Micellization Studies on Binary Mixture of Methionine with Polyoxyethylene (10) Cetyl Ether (Brij-56) and Polyoxyethylene (20) Cetyl Ether (Brij-58)

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Abstract: The measurement of cloud point (CP) under the influence of additives provides an excellent tool for investigation of surfactant macromolecule interaction. The CP of pure surfactant polyoxyethylene (10) cetyl ether (Brij-56) and polyoxyethylene (20) cetyl ether (Brij-58) declined with increased [Bj-56] and [Bj-58]. The CP of mixed systems Brij-56/methionine and Brij-58/methionine shows same trends with increased [Met.]. This is mainly due to increased micelle concentrations. The influence of amino acid on the cloud point of Brij-56 and 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 energetic of clouding process (ΔG_{cl}^0 , ΔH_{cl}^0 and ΔS_{cl}^0) have been evaluated using "Phase Separation Model". It is found that the overall clouding process is exothermic and $\Delta H_{cl}^0 > T\Delta S_{cl}^0$ indicating that the process of clouding is guided by both enthalpy and entropy. This work supports the conjecture that the cloud point is critical phenomenon rather than the growth of micelles.

Keywords: Cloud Point, Brij-56, Brij-58, Methionine, Phase separation model.

Introduction

Cloud point is one of the important characteristic properties of nonionic surfactant. It is well known that the phase separation occurs in aqueous solution of nonionic surfactant with increase in temperature. The temperature at which this phase separation occurs is known as 'cloud point' (CP). Since this process involved drastic increase in turbidity of solution¹, a single phase of molecular solution or micellar solution exists below its CP and above the CP

water solubility of surfactant is reduced, this results into cloudy dispersion². The nature of cloud point has been of interest to discuss from two point of view³⁻⁵. The first one assumes that the nonionic surfactant micelles grow up as one heat the solution to the cloud. Secondly interpreting the observed data in the light of scattering intensity due to the growth of micelles, aggregation number of micelles as a function of the temperature was measured⁶. Cloud point values for mixed system might be a guide to its hydrophilic or hydrophobic character. This information might be useful in pharmaceutical preparations, biomedical formulations or medicinal *etc.* On contrary, Corti and Degiorgio have interpreted the cloud point as critical point of a binary mixture with a lower consolute point⁴. The critical phenomenon in micellar solution and the micro emulsions is increasingly becoming important and investigated by a number of techniques⁷⁻⁹. 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. Various mechanisms have been suggested to explain the phenomenon that includes formation of micelles, solubilization and complex formation¹⁰. The measurement of CP is of great importance in judging the quality and characteristics of surfactant alone or in a mixture prior to its possible use in a process especially where elevated temperature prevails¹¹.

In this paper, the results of our study on the clouding phenomenon of pure Brij-56, Brij-58 and in presence of said amino acid at various concentrations have been reported. These studies are supposed to be landmark 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_{cl}^0 , ΔH_{cl}^0 and ΔS_{cl}^0) have been evaluated using "Phase Separation Model".

Experimental

The non-ionic surfactant Brij-56 was the product of Aldrich (m.wt.682) and Brij-58 was the product of sigma, USA (m.wt.1122). These surfactants were used as received. The amino acid methionine (m.wt.149.21) was the products of Thomas Baker (99% Purity). Doubly distilled water with Sp.conductance $2-4 \mu S cm^{-1}$ 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 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 $1 ^\circ C/min$. The detailed procedure was given in our previous publications¹². The reproducibility of the measurement found to be within $\pm 0.2 ^\circ C$. 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

Additives amino acid

Figure 1. Molecular structures of clouding species and additives

Results and Discussion

Cloud points of pure Brij-56 and Brij-58

The cloud points of pure surfactant, Brij-56 at various concentrations in wt% are given in Table 1. 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 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-56

Wt % Brij-56	Molarity $\times 10^{-3}$	Mole fraction $\times 10^{-4}$	Cp/ $^{\circ}$ C
0.5	7.331	1.3184	66.0
1.0	14.663	2.6365	63.2
2.0	29.326	5.2716	62.0
3.0	43.988	7.9053	61.0
4.0	58.651	10.538	60.2
5.0	73.314	13.167	58.6

Similar results as said above was observed for pure surfactant Brij-58 at various concentrations in wt%, which are given in Table 2. It should be noted that the phase separation in Brij-58 occurs slightly at temperature than in Brij-56. This might be indicated the micelle-micelle interaction is greater in Brij-58 than in Brij-56.

Table 2. Cloud points of pure Brij-58

Wt % Brij-58	Molarity $\times 10^{-3}$	Mole fraction $\times 10^{-4}$	Cp/ $^{\circ}$ 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

Brij-56 / methionine and Brij-58 /methionine systems

The influence of methionine (Met.) on the CP of Brij-56 and Brij-58 at different [methionine] has been given in Table 3 & 4. These results indicating that the cloud point of surfactant declined considerably with increased [methionine]. This is due to the removal of water from surfactant by added amino acid and helps the surfactant micelles to come closer with each other resulting into lowering of CP. In both systems below 0.5 wt% concentration, there is no remarkable change in CP but at higher concentration the surfactant molecules get saturated with added amino acid moieties and makes more hydrophobic to manifest rapid lowering of CP¹³. The dependence of CP of Brij-56 and Brij-58 on [methionine] is depicted in Figure 2a and 2b.

Table 3. Influence of methionine on CP of Brij-56

Wt% Brij-56	Wt % of methionine					
	0.5	1.0	2.0	3.0	4.0	5.0
0.5	63.0	61.5	60.2	59.4	57.8	56.3
1.0	62.5	60.7	58.5	58.0	56.4	53.5
2.0	61.2	59.0	57.2	56.5	56.0	52.6
3.0	60.7	58.2	56.0	55.2	54.0	51.0
4.0	60.0	57.4	55.0	54.7	53.3	50.7
5.0	57.0	56.5	53.7	53.0	50.2	48.0

Figure 2 (a). CP of Brij56

Figure 2 (b). CP of Brij-58

Thermodynamics of clouding

All physicochemical 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, Brij-58 and mixed system Brij-56/methion, Brij-58/methionine are given in Table 4-8. 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 very detached from the micelles.

Table 4. Influence of methionine on CP of Brij-58

Wt% Brij-58	Wt % of methionine					
	0.5	1.0	2.0	3.0	4.0	5.0
0.5	92.0	90.2	84.5	83.3	82.4	78.5
1.0	90.4	89.0	82.6	81.0	80.2	75.4
2.0	89.0	86.3	82.0	80.0	79.4	74.5
3.0	87.0	84.4	80.8	79.0	78.0	72.8
4.0	86.7	83.0	80.0	78.0	76.5	71.6
5.0	85.2	82.0	78.5	76.5	75.5	70.6

Table 5. Thermodynamic parameter CP of Brij-56

Wt% Brij-56	ΔG_{cl} kJmole ⁻¹	$-\Delta H_{cl}$ kJmole ⁻¹	$-\Delta S_{cl}$ Jmole ⁻¹
0.5	25.1		493.07
1.0	23.0	141.97	490.78
2.0	21.0		486.54
3.0	19.8		484.43
4.0	18.9		483.07
5.0	18.3		483.26

Table 6. Thermodynamic parameter CP of Brij-58

Wt% Brij-58	ΔG_{cl} kJmole ⁻¹	$-\Delta H_{cl}$ kJmole ⁻¹	$-\Delta S_{cl}$ Jmole ⁻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 7. Thermodynamic parameter of Brij-56/methionine

Wt% Brij-56	$\Delta G_{cl}^0 \text{ kJmole}^{-1}$	$-\Delta H_{cl}^0 \text{ kJmole}^{-1}$	$-\Delta S_{cl}^0 \text{ J mole}^{-1}$
0.5	20.7	224.19	728.87
1.0	18.7	192.45	629.49
2.0	16.7	128.05	433.26
3.0	15.6	126.92	427.08
4.0	14.8	118.00	398.71
5.0	14.0	114.66	389.95

Table 8. Thermodynamic parameter of Brij-58/methionine

Wt% Brij-58	$\Delta G_{cl}^0 \text{ kJmole}^{-1}$	$-\Delta H_{cl}^0 \text{ kJmole}^{-1}$	$-\Delta S_{cl}^0 \text{ Jmole}^{-1}$
0.5	22.5	176.14	544.22
1.0	20.3	144.54	453.62
2.0	18.1	143.55	446.66
3.0	16.8	140.19	436.16
4.0	15.9	135.50	421.05
5.0	15.2	134.30	417.43

Considering cloud point as the phase separation point, the thermodynamic parameters such as standard free energy (ΔG_{cl}^0), enthalpy (ΔH_{cl}^0) and entropy (ΔS_{cl}^0) for the clouding process have been calculated using the Phase separation Model¹⁴.

$$\Delta G_{cl} = -RT \ln X_s \quad (1)$$

Where “cl” stands for clouding process and $\ln X_s$ is the mole fractional solubility of the solute. The standard enthalpy (ΔH_{cl}^0) for the clouding process have been calculated from the slope of the linear plot of $\ln X_s$ vs. $1/T$ in Figure 3(a) and Figure 3(b).

$$d \ln X_s / dT = \Delta H_{cl} / RT^2 \quad (2)$$

Figure 3(a). CP of Brij 56 at different conc. **Figure 3 (b).** CP of Brij 58 at different conc.

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

$$\Delta S_{cl}^0 = (\Delta H_{cl}^0 - \Delta G_{cl}^0) / T \quad (3)$$

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table 3 and Table 4. $\Delta H_{cl}^0 < \Delta G_{cl}^0$ indicating that overall clouding process is exothermic and also $\Delta H_{cl}^0 > T\Delta S_{cl}^0$ indicate that the process of clouding is guided by both enthalpy and entropy¹⁵.

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.

Conclusion

- The CP of pure surfactant polyoxyethylene (10) cetyl ether and polyoxyethylene (20) cetyl ether declines with increased in its concentration due to increased micelle concentration.
- The CP of mixed system Brij-56/methionine and Brij-58/methionine shows same trend with the different micelle coalescing.
- At elevated temperature phase separation results from micelle-micelle interactions.
- Energetic of clouding process found to be exothermic and $\Delta H_{cl}^0 > T\Delta S_{cl}^0$ indicating that the process of clouding is guided by both enthalpy and entropy.

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