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Influence of amino acids on the micellar behaviour of non-ionic surfactant in aqueous medium

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Abstract: The phenomenon of micellization in non-ionic surfactant Brij-58 (Bj-58) have been studied by measuring the cloud points (CP) of the pure surfactant and mixed system with Alanine (Ala) and Phenylalanine (PA). The CP of pure surfactant found to be decreased with increased [Bj-58]. The CP of mixed system also shows same trends with increased [Ala] and [PA]. This is mainly due to increase in micelle concentration. The phase separation results from micelle-micelle interaction. Considering CP as a threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG^0_{cl}, ΔH^0_{cl} and ΔS^0_{cl}) have been evaluated using "Phase Separation Model". The findings of the present work supports to made the probable evidence of macromolecule-surfactant interactions in aqueous medium.
Key Words: Micellization, Cloud Point (CP), Brij-58 (Bj-58), Alanine (Ala), Phenylalanine (PA), Phase Separation Model.

INTRODUCTION

The interaction of surfactants with the macromolecules in aqueous solution has been studied during past several years.Non-ionic surfactants can not withstand at elevated temperature and become perceptible even with the naked eye is known as "clouding". This temperature is referred as "Colud Point [1] (CP), the cloud point is an important property of non-ionic surfactants, below CP a single phase of molecular solution or micellar solution exists; above CP the water solubility of surfactant is reduced and it results into cloudy dispersion [2] **.** The nature of cloud point has been of interest recently and has been discussed from two points of view [3-5] . The first one assumes that the non-ionic micelles grow up as one heat the solution to the cloud point. Interpreting the observed data in the light of scattering intensity as due to the growth of micelles, the aggregation number of micelles as a function of the temperature has been measured [6]. On contrary, Corti and Degiorgio have interpreted the cloud point as critical point of a binary mixture with a lower consulate point [4]**.** They were able to evaluate the critical exponents from the light scattering data. The critical phenomenon in micellar solution and the microemulsions is increasingly becoming important and has been investigated by a number of techniques [6-11] . The interpretation of cloud point as a critical point implies that the critical point is approached the micelle come together and above the critical point they separate out as the second phase.

In this paper, the results of our study on the clouding phenomenon of Brij-58 in pure and in presence of said amino acids at various concentrations have been reported. These studies are supposed to be land mark in the field of interaction of medicinal preparations, agrochemicals, detergents etc.

MATERIALS AND METHODS

The non-ionic surfactant Brij-58 was the product of SIGMA, USA.(M.Wt. 1122) and it was used as received. The amino acids; Alanine (M.Wt.89.09) and Phenylalanine (M.Wt.165.19) were the products of Thomas Baker (99% Purity). Doubly distilled water with Sp.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 (CP) was determined by controlled heating in well stirred surfactant solution as well as surfactant-amino acid mixture until it clouded or got turbid. The turbid solution was then allowed to cool slowly while being stirred and the temperature for the appearance and disappearance of the turbidity is noted as the cloud point of the test solution. Heating and cooling was regulated to about 1^0C per minute around CP. The reproducibility of the measurement was found to be within $\pm 0.2^0$C.

Clouding species:

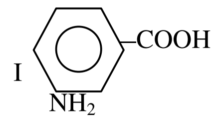
$C_{16}H_{33}(-OCH_2-CH_2)_{20}OH$ n=20

Brij-58 (Bj-58)

Additives:Amino acids

CH_3—CH—COOH
I
NH_2

Alanine (Ala)



Phenylalanine (PA)

Fig.1: Molecular structures of clouding species and additives.

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 CP of the surfactant was found to be decreased with increased [Bj-58] this is due to increase in micelle concentration. The phase separation occurs from 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.

Brij-58 /Alanine and Brij-58 / Phenylalanine Systems:

The influence of Alanine and Phenylalanine on the CP of Brij-58 at different [Ala] and [PA] has been given in Table: 2 and Table: 3. these results indicating that the cloud point of surfactant declined considerably with increased [Ala] and [PA], this is due to the removal of water from surfactant by added amino acids. In case of Brij-58 / Phenylalanine System it was found that above 4.0 Wt% concentration the effect on CP is very mild this might be due to the presence of phenyl group as compared to the methyl group in alanine. The dependence of CP on [Ala] and [PA] is depicted in Fig. 2a and 2b.

Table1: Cloud Points of Pure Brij-58:

Wt %	Molarity x 10^{-3}	Mole fraction x10^{-4}	Cp/^{0}C
0.5	4.456	0.8014	96.3
1.0	8.913	1.6028	95.0
2.0	17.825	3.2060	94.2
3.0	26.738	4.8090	93.5
4.0	35.651	6.4120	92.1
5.0	44.563	8.0150	91.7

Table 2: Influence of Alanine on CP of Brij-58:

[Brij-58]	Wt % of Alanine					
Wt%	0.5	1.0	2.0	3.0	4.0	5.0
0.5	90.1	88.6	86.2	75.2	72.0	69.0
1.0	89.0	87.7	85.3	74.2	70.7	68.2
2.0	87.8	85.2	83.5	72.6	69.0	67.4
3.0	86.3	84.5	81.8	69.5	68.4	65.6
4.0	85.2	83.4	79.2	68.2	66.2	63.8
5.0	84.5	82.0	76.5	65.5	64.3	61.5

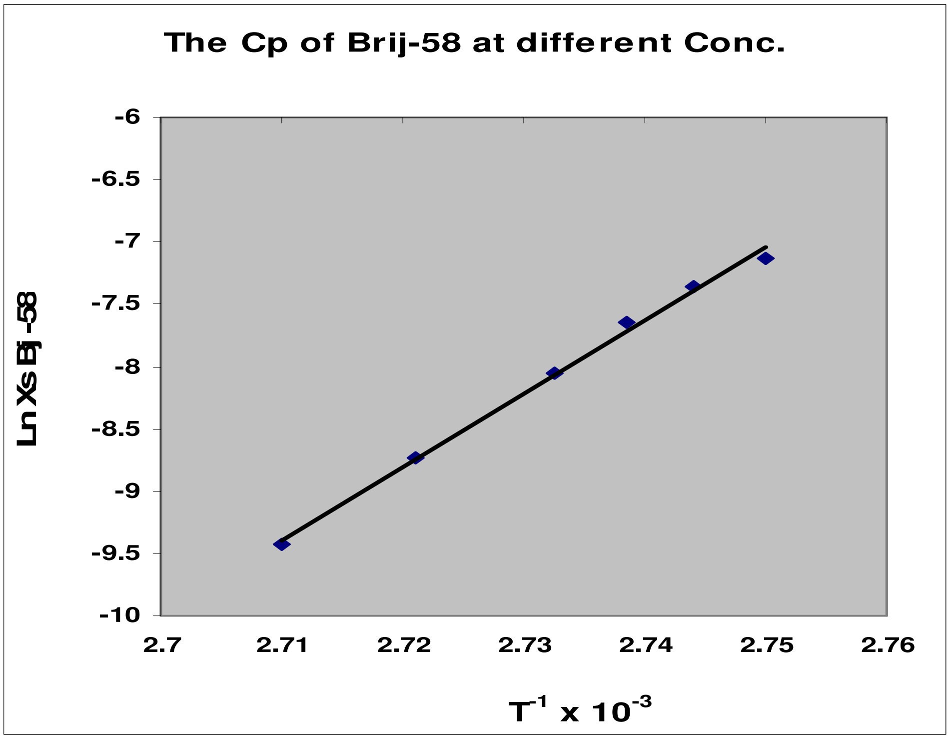
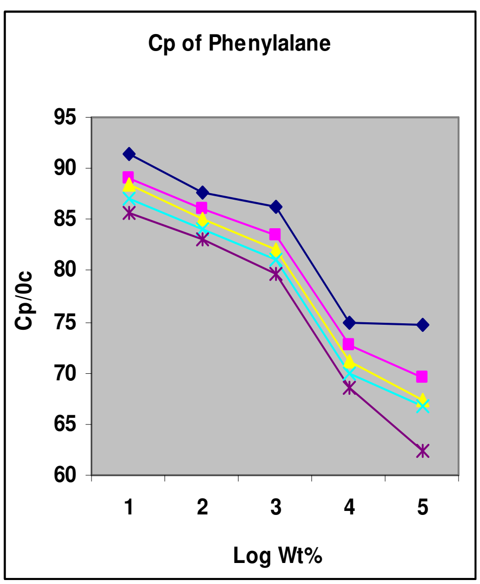


Fig.1 CP 0f Brij-58 at different concentration



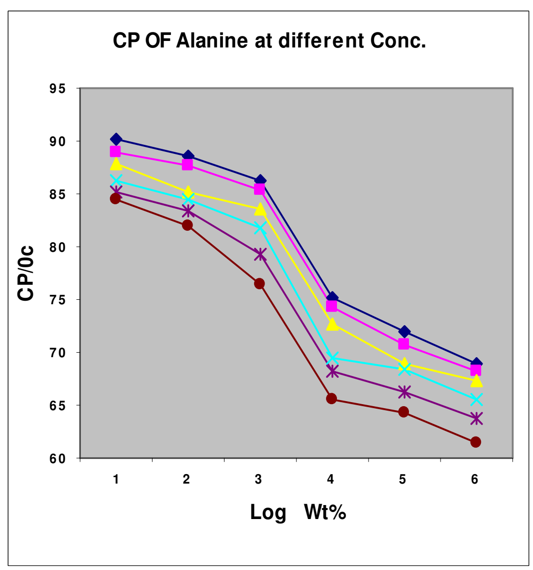


Fig: 2(a); CP of Alanine

Fig:2 (b); CP of Phenylalanine

Table 3: Influence of Phenylanine on CP of Brij-58:

[Brij-58] Wt%	Wt % of Phenylanine 0.5	1.0	2.0	3.0	4.0
0.5	91.4	87.6	86.2	75.0	74.7
1.0	89.0	86.0	83.5	72.7	69.5
2.0	88.4	85.0	82.1	71.2	67.3
3.0	87.0	84.0	81.1	70.0	66.8
4.0	85.6	83.0	79.6	68.6	62.6

Thermodynamics of Clouding:

Thermodynamic parameters of pure Brij-58, Brij-58 /Alanine System and Brij-58 / Phenylalanine System are given in Table 4, 5 and 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 get totally detached from the micelles.

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[12].

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

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 slop of the linear plot of d ln Xs Vs T^{-1} as shown in Fig. 1.

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

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

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

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table: 3 and Table: 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[13].

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.

Table 4: Thermodynamic Parameters of Brij-58:

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

Table 5: Thermodynamic Parameters of Brij-58 / Alanine System:

[Ala] Wt %	ΔG^{0}_{cl} KJ mol^{-1}	$-\Delta H^{0}_{cl}$ KJ mol^{-1}	$-\Delta S^{0}_{cl}$ J mol^{-1}K^{-1}
0.5	20.8	188.98	577.74
1.0	18.7	163.67	503.78
2.0	16.5	117.37	371.04
3.0	15.2	108.49	344.25
4.0	14.4	106.38	337.18
5.0	13.7	103.79	328.64

Table 6: Thermodynamic Parameters of Brij-58 / Phenylanine System:

[PA] Wt %	ΔG^{0}_{cl} KJ mol^{-1}	$-\Delta H^{0}_{cl}$ KJ mol^{-1}	$-\Delta S^{0}_{cl}$ J mol^{-1}K^{-1}
0.5	22.8	234.03	704.80
1.0	20.5	214.86	650.17
2.0	18.4	150.88	468.40
3.0	17.1	134.66	421.56
4.0	16.1	72.41	246.81

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