RESEARCH ARTICLE

CLOUDING BEHAVIOUR AND THERMODYNAMICS INVESTIGATION OF NON-IONIC SURFACTANT BRIJ-56 IN PRESENCE OF POLYMETHACRYLIC ACID (PMA) USING PHASE SEPARATION MODEL

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ABSTRACT:

The addition of foreign additive material to the non-surfactants shows the change in temperature at which the clouding process occurs. The phenomenon of micellization of non-ionic surfactant Tween 80 has been studied through the effect of additives PMA in aqueous medium by measuring the cloud points (CP) of the pure surfactant Brij-56 and with PMA. The CP of pure surfactant Brij-56found to be decreased with increased concentration of Tween-80. The CP of Brij-56and PMA mixed system found to be increased with increased concentration of PMA. The effect of PMA on the cloud point of Brij-56is a clear indication that, the phenomenon of clouding is associated with the different micelles coalescing. This work evaluates the effect of PMA on Cloud Point (CP) of non-ionic surfactant Brij-56at variable concentrations. Considering CP as a threshold temperature of the solubility, the thermodynamic parameters of clouding process (ΔG0cl , ΔH0cl and ΔS0cl) have been evaluated using "Phase Separation Model". The phase separation results from micelle-micelle interaction. It is found that the overall clouding process is exothermic and ΔH0cl > TΔS0cl, indicating that the process of clouding is guided by both enthalpy and entropy. This work supports the conjecture that the clouding is critical phenomenon rather than the growth of micelles. The outcomes of the present work support to made the probable evidence of polymer-surfactant interactions in aqueous medium.

KEYWORDS: *Non-ionic surfactant, Micellization, Cloud Point (CP), Brij-56 (Bj-56), Sodium salt of Polymethacrylic acid (PMA), Phase Separation Model.*

INTRODUCTION

While comparing clouding behavior; the ionic surfactants hardly show the clouding behaviour while number of Non-ionic surfactants cannot withstand at elevated temperature and become perceptible even with the naked eye is known as "clouding", and that temperature is referred as Cloud Point[1]. Thus, phase separation occurs due to difference in density of the micelle rich and micelle poor phase[1]. This process depends on the existence of the phase separation phenomenon which can be induced by changes in the temperature of micellar solution of non-ionic surfactant also called as CP[2,3]. Non-ionic surfactants and polymers in their aqueous solution may cloudy or become turbid at and above a specific temperature by way of desolvation[4]. An understanding of the clouding behavior in non-ionic surfactant solution is of practical and theoretical interest[5-7] 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[8].

The cloud point (CP) 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[9] by formation of giant molecular aggregates in the state of separate phase and the critical phenomenon in micellar solution and the micro-emulsions is increasingly becoming important and investigated by a number of workers[10,11]. The Nonionic surfactants has vast applications in various fields viz; for separation of organic compounds[12], Metal ions[13], as a novel separation technique[14], as it does not harm to protein and act as a biocatalyst[15].

The critical point is approached when the micelle come together and above the critical point, they separate out as the second phase. This CP behavior can be altered by surfactant concentration, ionic strength, pressure and presence of additives[16,17]. There are different mechanisms used to explain phenomenon such as formation of micelles, solubilization and complex formation[18]. The CP measurement has great importance for judging the quality and characteristics of surfactant alone or in a mixture prior to its possible use in a processes viz pharmaceutical preparations, biomedical formulations, oil recovery processes etc. especially where elevated temperature prevails[19].

The Polymer-Surfactant interaction has been studied by various methods[20-22]. The interaction of surfactants with the polymers in aqueous solution shows great industrial importance[23-25].

Such interactions might be a solute-solute, solute-solvent and solvent-solvent type. The effect of additives is mainly responsible for the change in CP values of surfactant[26]. Polymer-Surfactant interactions have studied measurement of CP of ionic or nonionic surfactants and polymers alone and mixture[27-31].

In this paper, the results of our study on the clouding phenomenon of pure Brij-56 alone and also in presence PMA at various concentrations have been reported. The clouding studies and thermodynamic investigation are supposed to be applied in the field of interaction of medicinal preparations, agrochemicals, detergents etc. By considering cloud point as threshold temperature of the solubility, the thermodynamic investigation of clouding process with respect to thermodynamic parameters (ΔG^0_{cl}, ΔH^0_{cl} and ΔS^0_{cl}) have been evaluated using "Phase Separation Model".

MATERIALS AND METHODS:

The non-ionic surfactant Brij-56 (M.Wt. 682) is the product of E-Merck (Germany) and the water-soluble polymer polymethacrylic acid 15% aqueous sodium salt solution (MW 8415337) is a product of National Chemicals Baroda (India). Both these products were used as received. 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 (CP) was determined by controlled heating of the sample solution is taken in a Pyrex glass tube, and the solution was heated gently, with constant stirring in the heating apparatus[32]. The heating rate of sample was controlled by less than $1^{o}C$/min. The reproducibility of the measurement was found to be within $\pm 0.2^{0}C$. As the CP values are not small, the observed values have been rounded off to the nearest degree and presented in the tables.

Clouding species: **Additive:**

Brij-56 **PMA**

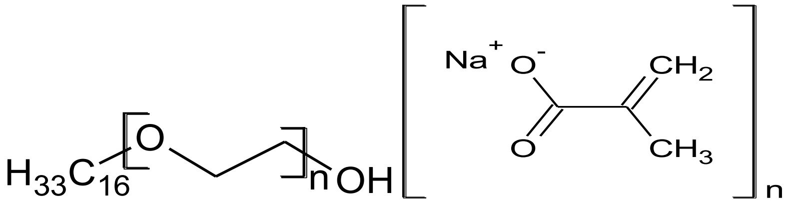

Figure 1: Molecular structures of clouding species and additive

RESULTS AND DISCUSSION

Cloud Points of Pure Brij - 56:

The cloud points of pure surfactant Brij-56 at various concentrations in Wt % are given in Table-1 (A). The CP of the surfactant was found to be decreased with increased [Bj-56] 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 decreases in cloud point. This is mainly due to lower concentration of surfactant moiety required to form agglomerate of visible micelle. Since very mild change in CP has been also observed for some non-ionic surfactants viz Triton X-100, Tween 20, Brij-35, Brij-56[33].

Mixed system of Brij-56 and PMA:

The effect of PMA on the CP of Brij-56 at different [PMA] has been given in Table-2 (A). The cloud point of non-ionic surfactant Brij-56 decreased considerably with increased concentration of water soluble polymer PMA which shows that, for same surfactant concentration when concentration of polymer increased then in general the CP increase[34] but due to strong attractive interactions and complex formation between the surfactant micelles and the polymer chains, which promote the dehydration and subsequent aggregation of the micelles at lower temperatures decreasing the cloud point as in Table-2 (A) 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 [35, 36]

Thermodynamics of Clouding:

All physico-chemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. The energetic of such processes are required for formulation, uses and basic understanding. Thermodynamic parameters of pure Brij-56 are given in Table1 (B). The Thermodynamic parameters of Brij-56/ PMA mixed System are given in Table 2 (B). 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 detached from the micelles.

Table 1: A] CP of pure TW-80 at different concentration in wt% and B] Thermodynamic parameters of solubilization of Tw- 80

A] CP of pure Bj-56				B] Thermodynamic parameter of solubilization of Bj-56			
[Bj-56] Wt%	Molarity x 10^{-3}	Mole Fraction x 10^{-4}	CP /^{0}C	[Bj-56] Wt%	$-\Delta G^0_{cl}$ KJmole^{-1}	$-\Delta H^0_{cl}$ KJmole^{-1}	$-\Delta S^0_{cl}$ J mole^{-1}K^{-1}
0.5	0.7331	1.3195	66.0	0.5	25.18		463.3
1	1.4663	2.6386	63.3	1	23.04		460.6
2	2.9326	5.2759	62.1	2	21.03	131.9	456.3
3	4.3988	7.9117	61.0	3	19.83		454.2
4	5.8651	10.5462	60.3	4	18.99		452.6
5	7.3314	13.1792	58.3	5	18.27		453.2

Table 2: A] Influence of PMA on CP of Bj-56 and B] Thermodynamic parameters of Bj-56 in presence of PMA

A] Influence of PMA on CP of Bj-56						B] Thermodynamic parameter of Bj-56 in presence of PMA			
[Bj-56] Wt%	Wt % of PMA					[PMA] Wt%	$-\Delta G^0_{cl}$ KJmole^{-1}	$-\Delta H^0_{cl}$ KJmole^{-1}	$-\Delta S^0_{cl}$ J mole^{-1}K^{-1}
	0.010	0.025	0.050	0.075	0.1				
0.5	84.4	83.8	82.4	81.2	80.9	0.01	66.16	152.4	611.5
1	83.6	82.7	81.6	80.8	80.5	0.025	63.30	182.1	688.2
2	81.3	81.4	80.1	79.9	79.6	0.05	60.95	218.1	786.2
3	80.1	79.6	79.2	78	77.7	0.075	59.45	208.7	759.5
4	79.0	78.8	78.3	77.8	77.4	0.1	58.42	197.4	726.7
5	78.7	78.6	77.9	76.6	76.2				

The dependence of CP on [PMA] is depicted in Fig. 3

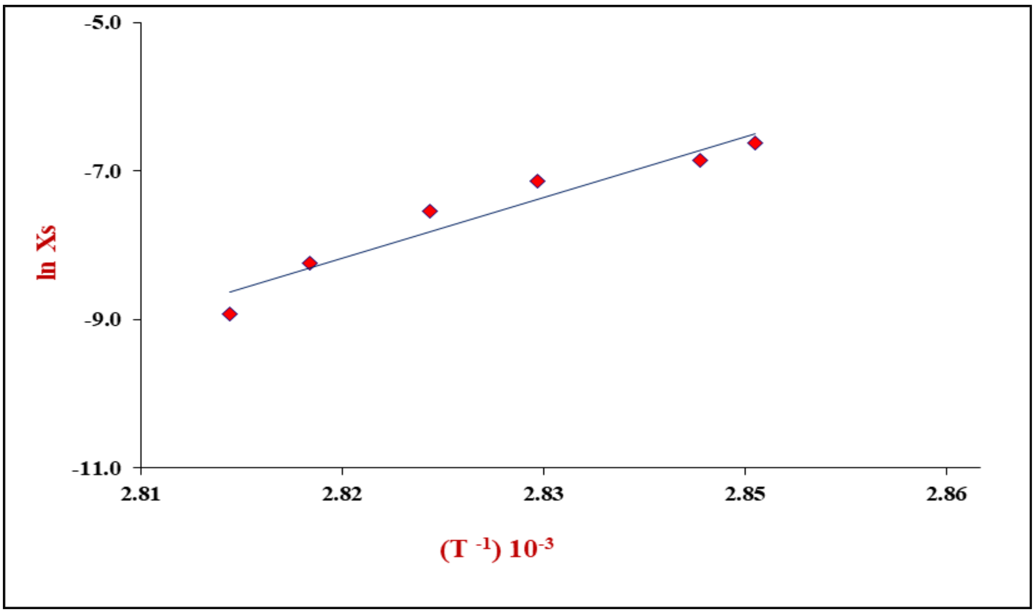

Figure 2: CP of Bj-56 at different concentrations

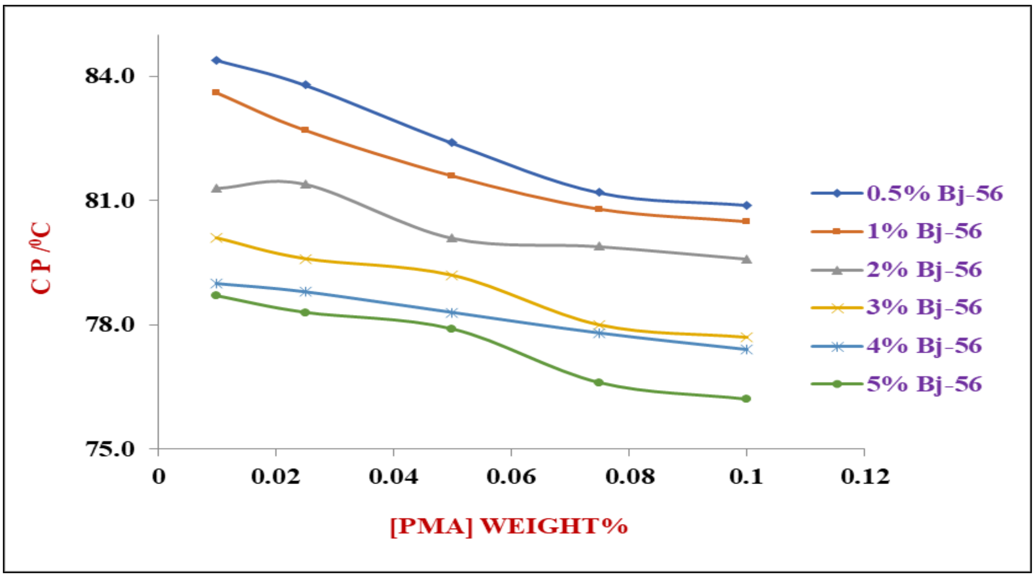

Figure 3: Influence of PMA on CP of Bj-56

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[37],

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

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 has been calculated from the slope of the linear plot of of ln Xs Vs 1/T in Fig.2 for pure nonionic surfactants.

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

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

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

$\Delta H^0_{cl} < \Delta G^0_{cl}$ 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[36].

The present work would be supportive evidence for the probable interaction between non-ionic surfactant and polyions leading to the phase separation at the cloud point. The effect of PMA 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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