Oriental Journal of Chemistry Vol. **26**(2), 623-627 (2010)

Influence of Polyvinyl sulphonic acid (PVSA) on the thermodynamics of clouding behaviour of non ionic surfactant Tween 80

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(Received: January 09, 2010; Accepted: February 19, 2010)

ABSTRACT

The phenomenon of micellization of non-ionic surfactant Tween 80 has been studied through the influence of additives PVSA in aqueous medium by measuring the cloud points (CP) of the pure surfactant and with PVSA. The CP of pure surfactant Tween 80 found to be declined with increased [Tween-80]. The CP of mixed system shows same trends with increased [PVSA]. The influence of PVSA on the cloud point of Tween-80 is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. Considering cloud point as 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 phase separation results from micelle-micelle interaction. It is found that the overall clouding process is exothermic and $\Delta H^0_{cl} > T\ \Delta S^0_{cl}$ 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. Findings of the present work supports to made the probable evidence of polymer-surfactant interactions in aqueous medium.

Key words: Micellization, Cloud Point (CP), Tween 80 (Tw-80), Polyvinylsulphonicacid sodium salt (PVSA), Phase Separation Model

INTRODUCTION

The Polymer-Surfactant interaction has been studied by various methods[1-3]. The interaction of surfactants with the polymers in aqueous solution is of great importance regarding their industrial importance[4-10]. 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[11]. Hence many workers[12-20] provides an excellent tool for investigating Polymer-Surfactant interactions have studied measurement of CP of ionic or nonionic surfactants and polymers alone and mixture.

The ionic surfactants hardly show the property of clouding 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[21]. 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[22] by formation of gaint 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[23-25]. The interpretation of cloud point as a critical point implies that as the critical point is approached when 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[26]. 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 prevails[27], such as pharmaceutical preparations, biomedical formulations, oil recovery processes etc.

In this paper, the results of our study on the clouding phenomenon of pure Tween 80 also in presence PVSA 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^0_{cl}, ΔH^0_{cl} and ΔS^0_{cl}) have been evaluated using "Phase Separation Model".

MATERIALS AND METHODS

The non-ionic surfactant Tween 80 (M.Wt. 1310) and the water-soluble polymer polyvinylsulphonicacid sodium salt (M.Wt. 130.09819 gm mol^{-1}) were the product of SIGMA-ALDRICH, USA. and 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 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°C/min. The detailed procedure is given in previous publication[28]. The reproducibility of the measurement is found to be within ±0.2°C. As the CP values are not small, the observed values have been rounded off to the nearest degree and presented in the tables.

RESULTS AND DISCUSSION

Cloud Points of Pure Tween - 80

The cloud points of pure surfactant Tween-80 at various concentrations in Wt% are given in Table-1 (A). The CP of the surfactant was found to be decreased with increased [Tw-80] 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[29].

Tween-80 / PVSA Systems

The influence of PVSA on the CP of Tween-80 at different [PVSA] has been given in Table-2 (A). These results indicating that the cloud point of surfactant declined considerably with increased [PVSA]. This is due to the removal of water from surfactant by added polymer and helps the surfactant micelles to come closer with each other

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 TW-80				b) Thermodynamic parameter of solubilization of Tw- 80			
[Tw-80] Wt%	Molarity x 10^{-3}	Mole Fraction x 10^{-4}	CP /°C	[Tw-80] Wt%	$-\Delta G^0_{cl}$ KJ$mole^{-1}$	$-\Delta H^0_{cl}$ KJ$mole^{-1}$	$-\Delta S^0_{cl}$ J $mole^{-1}K^{-1}$
0.5	3.8168	0.6870	91.8	0.5	29.07		648.0
1	7.6336	1.3739	91.4	1	26.94		642.8
2	15.2672	2.7474	90.2	2	24.76	207.3	638.9
3	22.9008	4.1205	89.1	3	23.46		637.3
4	30.5344	5.4932	87.8	4	22.52		637.0
5	38.1679	6.8656	86.4	5	21.76		637.4

resulting in to 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 polymer moieties and makes more hydrophobic to manifest rapid lowering of CP as in Table-2 (A)

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 Tween-80 are given in Table1 (B). The Thermodynamic parameters of Tween-80/ PVSA 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.

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[30].

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

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 have been calculated from the slope of the linear plot of of ln Xs Vs 1/T in Fig.2 for pure nonionic surfactants Tw-80.

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

Clouding species:
Tween 80

Additive:
PVSA

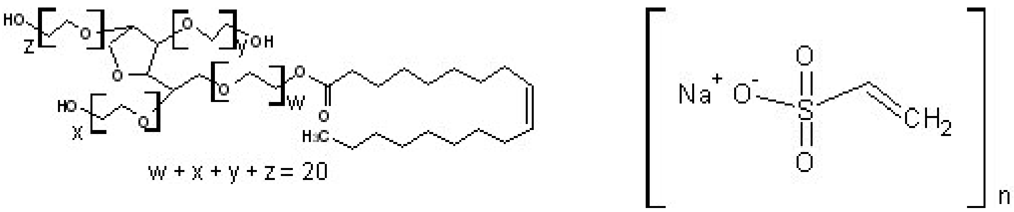

Fig. 1: Molecular structures of clouding species and additive

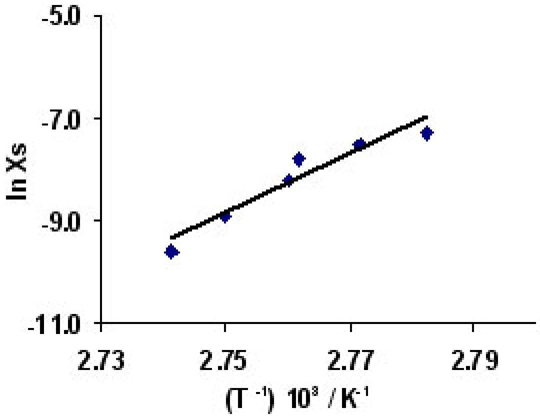

Fig. 2: CP of Tw- 80 at different concentrations

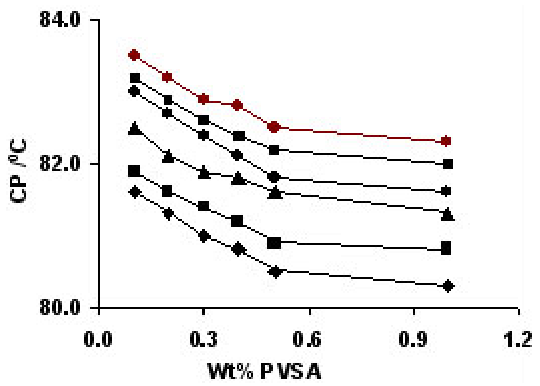

Fig. 3: Influence of PVSA on CP of Tw-80

Table 2 : A] Influence of PVSA on CP of TW-80 and B] Thermodynamic parameters of Tw- 80 in presence of PVSA

A] Influence of PVSA on CP of TW-80							B] Thermodynamic parameter of Tw-80 in presence of PVSA			
[Tw-80] Wt%	Wt % of PVSA 0.1	0.2	0.3	0.4	0.5	1	[PVSA] Wt%	$-\Delta G^0_{cl}$ KJ mole^{-1}	$-\Delta H^0_{cl}$ KJ mole^{-1}	$-\Delta S^0_{cl}$ J mole^{-1} K^{-1}
0.5	81.6	81.3	81.0	80.8	80.5	80.3	0.1	26.20	528.4	1564.0
1	81.9	81.6	81.4	81.2	80.9	80.8	0.2	24.17	521.5	1537.6
2	82.5	82.1	81.9	81.8	81.6	81.3	0.3	23.02	541.5	1588.0
3	83.0	82.7	82.4	82.1	81.8	81.6	0.4	22.20	529.8	1550.7
4	83.2	82.9	82.6	82.4	82.2	82.0	0.5	21.55	519.5	1518.9
5	83.5	83.2	82.9	82.8	82.5	82.3	1	19.52	530.0	1541.5

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

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

$\Delta H^0_{cl} < \Delta G^0_{cl}$ 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[31].

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

ACKNOWLEDGEMENTS

The author (V. B. Jadhav) wishes to acknowledge UGC, WRO, Pune for financial assistance under Minor research project 47- 098/07 (WRO) dated 16-1-2008. The author also thankful to Hon’ble Chairman, Dr. A.Z. Patil, JET’s Z.B.Patil College, Dhule and Hon’ble Principal, Dr. P. H. Pawar, Z.B.Patil College, Dhule and Vice Principals, also Head, Department of Chemistry and all colleagues of Chemistry Department, Z.B.Patil College, Dhule.

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