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Influence of Polyvinyl Sulphonic Acid on the Thermodynamics of Clouding Behaviour of Non-Ionic Surfactant Tween 40

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The phenomenon of micellization of non-ionic surfactant Tween 40 has been studied through the influence of additives polyvinyl sulphonic acid in aqueous medium by measuring the cloud points of the pure surfactant and with polyvinyl sulphonic acid. The cloud points of pure surfactant Tween 40 found to be increased with increased [Tween-40]. The cloud points of mixed system shows same trends with increased [concentration of polyvinyl sulphonic acid]. The influence of polyvinyl sulphonic acid on the cloud point of Tween 40 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^o_{cl}, ΔH^o_{cl} and ΔS^o_{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 ΔH^o_{cl} > $T\Delta S^o_{cl}$ 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, Tween 40 (Tw-40), Polyvinyl sulphonic acid sodium salt, 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 cloud points values of surfactant[11]. Hence many workers[12-20] provides an excellent tool for investigating polymer-surfactant interactions by measurement of cloud points of ionic or non-ionic surfactants and polymers alone and mixture.

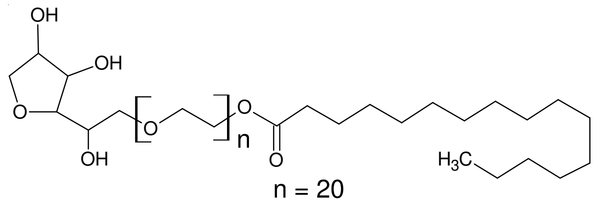
The ionic surfactants hardly show the property of clouding while number of non-ionic surfactants cannot withstand at elevated temperature and become perceptible even with the naked eye is known as "clouding" and that temperature is referred as cloud point[21]. The cloud point (CP) is an important property of non-ionic surfactants. Below cloud points a single phase of molecular solution or micellar solution exists, above cloud points 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 cloud points 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 present study on the clouding phenomenon of pure Tween 40 in presence polyvinyl sulphonic acid (PVSA) at various concentrations have been reported. 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".

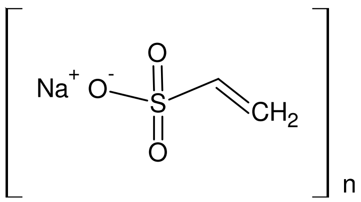
EXPERIMENTAL

The non-ionic surfactant Tween 40 (m.w. 1283.65) is product of SRL chemicals, India and the water soluble polymer polyvinyl sulphonic acid sodium salt (m.w. 130.09819 g mol^{-1}) is the product of Sigma-Aldrich, USA and these products were used as received. Doubly distilled water with specific conductance 2-4 μS 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 ºC/min. The detailed procedure is given in previous publication[28]. The reproducibility of the measurement is found to be within ± 0.2 ºC. As the cloud points values are not small, the observed values have been rounded off to the nearest degree and presented in the tables.



Clouding species: Tween 40



Additive: PVSA

Molecular structures of clouding species and additive

RESULTS AND DISCUSSION

Cloud points of pure Tween-40: The cloud points of pure surfactant Tween-40 at various concentrations in wt. % are given in Table-1 (A). The cloud points of the surfactant was found to be increased with increased [Tw-40]. This is because at higher surfactant concentration structured water-surfactant system is present[29]. It is also observed that below 1 wt. % there is very mild change in cloud point. This is mainly due to lower concentration of surfactant moiety required to form agglomerate of visible micelle.

TABLE-1
(A) CLOUD POINTS OF PURE TW-40 AT DIFFERENT CONCENTRATION IN wt. % AND (B) THERMODYNAMIC PARAMETERS OF SOLUBILIZATION OF TWEEN-40

(A) Cloud pointof pure Tw-40

[Tw-40] (wt. %)	Molarity × 10^{-2}	Mole fraction × 10^{-4}	Cloud point (ºC)
2	1.5581	2.8037	94.9
4	3.1161	5.6059	95.7
6	4.6742	8.4065	96.4
8	6.2322	11.2056	96.7
10	7.7903	14.0030	97.2

(B) Thermodynamic parameters of solubilization of Tw-40

[Tw-40] (wt. %)	$-\Delta G^o_{cl}$ (KJ mol^{-1})	$-\Delta H^o_{cl}$ (KJ mol^{-1})	$-\Delta S^o_{cl}$ (J mol^{-1} K^{-1})
2	25.02		1007.8
4	22.95		1000.0
6	21.75	345.8	994.9
8	20.88		991.7
10	20.22		988.6

Tween-40/PVSA systems: The influence of polyvinyl sulphonic acid (PVSA) on the cloud points of Tween-40 at different [concentration of polyvinyl sulphonic acid] has been given in the Table-2 (A). These results indicating that the cloud point of surfactant increased considerably with increased [concentration of polyvinyl sulphonic acid]. This is because for same surfactant concentration when additive concentration increased then in general the cloud points increase indicating the increase in miceller charge density, hence it is suggest that charge density on mixed micelle will determine the cloud point *i.e.*, higher the charge density higher is the cloud point, the increase in [additive] need not always increase the charge density because charge density will be depend upon micelle size *i.e.*, micelle size might be change due to addition of additive[29]. In both systems below 1 wt. % concentration, there is no remarkable change in cloud points but at higher concentration the surfactant molecules get saturated with added polymer moieties and makes more hydrophobic to manifest lowering of cloud points as in Table-2 (A).

TABLE-2
(A) INFLUENCE OF PVSA ON CLOUD POINT OF Tw-40 AND (B) THERMODYNAMIC PARAMETERS OF Tw-40 IN PRESENCE OF PVSA

(A) Influence of PVSA on cloud point of Tw-40

[Tw-40] (wt. %)	PVSA (wt. %)				
	0.1	0.2	0.3	0.4	0.5
2	91.4	92.0	92.3	92.6	93.2
4	92.5	92.8	93.1	93.3	93.9
6	93.2	93.4	93.7	93.9	94.3
8	93.5	93.8	94.2	94.5	94.7
10	94.4	94.6	94.7	95.1	95.3

(B) Thermodynamic parameters of Tw-40 in presence of PVSA

[PVSA] (wt. %)	$-\Delta G^o_{cl}$ (KJ mol^{-1})	$-\Delta H^o_{cl}$ (KJ mol^{-1})	$-\Delta S^o_{cl}$ (J mol^{-1} K^{-1})
0.1	26.92	269.2	812.6
0.2	24.90	305.5	904.0
0.3	23.71	325.7	954.1
0.4	22.85	308.3	903.7
0.5	22.23	381.7	1099.4

The dependence of cloud points on [PVSA] is depicted in Fig. 1.

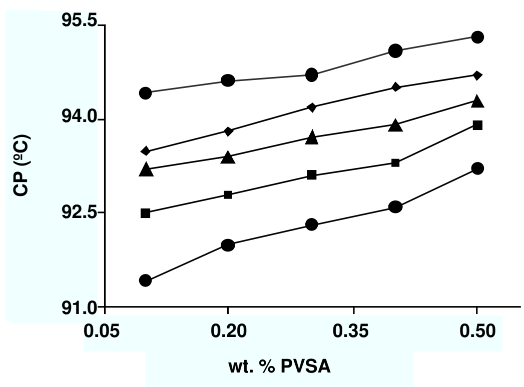


Fig. 1. Influence of PVSA on cloud points of Tw-40

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 40 are given in Table-1(B). Thermodynamic parameters of Tween-40/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^o_{cl}),enthalpy (ΔH^o_{cl}) and entropy (ΔS^o_{cl}) for the clouding process have been calculated using the phase separation model[30].

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

where "cl" stands for clouding process and ln Xs = mole fractional solubility of the solute. The standard enthalpy (ΔH^o_{cl}) for the clouding process have been calculated from the slope of the linear plot of of ln Xs *versus* 1/T in Fig. 2 for pure non-ionic surfactants Tw-40.

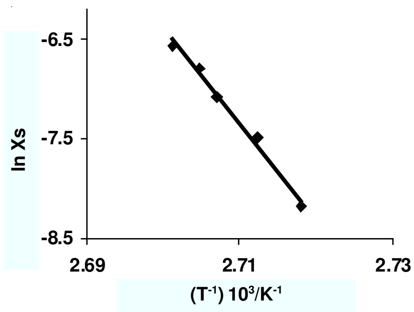


Fig. 2. Cloud points of Tw-40 at different concentrations

$$d \ln \frac{Xs}{dT} = \frac{\Delta H^o{}_{cl}}{RT^2} \quad (2)$$

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

$$\Delta S^o{}_{cl} = \frac{(\Delta H^o{}_{cl} - \Delta G^o{}_{cl})}{T} \quad (3)$$

$\Delta H^o_{cl} < \Delta G^o_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H^o_{cl} > T\Delta S^o_{cl}$ 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 polyvinyl sulphonic acid 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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