with glycine (Gly) and serine (Ser). The cloud point of pure surfactant found to be decreased with increased [Bj-58]. The cloud point of mixed system also shows same trends with increased [Gly] and [Ser]. This is mainly due to increased micelle concentrations. The influence of amino acids on the cloud point of Brij-58 is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. The phase separation results from micelle-micelle interaction. Considering cloud point as threshold temperature of the solubility. The thermodynamic parameters of clouding process (ΔG^{o}_{Cl} , ΔH^{o}_{Cl} and ΔS^{o}_{Cl}) have been evaluated using 'Phase Separation Model'. It is found that the overall clouding process is exothermic and $\Delta H^{o}_{Cl} > T\Delta S^{o}_{Cl}$ indicating that the process of clouding is guided by both enthalpy and entropy. This work support the conjecture that the clouding is critical phenomenon rather than the growth of micelles. The findings of the present work supports the probable evidence of macromolecule-surfactant interactions in aqueous medium.

Key Words: Solubilization, Cloud point, Brij-58, Glycine, Serine, Phase separation model.

INTRODUCTION

The interaction of surfactants with the macromolecules in aqueous solution is of great importance in the technical systems[1]. Various techniques have been used to study the surfactant-macromolecule interactions[1,2]. Such interactions might be a solute-solute, solute-solvent and solvent-solvent type. The influence of additives is mainly responsible for the change in cloud point values of surfactant[3]. Hence, measurement of cloud point of such systems provides an excellent tool for investigating surfactant-macromolecule interactions[4].

Non-ionic surfactants cannot withstand at elevated temperature and become perceptible even with the naked eye is known as 'clouding' and that temperature is

†Department of Chemistry, Z.B. Patil College, Deopur-424 002, India.

referred as cloud point[5] (CP). The cloud point is an important property of non-ionic surfactants, below cloud point a single phase of molecular solution or micellar solution exists. Above cloud point of the water solubility of surfactant is reduced and it results into cloudy dispersion[6]. The critical phenomenon in micellar solution and the microemulsions is increasingly becoming important and investigated by a number of workers[7-9]. The interpretation of cloud point as a critical point implies that as the critical point is approached the micelle come together and above the critical point they separate out as the second phase. Various mechanisms have been suggested to explain the phenomenon that includes formation of micelles, solubilization and complex formation[10]. The measurement of cloud point is of great importance in checking the quality and characteristics of surfactant alone or in a mixture prior to its possible use in a process especially where elevated temperature prevails[11], such as pharmaceutical preparations, biomedical formulations, oil recovery processes, *etc*.

In this paper, the results of present study on the clouding phenomenon of pure Brij-58 and in presence of glycine and serine at various concentrations have been reported. These studies are important in the field of interaction of medicinal preparations, agrochemicals, detergents *etc.* Considering cloud point as threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG^o_{Cl}, ΔH^o_{Cl} and ΔS^o_{Cl}) have been evaluated using phase separation model.

EXPERIMENTAL

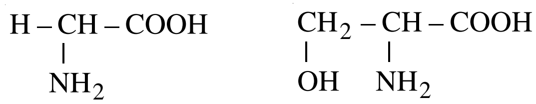
The non-ionic surfactant Brij-58 was the product of Sigma, USA (m.w. 1122) and was used as received. Glycine (m.w. 75.07) and serine (m.w. 105.09) were the products of Thomas Baker (99 % purity). Doubly distilled water with specific conductance 2-4 μ S cm^{-1} at 303.15 K was used in the preparation of all solutions of different concentrations.

The cloud point 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 controlled by less than 1 ºC/min. The detailed procedure is given in previous publications[12]. The reproducibility of the measurement is found to be within ± 0.2 ºC.

Clouding species: $C_{16}H_{33}(-OCH_2-CH_2)_{20}OH$ n = 20

Brij-58 **(Bj-58)**

Additives: Amino acids



Glycine **(Gly)** Serine **(Ser)**

Fig. 1. Molecular structures of clouding species and additives

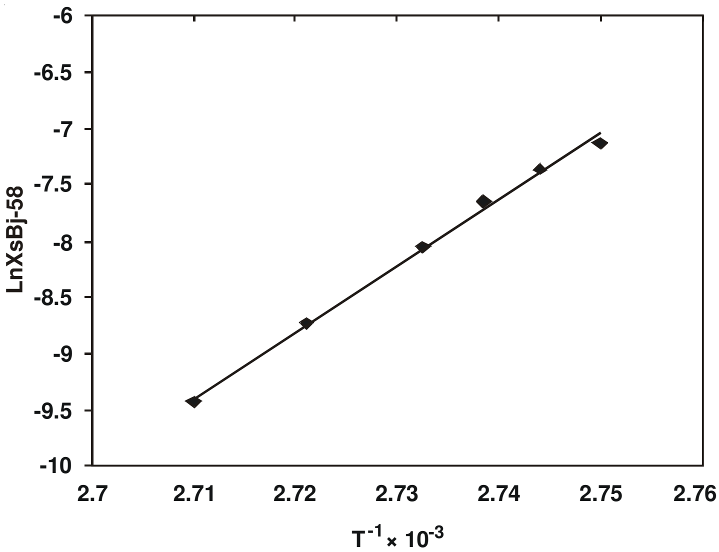


Fig. 1. Cloud points of Brijj-58 at different concentration

RESULTS AND DISCUSSION

Cloud points of pure Brij-58: The cloud points of pure surfactant, Brij-58 at various concentrations in wt % are given in Table-1. The cloud point of the surfactant was found to be decreased with increased [Bj-58] 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 form agglomerate of visible micelle.

TABLE-1
CLOUD POINTS OF PURE Brij-58

Wt (%)	Molarity × 10^{-3}	Mole fraction × 10^{-4}	Cloud point (ºC)
0.5	4.4560	0.8014	96.3
1.0	8.9130	1.6028	95.0
2.0	17.8250	3.2060	94.2
3.0	26.7380	4.8090	93.5
4.0	35.6510	6.4120	92.1
5.0	44.5630	8.0150	91.7

Brij-58/glycine and Brij-58/serine systems: The influence of glycine (Gly) and serine (Ser) on the cloud point of Brij-58 at different [Gly] and [Ser] has been given in Tables 2 and 3. These results indicating that the cloud point of surfactant declined considerably with increased [Gly] and [Ser]. This is due to the removal of water from surfactant by added amino acids and helps the surfactant micelles to come closer with each other resulting in to lowering of cloud point. In both systems below 0.5 wt % concentration, there is no remarkable change in cloud point but at higher concentration the surfactant molecules get saturated with added amino acid moieties and makes more hydrophobic to manifest rapid lowering of cloud point[13].The dependence of cloud point on [Gly] and [Ser] is depicted in Figs. 2a-2b.

TABLE-2
INFLUENCE OF GLYCINE ON CLOUD POINT OF Brij-58

[Brij-58]	Weight % of glycine					
wt %	0.5	1.0	2.0	3.0	4.0	5.0
0.5	95.0	93.4	91.8	89.0	86.2	84.2
1.0	94.2	91.5	85.0	81.4	82.6	80.2
2.0	93.0	85.5	82.0	78.2	71.0	67.2
3.0	89.4	84.0	81.2	74.5	66.0	62.5
4.0	83.6	78.5	75.0	68.7	62.5	61.5
5.0	79.8	76.8	74.6	68.3	61.5	61.0

TABLE-3
INFLUENCE OF SERINE ON CLOUD POINT OF Brij-58

[Brij-58]	Weight % of serine					
wt %	0.5	1.0	2.0	3.0	4.0	5.0
0.5	89.2	87.0	81.8	75.4	73.4	63.4
1.0	87.8	83.2	79.0	73.2	71.0	61.3
2.0	85.1	80.0	76.2	70.4	67.0	60.0
3.0	84.4	79.5	74.7	69.2	65.4	58.0
4.0	83.0	76.0	73.6	68.2	64.2	57.1
5.0	81.3	74.0	72.4	67.0	62.0	56.0

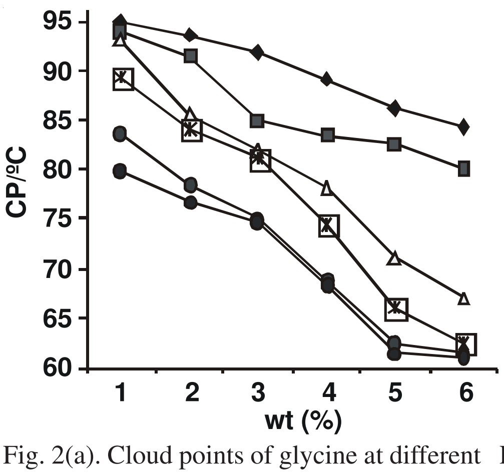


Fig. 2(a). Cloud points of glycine at different concentration

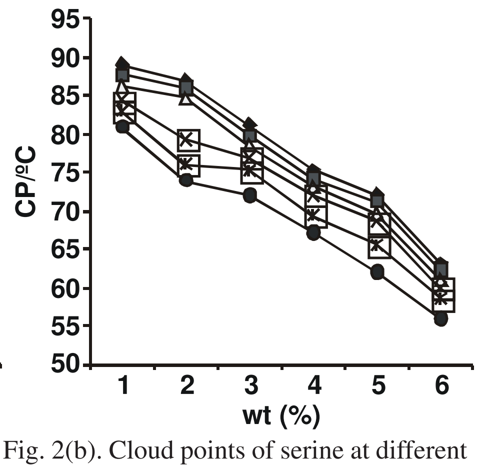


Fig. 2(b). Cloud points of serine at different concentration

Thermodynamics of clouding: All physico-chemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. The energies of such processes are required for formulation, uses and basic understanding. Thermodynamic parameters of pure Brij-58, Brij-58/glycine and Brij-58/serine system are given in Tables 4-6. In case of non-ionic surfactant, the desolvation of hydrophilic groups of the surfactant leads to the formation of cloud or turbidity in the surfactant solution at elevated temperature. The appearance of cloud point is entropy dominated. At the cloud point, the water molecules detached from the micelles.

TABLE-4
THERMODYNAMIC PARAMETERS OF Brij-58

[Brij-58] wt %	ΔG^0_{Cl} KJ mol^{-1}	$-\Delta H^0_{Cl}$ KJ mol^{-1}	$-\Delta S^0_{Cl}$ KJ mol^{-1} K^{-1}
0.5	29.0		654.56
1.0	26.7		650.84
2.0	24.6	212.78	646.57
3.0	23.3		644.09
4.0	22.3		643.90
5.0	21.6		642.70

TABLE-5
THERMODYNAMIC PARAMETERS OF Brij-58/GLYCINE SYSTEM

[Gly] wt %	ΔG^0_{Cl} KJ mol^{-1}	$-\Delta H^0_{Cl}$ KJ mol^{-1}	$-\Delta S^0_{Cl}$ KJ mol^{-1} K^{-1}
0.5	20.6	75.04	259.83
1.0	18.2	62.55	219.82
2.0	16.2	61.40	212.15
3.0	14.9	47.20	171.28
4.0	13.8	34.71	135.99
5.0	13.0	29.50	120.41

TABLE-6
THERMODYNAMIC PARAMETERS OF Brij-58/SERINE SYSTEM

[Gly] wt %	ΔG^0_{Cl} KJ mol^{-1}	$-\Delta H^0_{Cl}$ KJ mol^{-1}	$-\Delta S^0_{Cl}$ KJ mol^{-1} K^{-1}
0.5	21.3	136.81	436.53
1.0	19.1	102.96	338.30
2.0	16.9	90.040	298.64
3.0	15.7	87.850	289.73
4.0	14.1	72.710	245.81
5.0	14.0	70.140	237.48

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[14].

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

where 'Cl' stands for clouding process and ln Xs is the mole fractional 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 of ln Xs, *vs.* 1/T in Fig. 1.

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

The standard free energy (ΔS^0_{Cl}) of the clouding process 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-3-4. $\Delta H^0_{Cl} < \Delta G^0_{Cl}$ indicating that overall clouding process is exothermic and also $\Delta H^0_{Cl} > T\Delta S^0_{Cl}$ indicate that the process of clouding is guided by both enthalpy and entropy[15].

The present work would be supportive evidence regarding the probable interaction between non-ionic surfactant and macromolecules leading to the phase separation at the cloud point. The effect of amino acids on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. This paper supports the conjecture that the cloud point is a critical phenomenon.

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