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Influence of water soluble polymer – Polyvinyl alcohol (PVA) on the micellar behavior of nonionic surfactant Triton- X- 100 - Thermodynamics and clouding approach

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ABSTRACT

The mechanism of clouding in the non-ionic surfactant is investigated through the effect of additives. The cloud point of Triton- X -100 is shown to be very sensitive to the additions of small amounts (10^{-5} M) of charged surface molecule of poly vinyl alcohol (PVA). The clouding phenomenon is a phase-changing process which is very common in the case of non-ionic surfactants. The purpose of this study was to determine the cloud point of non-ionic surfactant with and without water soluble polymer and to search for means to boost or suppress the cloud point, used in pharmaceutical formulations. The energetics of clouding in non-ionic surfactant in the presence of PVA is reported. The additives which assist in micellar growth like long chain alcohols gives negative ΔH^o_{C1} and $T\Delta S^o_{C1}$ values whereas the standard Gibb's energy change of clouding (ΔG^o_{c1}) for additive PVA is found to be positive. The results are explained on the basis of their nature, effect on the water structure and solubilization of this PVA either in the micellar or aqueous phase.

Keywords: Cloud point, Micellization, poly vinyl alcohol (PVA), Triton- X -100, Non ionic surfactant.

INTRODUCTION

The study of the interactions between soluble polymers and surfactants is of importance in technological systems. A large variety of techniques have been used to study the polymer surfactant complexes [1, 2]. In recent years, several theories have been developed to explore the nature of these systems [3-5]. Solutions of nonionic surfactants, upon heating become cloudy at a well-defined temperature. This temperature is known as the cloud point for the surfactant [6]. This temperature is not very sensitive to the concentration of the surfactant. Above the cloud point the solution separates into two phases if it is maintained at a constant temperature for a long time. The nature of the cloud point has been of interest recently and has been discussed from two points of view [7, 8]. The first one assumes that the nonionic micelles grow, as one heats the solution to the cloud point. Carti and Degiorgio have interpreted the cloud point as a critical point of a binary mixture with a lower consolute point [8]. The interpretation of the cloud point as a critical point implies that as the critical point is approached the micelles came together and above the critical point they separate one as the second phase [9]

Triton -X - 100 is a nonionic surfactant that is easily available. Its chemical name is iso octylphenoxy polyethoxyethanol with an average chain length of 9.5 oxyethylene units and having lower consolute point (cloud point) at 63^{o}C. The cloud point of a nonionic surfactant depends on its molecular structure, which is on lipophilic nonpolar and the hydrophilic parts. Increasing hydrophobicity decreases the cloud point whereas increasing the hydrophilicity increases the cloud point. The CP of non-ionic surfactants can be conveniently decreased or increased by the presence of additives [10]. When surfactants are added to water at low concentration, they are dispersed as discrete molecules. However at a particular concentration surfactant molecules get associated to form aggregates or micelles [11-13]. This concentration is known as critical micellar concentration (CMC) which is as important property of surfactant. Above CMC the surfactant molecules exists as aggregates or micelles. CMC of surfactant is determined by several methods such as conductance, solubilization, surface tension etc.

In this paper the results of our study on the clouding phenomenon of pure Triton -X - 100 and in presence of water soluble polymer - Polyvinyl alcohol (PVA) at various concentrations has reported. These studies are important in the field of medicinal preparations, agrochemicals, detergents etc. considering cloud point as threshold temperature of the solubility, the thermodynamic parameters of clouding process ($\Delta H^{o}_{C1,}$ $T\Delta S^{o}_{C1}$ and ΔG^{o}_{c1}) have been evaluated using, “Phase Separation Model”.

MATERIALS AND METHODS

Nonionic surfactant Triton -X -100 was obtained from Fluka Chemie and it was used as received. Water soluble polymer (Polyvinyl alcohol) PVA was the product of Sigma Aldrich USA (Mol.Wt. 1,15,000 and 1,25,000) both the PVA polymers are dialyzed to remove low molecular weight fractions and other associated electrolytic impurities before use. Doubly distilled water with specific conductance 2 - 4 x 10^{6} Scm^{-1} at 303.15 K was used in preparation of solutions of different concentrations.

Experimental: The cloud point was determined by controlled heating in well stirred surfactant solution as well as surfactant PVA mixture until it clouded or got turbid. The turbid solution was then allowed to cool slowly while being stirred and the temperature for the disappearance of turbidity was considered as the cloud point of the test solution, heating and cooling was regulated to about 1^{o}C per minute around the CP. The reproducibility of the measurement was found to be within ±0.2 ^{o}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:

Surfactant-

$$CH_3C\,(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}C_6H_4{-}O{-}({-}CH_2CH_2O)_{8\text{-}9}{-}H$$

Iso-Octyl phenoxy polyehtoxy- ethanol
Triton-X-100 (TX-100)

Water soluble polymers (Additive)-

$$[\text{-}CH_2\,CH\,(OH)\text{-}]_n$$

Poly-vinyl alcohol [PVA]

RESULTS AND DISCUSSION

Cloud Points (CP) of pure TX-100: The cloud points of TX-100 pure non ionic surfactant at different concentrations in (Wt %) are given in Table 1. The CP of TX-100 is substantially constant over a wide range of concentration. The values of CP increases mildly from 63ºC to 67ºC with increase in concentration of surfactant from 1 to 10 Wt %. In fact CP of TX-100 has been reported to change very slowly [14]. The cloud point depends on the surfactant concentration. If the heating proceeds above the cloud point the small droplets responsible for the turbidity grow up and a phase separation occurs, between an aqueous phase with a very small amount of solubilized surfactant, and a surfactant phase which contains same amounts of water. The phenomena can explained in the following way, when the temperature increases the thermal agitation decreases the polar interaction between the water molecules and the ether links of the non-ionic surfactant TX-100, hydrophilic poly oxyethylene chain. As a consequence the hydrophilic group is less and less hydrated as the temperature increases. As the solvation decreases, this favor the micelle formation, then CMC decreases. Added electrolytes tend to reduce the interaction between the surfactant hydrophilic group and the water molecules as a consequence they produce a CMC decreases and they make easier the phase separation, which then occurs at a lower temperature.

Table 1. CP of Triton -X-100 at different concentrations (Wt %)

Wt %	Molarity x 10^2	Mole fraction x 10^4	ln X_s	CP/^{0}C
1	1.548	2.783	-8.1867	63
2	3.096	5.565	-7.49384	64
3	4.644	8.338	-7.0895	64.5
4	6.192	11.124	-6.80123	65
5	7.740	13.901	-6.5783	65.5
6	9.288	16.677	-6.39630	65.8
7	10.836	19.451	-6.2424	66
8	12.380	22.216	-6.10952	66.5
9	13.931	24.991	-5.99182	66.8
10	15.480	27.834	-5.8840	67.00

Cloud Points (CP) Triton X – 100 – Polyvinyl alcohol (PVA): The influence of PVA (Mol. Wt. 1, 15,000) and PVA (Mol. Wt. 1, 25,000) on the CP, cloud point of TX-100 at different concentrations has been also studied. The results are given in Table 2 and Table 3. These results indicating that the cloud point of surfactant declined considerably with increased molecular weight of PVA from 1,15,000 to 1,25,000. It has been found that the low concentration of PVA, below 0.005 Wt% did not have much effect on the CP of pure Triton X- 100 and it remain around 63ºC, with addition of PVA (Mol. Wt. 115000) CP of TX-100 increases (Table 1). As concentration of PVA increases from 0.005 to 0.05 % CP decreases from 67.5 to 64.3ºC. As concentration of TX-100 increases from 1 to 10 Wt% CP decreases from 67.5 to 59.2ºC for 0.005 Wt% of PVA. As molecular weight of PVA was increased from 1,15,000 to 1,25,000 the CP of TX-100 decreases with addition of PVA for all concentration pairs studied. The influence of [PVA] on CP of TX-100 for Mw = 1,15,000 and 1,25,000 are shown in a graph, 1, 2, 3 and 4 respectively.

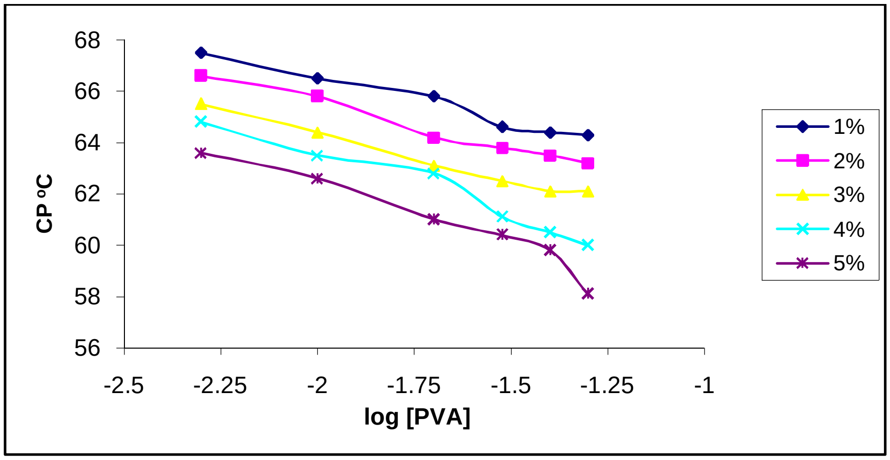

Fig.1. CP Vs. log [PVA] (Mw = 1,15,000) plot at different TX-100 in Wt % [1 to 5 %]

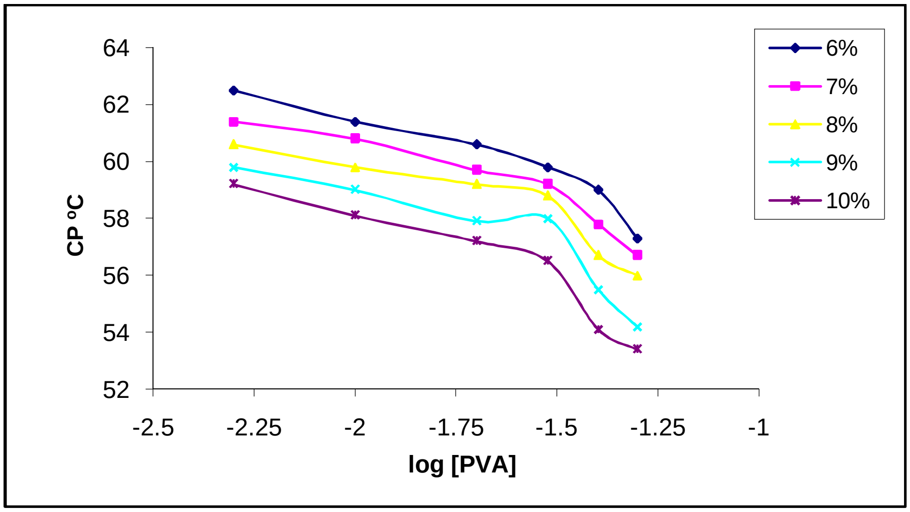

Fig.2. CP Vs. log [PVA] (Mw = 1,15,000) plot at different TX-100 in Wt % [6 to 10 %]

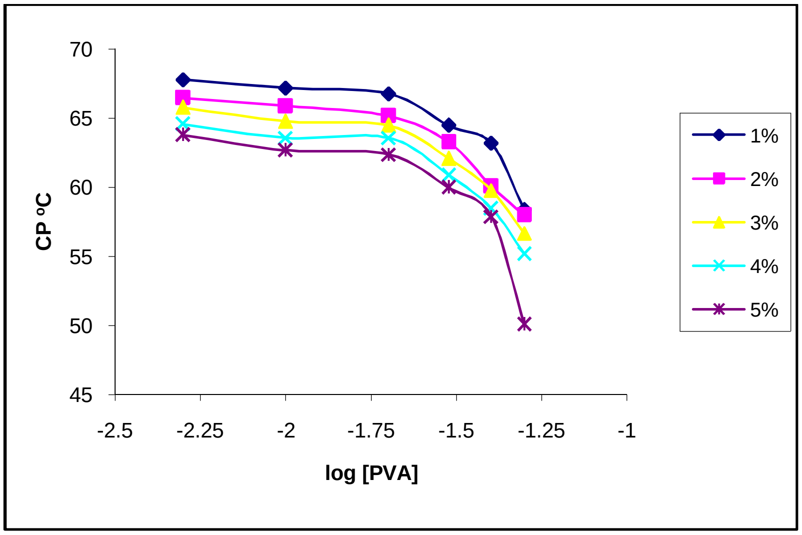

Fig.3. CP Vs. log [PVA] (Mw = 1,25,000) plot at different TX-100 in Wt % [1 to 5 %]

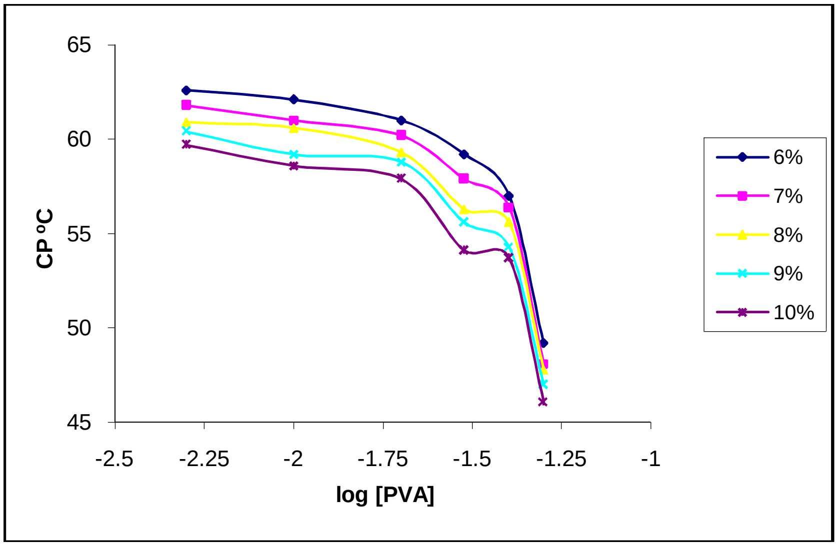

Fig.4. CP Vs. log [PVA] (Mw = 1,25,000) plot at different TX-100 in Wt % [6 to 10 %]

The values of CP in tables 2 and 3 show that CP declines with increase in PVA concentration effectively. This is mainly due to removal of water molecules by added polymers which helps the surfactant micelles to came closer with each other resulting into lowering of CP of the present [PVA]-surfactant systems. Due to polymer interaction, the CP of Triton-X-100 surfactant decline is observed. The decrease in CP is due to molecular size and solubility of CP depressed. At higher concentration of polymers, the surfactant molecules are preferentially bound to polymers making them more hydrophobic to manifest rapid lowering of CP.

Table 2. Influence of [PVA] (M_w = 1,15,000) on CP of Triton X – 100

Triton X-100 Wt %	CP^0/C at [PVA] (Wt %)					
	0.005	0.01	0.02	0.03	0.04	0.05
1	67.5	66.5	65.8	64.6	65.1	64.3
2	66.6	65.8	64.2	63.8	63.5	63.2
3	65.5	64.4	63.1	62.5	62.1	62.1
4	64.8	63.5	62.8	61.6	60.5	60.0
5	63.6	62.6	61.0	60.4	59.8	58.1
6	62.5	61.5	60.6	59.8	59.0	57.3
7	61.4	60.8	59.7	59.2	57.8	56.7
8	60.6	59.8	59.2	58.8	56.7	56.0
9	59.8	59.0	57.9	58.0	55.5	54.2
10	59.2	58.1	57.2	56.5	54.1	53.4

Table 3. Influence of [PVA] (M_w = 1,25, 000) on CP of Triton X – 100

Triton X-100 Wt %	CP^0/C at [PVA] (Wt %)					
	0.005	0.01	0.02	0.03	0.04	0.05
1	67.8	67.2	66.8	64.5	63.2	58.4
2	66.5	65.9	65.2	63.3	60.1	58.0
3	65.8	64.8	64.5	62.1	59.8	56.7
4	64.6	63.6	63.6	60.9	58.5	55.2
5	63.8	62.7	62.4	60.0	57.9	50.1
6	62.6	62.1	61.0	59.2	57.0	49.2
7	61.8	61.0	60.2	57.9	56.4	48.1
8	60.9	60.6	59.2	56.3	55.6	47.8
9	60.4	59.2	58.8	55.6	54.3	47.0
10	59.7	58.6	57.9	54.1	53.7	46.1

Thermodynamics of clouding: All physicochemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principles. Cloud points are the characteristics of non-ionic surfactants. Thermodynamic parameters of pure Triton-X-100 are given in Table 4 and Triton-X-100 - PVA mixed systems are given in Table 5 and 6 respectively. In case of non-ionic surfactant the desolvation of hydrophilic groups of the surfactant leads to the formation of cloud 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 4. Thermodynamic parameter of solubilization of TX-100.

[Triton X-100] Wt %	**ΔG^0_{Cl} kJmole^{-1}**	**$-\Delta H^0_{Cl}$ kJmole^{-1}**	**$-\Delta S^0_{Cl}$ Jmole^{-1} K^{-1}**
1	22.8696	208.82	689.55
2	20.9923		681.94
3	19.8930		677.67
4	19.1123		674.36
5	18.5132		671.59
6	18.0170		669.53
7	17.5939		667.89
8	17.2447		665.88
9	16.9274		664.35
10	16.6327		663.09

Considering cloud point as the phase separation point, the thermodynamic parameters such as standard free energy (ΔG°_{cl}), enthalpy (ΔH°_{cl}) and entropy (ΔS°_{cl}) for the clouding process have been calculated using the Phase Separation Model [16]. The following relation can be written as –

$$\Delta G^{\circ}_{cl} = -RT \ln X_s \qquad ......1$$

Where "cl" stands for clouding process and $\ln X_s$ is the mole fractional solubility of the solute. The standard enthalpy (ΔH°_{cl}) for the clouding process have been calculated from the slope of the linear plot of $\ln X_s$ Vs 1/T in Fig.5,6.

$$d \ln X_s / dT = \Delta H^{\circ}_{cl} / RT^2 \qquad ......2$$

Table 5. Thermodynamic parameters of TX-100 in presence of PVA (M_w=1,15,000)

Wt % [PVA]	**ΔG^0_{Cl} kJmole^{-1}**	**$-\Delta H^0_{Cl}$ kJmole^{-1}**	**$-\Delta S^0_{Cl}$ Jmole^{-1} K^{-1}**
0.05	52.84	101.8065	454.17
0.01	50.72	100.36	445.00
0.02	48.67	87.00	400.44
0.03	47.35	82.67	385.13
0.04	46.60	67.51	337.50
0.05	45.88	62.46	321.20

Table 6. Thermodynamic parameters of TX-100 in presence of PVA (M_w=1,25,000)

Wt % [PVA]	**ΔG^0_{Cl} kJmole^{-1}**	**$-\Delta H^0_{Cl}$ kJmole^{-1}**	**$-\Delta S^0_{Cl}$ Jmole^{-1} K^{-1}**
0.05	5.13	105.06	464.16
0.01	51.08	100.72	446.21
0.02	49.04	96.03	426.93
0.03	47.59	86.51	379.55
0.04	46.60	61.73	322.23
0.05	45.30	44.55	271.11

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

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

The thermodynamic parameters for pure surfactant and in mixed systems are given in tables 4 5 and 6. $\Delta H^{\circ}_{cl} < \Delta G^{\circ}_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H^{\circ}_{cl} > T\Delta S^{\circ}_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy [17].

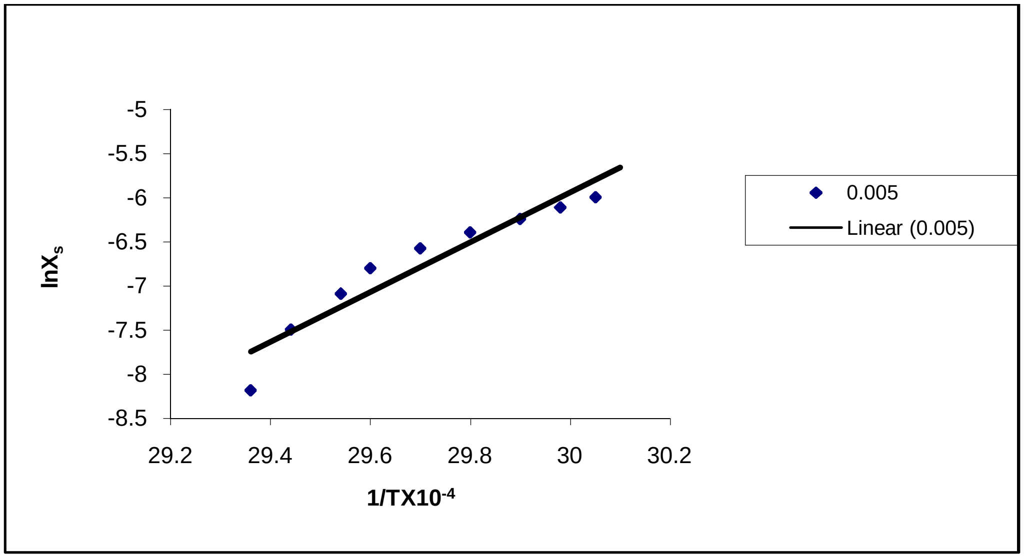

Fig.5. $\ln X_s$ Vs $1/T \times 10^{-4}$ Plot for TX-100 – PVA (M_w = 115000) for 0.005 %

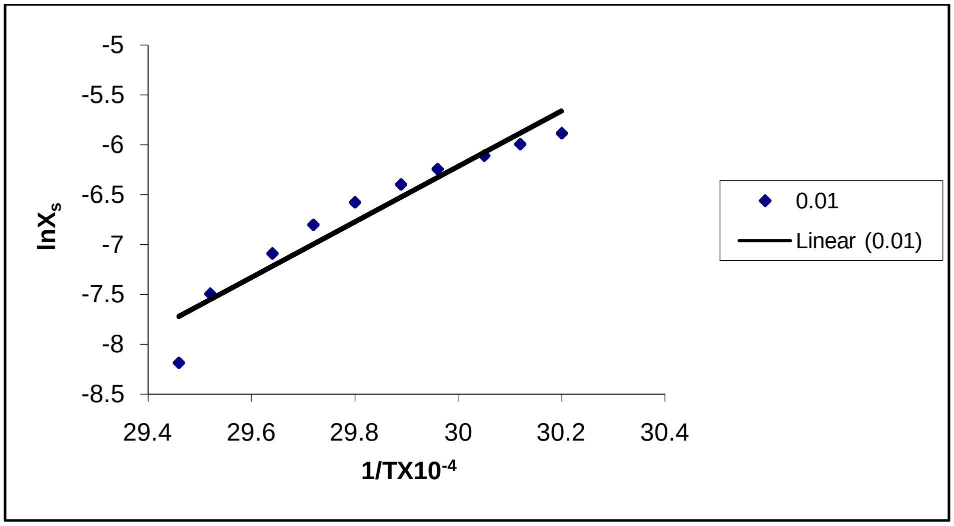

Fig.6. $\ln X_s$ Vs 1/T x 10^{-4} Plot for TX-100 – PVA (M_w = 115000) for 0.01 %

The present work would be supportive evidence regarding the probable interaction between non-ionic surfactant and macromolecules, water soluble polymer leading to the phase separation at the cloud point. The effect of PVA on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing.

APPLICATIONS

The mechanism of clouding in the non-ionic surfactant is useful to know the effect of additives.

CONCLUSIONS

It is observed that cloud point decreases with increases in Triton-X- 100 concentration, the cloud point decreases as the concentration increases, due to increased micelle concentration. For a fixed Triton-X-100 concentration the cloud point decreases as the concentration of PVA additives increases. The cloud point of mixed system Triton-X-100- PVA shows same trend with the different micelle coalescing. At elevated temperature phase separation results from micelle interactions. Energetic of clouding process found to be exothermic and $\Delta H^o_{C1} > \Delta S^o_{C1}$ indicating that the process of clouding is guided by both enthalpy and entropy. It has been observed that, concentration of pure Triton -X-100 decreases the ΔG^o_{c1} kJ mole^{-1} which decreases from 22.8696 kJ mole^{-1} to 16.6327 kJ mole^{-1} and ΔS^o_{C1} increases – 689.55 J mol^{-1} to -663.09 J mol^{-1} respectively. The value of ΔH^o_{C1} for pure Triton -X-100 was -208.82 kJ mole^{-1}. In case of Triton-X-100-PVA mixed systems ΔG^o_{c1} decreases and ΔH^o_{C1}, ΔS^o_{C1} increases respectively as concentration of PVA increases from 0.005 Wt% to 0.05 Wt%. As ΔG^o_{c1} is positive the clouding process is non-spontaneous and ΔH^o_{C1} is negative hence the process is exothermic.

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