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Physicochemical studies on effect of additives on clouding behavior and thermodynamics of polyoxyethylene (20) sorbitan monooleate

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Cloud point (CP) of nonionic surfactant, namely polyoxyethylene (20) sorbitan monooleate (Tween-80) in aqueous environment and in the presence of different additives such as salts (sodium chloride, NaCl; sodium sulfate, Na_2SO_4; sodium nitrate, $NaNO_3$) and polymers (polyvinylpyrrolidone, PVP; polyvinyl alcohol, PVA; polyethylene glycol, PEG) have been studied. The CP values of Tween-80 in aqueous medium are found to decrease with increase of surfactant concentration. The CP values of Tween-80 are lower in magnitude in the presence of sodium salts as compared to those in aqueous medium; the effect of sodium salts (between 0.1 and 10 mmol L^{-1}) in reducing CP values were found to be in the order: Na_2SO_4 > NaCl > $NaNO_3$. The CP values of Tween-80 solutions also decrease with increasing concentrations of polymers used. The values of ΔG^0_c are positive in all the cases, indicating the non-spontaneous nature of clouding. ΔH^0_c and ΔS^0_c values were found to be almost negative in the presence of salts and polymers, except in the case of the PEG-water system. The negative values of ΔH^0_c and ΔS^0_c decrease with increasing concentrations of salts and polymers.

Keywords: Cloud point, Tween-80, Surfactants, Hydrophobic interactions, Thermodynamic parameters

Nonionic surfactants have been widely used in practical and industrial formulations as solubilizers, emulsifiers and detergents[1-3]. They are used in cloud point separation of organic compounds, metal ions, proteins, and oily soil removal from substrates[1,2]. The aqueous solutions of nonionic surfactants upon heating turn cloudy and separate out into two liquid phases beyond a particular temperature. Such a phenomenon indicates their instability in solution and the threshold temperature at which such clouding is observed known as the cloud point (CP), a characteristic property of non-ionic surfactants[4,5]. The practical importance of the cloud point lies in the fact that suspensions, emulsions and ointments and foams stabilized with nonionic surfactants become unstable when heated in the vicinity of the cloud point, e.g., during manufacturing, steam sterilization, or some end uses[6,7].

The clouding behavior of nonionic surfactant is strongly affected by the presence of various additives in the solution and thus the change in the environment of the micelle[4,8]. The appearance of turbidity in the aqueous solution and its separation into two phases introduce certain disadvantages in its utilization. Knowledge of CP of nonionic surfactants is important because formulations at temperatures significantly higher than the CP may lead to phase separation and instable state. It is reported that nonionic surfactant is highly effective near and below CP of that surfactant[9]. Therefore, it is of vital importance to determine the effect of different additives on the CP of nonionic surfactants. Panchal *et al.*[10] investigated the effect of electrolytes on the CP of Triton X-100 (TX-100) as a function of added sodium dodecyl sulfate. They reported that an SDS increases the CP of TX-100 and the addition of an electrolyte diminishes the increase in CP. Mahajan *et al.*[11] studied the effect of glycol oligomers and triblock polymers on clouding behavior of Tweens and observed that increase of both in the repeating units of polymeric glycol additives and hydrophilic/hydrophobic ratio in triblock polymers decreases the CP values of Tweens. Recently, we have studied the clouding behavior and thermodynamics of *p-tert*-alkylphenoxy poly(oxyethylene)ether micelles in aqueous environment and in the presence of diols/polyols[12]. Although literature surveys[1,3,4,13] reveals the presence of a number of studies on the clouding phenomenon of non-ionic surfactants, a detail studies involving new model systems are still necessary.

Keeping these views in mind, a study of the cloud point measurement of a model non-ionic surfactant namely polyoxyethylene (20) sorbitan monooleate,

Tween-80, has been undertaken in aqueous medium and in the presence of some additives such as inorganic salts and polymers. This study also involves the determination of thermodynamic parameters such as $\Delta G^0_{c,}$ ΔH^0_c and $\Delta S^0_{c,}$ associated with the clouding process for varying concentrations of the pure Tween-80 in water as well as various concentrations of salts and polymers at a particular concentration of Tween-80.

Materials and Methods

Tween-80 (purity 0.98, CAS number 9005-65-6, molar mass = 1310 g mol^{-1}) was procured from Merck, Germany and used without any further treatment. PEG (purity >0.995, CAS number 25322-68-3, molar mass = 400 g mol^{-1}) from Merck, India, PVA (purity >0.98, CAS number 9002-89-5, molar mass =125000 g mol^{-1}) and PVP (purity >0.98, CAS number 9003-39-8, molar mass = 44000 g mol^{-1}) from BDH, England, sodium chloride (purity 1.00, CAS number 7647-14-5, molar mass = 58.44 g mol^{-1}) from BDH, England, sodium nitrate (purity >0.995, CAS number 7631-99-4, molar mass = 84.99 g mol^{-1}) from Riedel-de-haen, Germany and sodium sulphate (purity 0.995, CAS number 7757-82-6, molar mass = 142.04 g mol^{-1}) from E. Merck, India, were used as received where purity is expressed in mass fraction unit in this study. All solutions were prepared using distilled-deionized water.

Tween-80 solution prepared in pure water or water/salt or water/polymer mixed system was stirred for at least one hour to ensure the attainment of equilibrium conditions. Cloud point (CP) temperatures of surfactant solutions were determined by visual observation of the abrupt change in the appearance or disappearance of turbidity during the heating or cooling the surfactant solutions respectively following the procedure reported the literature[12,14-16]. The average temperatures of appearance and disappearance of turbidity was taken as the CP.

A fixed volume of Tween-80 solutions in water or Tween-80 solutions containing different salts/ polymers were taken in test tubes and gradually heated with constant stirring in a temperature-controlled water bath. The sample was heated slowly after the temperature reached a few degrees below the preestimated CP temperature. After the temperature exceeds the CP, the sample was cooled below the cloud point temperature and then it was heated again to check the reproducibility of the measurements. This procedure was repeated at least three times and the CP temperatures were determined with a reproducibility of ± 0.1K.

Results and Discussion

Cloud point of Tween-80 in water and (water+salt) media

The cloud point (CP) of Tween-80 solutions in water was measured within the concentration range of 7.63–76.34×10^{-2} mol L^{-1} (corresponding concentration range is 1-10%, *w*/*v*) and are represented in Table 1. (see also Supplementary Data, Fig. S1). The CP value of 7.63×10^{-2} mol L^{-1} Tween-80 in water was found to be 364.55 K (91.4 °C). Joyoti *et al*. observed the CP value of 91.1 °C (364.25 K) for 0.1 m*M* Tween-80 in water[9]. The CP values are found to decrease with increase of surfactant concentration. Such observation is in agreement with the literature report[17,18]. This result is expected due to the decrease of hydration of the oxyethylene oxygens in the polyoxyethylene hydrophilic group with decrease of temperature. The clouding of each solution of Tween-80 in water is likely to be due to a large decrease in the aggregation number of the Tween-80 micelles and an increase in intermicellar repulsion. The decrease in aggregation number and the intermicellar interaction produce small micellar aggregation at the cloud point temperature in the solution, which becomes visibly turbid and the two liquid phases separates out. Upon increasing the concentration of Tween-80 solution up to 76.34×10^{-2} mol L^{-1}, the spherical micelle becomes smaller in size and a shape transition occurs from disk-like to sphere. This shape transition may cause decrease of surface area of the micelle, which results in a decreased hydration and thereby decreasing the cloud point of solution[19,20].

The effect of different sodium salts such as NaCl, $NaNO_3$ and Na_2SO_4 on the CP of 7.63×10^{-2} and 15.27×10^{-2} mol L^{-1} solutions of Tween-80 was also studied and the results obtained are presented

Table 1—CP values of pure Tween-80 in aqueous medium[a]

$c_{Tween\text{-}80}$×10^{-2} (mol L^{-1})	CP (K)
7.63	91.40
15.27	90.00
22.90	89.00
30.53	87.30
38.17	86.30
45.80	85.09
61.07	83.09
76.34	81.50

[a]The uncertainty of CP values is within ± 0.1 K.

graphically in Figs 1, 2 and 3 as well as in Tables S1 and S2 (Supplementary Data). The cloud points of the system were found to be lower in magnitude in the presence of sodium salts as compared to those in aqueous medium. The effect of sodium salts (between 0.1 and 10 mmol L^{-1}) in reducing CP values were found to be in the order: $Na_2SO_4 > NaCl > NaNO_3$. According to Homeister series, anions from phosphate to bromide ions exhibit salting out effect since they attract and structure the water molecules and strengthen the hydrophobic interaction[16]. In addition, if one moves from left to right on the Homeister series, a decrease of formal charge density is observed[16]. Thus, the effect of sulfate ion in reducing CP values of Tween-80 is dominant compared to the chloride and nitrate ions. It is also reported in the literature that the CP values of TX-100 decreased more sharply in Na_2SO_4 solution compared to those in NaC1 solution[21]. This effect may be due to the nature of charge which determines the total of the effect. Such decrease in CP value of TX-100 by NaCl was also observed by Heusch[22]. Two mechanisms are used to describe the position of the anions in the Hofmeister series[16]. Usually the mechanism involved was believed to be related to the ability of the ions to alter the hydrogen bonding network of water. In this mechanism, ions on the left of the series (such as SO_4^{2-}) are water structure makers and induce entropy loss and immobilize water molecules. The resulting effect is due to the salting out of the anions of salts on the nonionic surfactant present in the system. Ions to the right of the series are water structure breakers because their high polarizibility leads to the disruption of self-associated water molecules. This releases more single water molecules which can form hydrogen bonds with the ether groups of the nonionic surfactant thereby exhibiting salting effect. In the alternative mechanism proposed recently, the ion effects are based on the direct ion-surfactant interaction rather than on water structure changes.

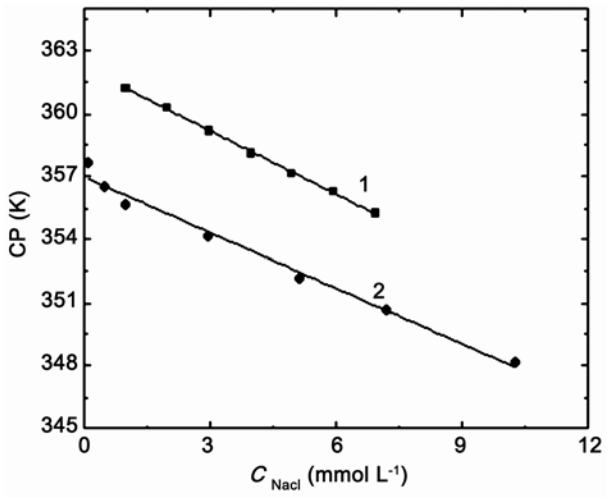

Fig. 1—Plot of cloud point versus different concentrations of sodium chloride for 7.63×10^{-2} mol L^{-1} (1, ■) and 15.27×10^{-2} mol L^{-1} (2, ♦) Tween-80 solution.

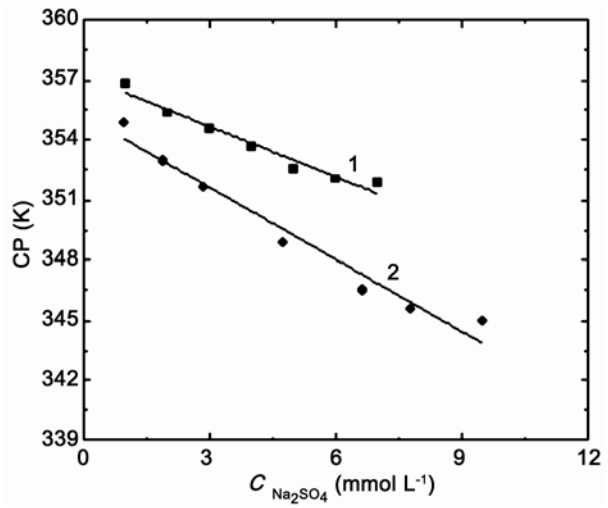

Fig. 2—Plot of cloud point versus different concentrations of sodium sulfate for 7.63×10^{-2} mol L^{-1} (1, ■) and 15.27×10^{-2} mol L^{-1} (2, ♦) Tween-80 solution.

Cloud point of Tween-80 in (water+polymer) media

The effect of the addition of some polymers such as PEG, PVP and PVA on the CP values of Tween-80 was investigated in this study. The CP values of

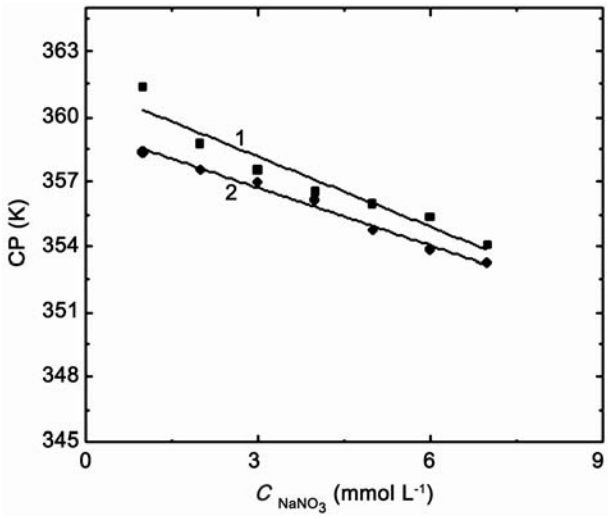

Fig. 3—Plot of cloud point versus different concentrations of sodium nitrate for 7.63×10^{-2} mol L^{-1} (1, ■) and 15.27×10^{-2} mol L^{-1} (2, ♦) Tween-80 solution.

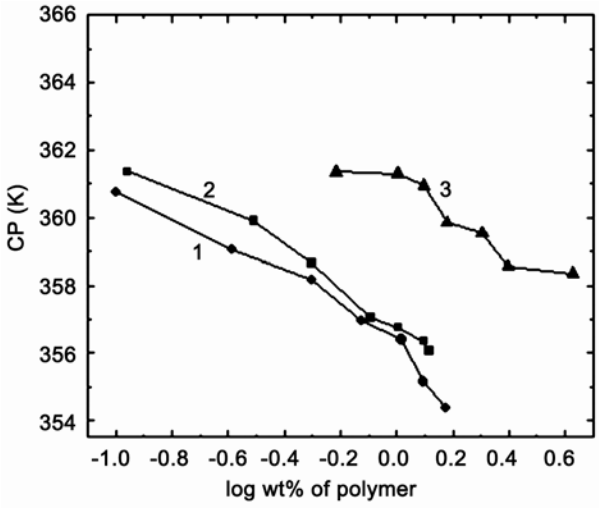

Fig. 4—Plot of cloud point versus log wt% of polymers for 7.63×10^{-2} mol L^{-1} Tween-80 solution. [1, (♦) PVP; 2, (■) PVA; 3, (▲) PEG].

7.63×10^{-2} and 22.90×10^{-2} mol L^{-1} Tween-80 solutions containing various concentrations of polymers are shown in Fig. 4 and Tables S3 and S4 (Supplementary Data). The CP values of Tween-80 solutions were found to decrease with increasing concentrations of polymers. Such a decrease of CP of surfactant solution due to addition of polymer is also reported in the literature[17,23]. This may be due to the removal of water from surfactant by added polymer which helps the surfactant micelles to come closer with each other, resulting in lowering of CP. In both systems below 0.1% (*w*/*v*) concentration of polymer, there is no remarkable change in CP but at higher concentrations of polymers, the surfactant molecules get saturated with added polymer moieties which makes it more hydrophobic, manifesting rapid lowering of CP.

Thermodynamic parameters of clouding phenomenon

Considering CP as the phase separation point, the thermodynamic parameters such as change in standard free energy (ΔG^0_c), enthalpy (ΔH^0_c) and entropy (ΔS^0_c) for the clouding process have been calculated using the following equations[12,16, 24-26],

$$\Delta G_c^0 = - RT \ln X_s \quad \ldots (1)$$

$$\Delta H_c^0 = RT^2 (\partial \ln X_s) / \partial T \quad \ldots (2)$$

$$\Delta S^0_c = (\Delta H^0_m - \Delta G^0_m)/ T \quad \ldots (3)$$

where X_s is the mole fractional solubility of the solute.

The CP dependence on X_s, the mole fractional solubility of the solute, can be expressed as a symmetrical parabolic curve according to Eq. (4)[27-30]:

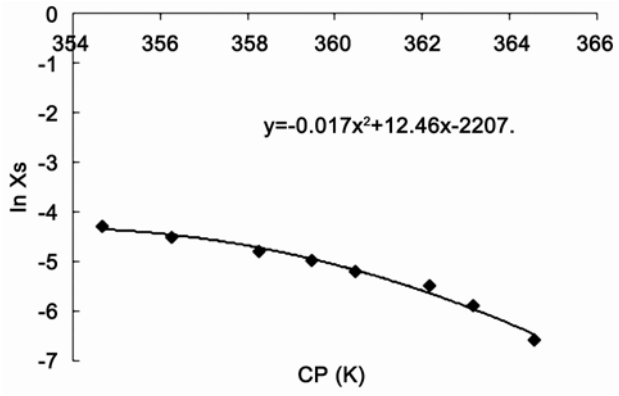

Fig. 5—The nonlinear plot of $\ln X_s$ versus. T (CP) for pure Tween-80-water system.

Table 2—Values of thermodynamic parameters of clouding for the Tween-80 in aqueous medium[a]

$c_{\text{Tween-80}} \times 10^{-2}$ (mol L^{-1})	$\triangle G^0_c$ (kJ mol^{-1})	$\triangle H^0_c \times 10^2$ (kJ mol^{-1})	$\triangle S^0_c$ (J mol^{-1} K^{-1})
7.63	26.98	0.72	-41.18
15.27	24.76	1.24	-36.97
22.90	23.47	1.60	-34.42
30.53	22.50	2.21	-32.02
38.17	21.77	2.56	-30.36
45.80	21.16	2.99	-28.78
76.34	19.44	3.67	-25.06
61.07	20.19	4.20	-25.47

[a]Uncertainty: $\triangle G^0_c$: ±0.05-0.2 kJ mol^{-1}; $\triangle H^0_c$: $\pm0.02\text{-}0.1\times10^2$ kJ mol^{-1}; $\triangle S^0_c$: $\pm0.02\text{-}0.05\times10^2$ J mol^{-1} K^{-1}.

$$\ln X_s = A + BT + CT^2 \quad \ldots (4)$$

where the constants A, B and C are determined by the regression analysis of least squares. A schematic parabolic curve for the plot of $\ln X_s$ versus T(CP) to determine enthalpy change (ΔH_c^0) of clouding process is shown in Fig. 5.

The values of the constants A, B and C are tabulated in Tables S1-S4 (Supplementary Data).

The enthalpy of clouding is then determined numerically by substituting Eq. (4) into Eq. (2).

$$\Delta H_c^0 = RT^2 [B + 2CT] \quad \ldots (5)$$

The values of thermodynamic parameters for pure Tween-80 in aqueous medium are given in the Table 2. The values of ΔG^0_c are found to be positive which indicates the clouding process is non spontaneous in nature. The positive values of ΔG^0_c are found to decrease with increase of concentration of Tween-80 in aqueous medium. The appearance of turbidity in the aqueous solution and its separation into two phases has led to investigations to

determine the effect of solubilization on the temperature at which clouding appears. The clouding components release their solvated water and separate out from the solution and can be considered as the limit of solubility[31]. As a result, the species attain maximum solubility at the CP and thus the standard free energy change of clouding (ΔG^0_c) is associated with the phase separation from a homogeneous phase (clear Tween-80 solution) to a heterogeneous phase (cloudy solution). The values of ΔH_c^0 are found to be positive and the positive values increase with increase of the mole fractional solubility of solute. Thus the values of ΔH_c^0 indicate that the clouding process is endothermic in nature. The values of ΔS^0_c are found to be negative while the negative values decrease with increase of concentration of Tween-80 in aqueous medium. Positive values of both enthalpies and entropies are characteristic of hydrophobic bonding whereas negative enthalpies and entropies are characteristic of hydrogen bonding and electrostatic interactions[32,33]. The positive values of ΔH_c^0 and negative values ΔS^0_c indicate that the interactions among surfactant molecules may be hydrophobic and electrostatic interactions during clouding process.

In the case of (Tween-80+water+sodium salts) systems, the thermodynamic parameters were determined considering the X_s values as the mole fractional solubility of the salt and the obtained values of thermodynamic parameters are summarized in Tables 3 and 4. In all these cases the $\ln X_s$ versus T plots are also found to be nonlinear. Some representative plots are shown in Figs S2-S4 (Supplementary Data). The values of ΔG^0_c for both 7.63×10^{-2} and 15.27×10^{-2} mol L^{-1} solutions of Tween-80 containing varying salts concentration are

Table 3—Values of thermodynamic parameters of clouding of 7.63×10^{-2} (mol L^{-1}) Tween-80 in (salt+water) medium[a]

c_{salt} (mol L^{-1})	$\triangle G^0_c$ (kJ mol^{-1})	$\triangle H^0_c \times10^2$ (kJ mol^{-1})	$\triangle S^0_c \times10^2$ (J mol^{-1} K^{-1})	$\triangle G^0_{c,t}$ (kJ mol^{-1})	$\triangle H^0_{c,t} \times10^2$ (kJ mol^{-1})
			NaCl-Water		
0.00	26.98	0.72	-0.41	-	-
0.99	32.84	3.50	11.56	5.86	-2.14
1.98	30.68	2.93	9.54	3.7	-2.71
2.98	29.37	2.36	7.47	2.39	-3.28
3.97	28.43	1.77	5.38	1.45	-3.87
4.96	27.69	1.18	3.26	0.71	-4.46
5.95	27.08	0.58	1.12	0.1	-5.06
6.94	26.55	-0.03	-1.04	-0.43	-5.67
			Na_2SO_4-Water		
0.00	26.98	0.72	-0.41	-	-
0.09	32.41	1.18	2.38	5.43	-4.46
0.49	30.23	2.17	5.25	3.25	-3.47
0.99	28.97	2.71	6.83	1.99	-2.93
2.96	28.05	3.32	8.58	1.07	-2.32
5.15	27.31	4.05	10.70	0.33	-1.59
7.21	26.74	4.38	11.66	-0.24	-1.26
10.30	26.27	4.51	12.06	-0.71	-1.13
			$NaNO_3$-Water		
0.00	26.98	0.72	-0.41	-	-
1.00	32.83	-0.31	-1.77	5.85	-5.95
2.00	30.52	0.08	-0.62	3.54	-5.56
3.00	29.22	0.26	-0.09	2.24	-5.38
4.00	28.28	0.40	0.35	1.3	-5.24
5.00	27.57	0.49	0.61	0.59	-5.15
6.00	26.99	0.58	0.88	0.01	-5.06
7.00	26.44	0.76	1.42	-0.54	-4.88

[a]Uncertainty: $\triangle G^0_c$: ±0.05-0.2 kJ mol^{-1}; $\triangle H^0_c$: ±0.03-0.1×10^2 kJ mol^{-1}; $\triangle S^0_c$: ±0.02-0.05×10^2 J mol^{-1} K^{-1}.

Table 4—Values of thermodynamic parameters of clouding of 15.27×10^{-2} (mol L^{-1}) Tween-80 in (salt+water) medium[a]

c_{salt} (mol L^{-1})	$\triangle G^0_c$ (kJ mol^{-1})	$\triangle H^0_c \times10^2$ (kJ mol^{-1})	$\triangle S^0_c \times10^2$ (J mol^{-1} K^{-1})	$\triangle G^0_{c,t}$ (kJ mol^{-1})	$\triangle H^0_{c,t} \times10^2$ (kJ mol^{-1})
			NaCl-Water		
0.00	24.76	1.24	-0.37	-	-
0.09	41.58	8.81	30.63	16.82	7.57
0.49	34.48	7.47	25.89	9.72	6.23
0.99	32.35	6.10	20.92	7.59	4.86
2.96	28.98	4.72	15.97	4.22	3.48
5.15	27.19	3.31	10.92	2.43	2.07
7.21	26.10	1.88	5.80	1.34	0.64
10.30	26.88	0.43	0.59	2.12	-0.81
			Na_2SO_4-Water		
0.00	24.76	1.24	-0.37	-	-
0.95	32.39	1.30	2.75	7.63	0.06
1.90	30.18	1.84	4.35	5.42	0.60
2.85	28.88	2.20	5.43	4.12	0.96
4.75	27.17	2.96	7.70	2.41	1.72
6.65	26.11	3.25	8.59	1.35	2.01
7.80	25.49	3.82	10.31	0.73	2.58
9.50	24.88	3.97	10.79	0.12	2.73
			$NaNO_3$-Water		
0.00	24.76	1.24	-0.37	-	-
1.00	32.55	-1.10	-0.19	7.79	-2.34
2.00	30.42	0.24	2.62	5.66	-1.00
3.00	29.17	1.23	6.33	4.41	-0.01
4.00	28.25	2.54	12.76	3.49	1.30
5.00	27.48	4.80	16.87	2.72	3.56
6.00	26.87	6.24	19.60	2.11	5.00
7.00	26.38	7.19	-3.97	1.62	5.95

[a]Uncertainty: ΔG^0_c: = ±0.05-0.2 kJ mol^{-1}; ΔH^0_c: ±0.05-0.1×10^2 kJ mol^{-1}; ΔS^0_c : ±0.01-0.05×10^2 J mol^{-1} K^{-1}.

found to be positive, indicating the processes are still non-spontaneous. The positive ΔG^0_c values are found to be higher in magnitude in presence of salts as compared to in aqueous medium. For all the salts used, the positive values of ΔG^0_c decrease with increase in the concentration of salts for both 7.63×10^{-2} and 15.27×10^{-2} mol L^{-1} solutions of Tween-80 solutions, which indicate that the process tends to move toward spontaneity with the increase of salt concentration.

For both 7.63×10^{-2} and 15.27×10^{-2} mol L^{-1} Tween-80 solutions containing varying concentrations of salts, the values of ΔH_c^0 and ΔS^0_c are found to be positive and the positive values decrease for NaCl. Thus, the values of ΔH_c^0 indicate that the clouding process is endothermic in nature and this endothermic nature decreases with increasing increase of salt concentration. In the case of $NaNO_3$ and Na_2SO_4 solution, the values of ΔH_c^0 and ΔS^0_c tend to increase with increase of concentration of salts. Thus, the interactions among surfactant molecules are mainly hydrophobic in nature in aqueous solution of salts during the clouding process.

For polymer-Tween-80 systems in aqueous medium, the values of thermodynamic parameters are summarized in Tables 5 and 6. The value of standard free energy (ΔG^0_c) change of Tween-80 solutions (7.63-15.27×10^{-2} mol L^{-1}) containing various polymer concentrations are positive indicating the processes are non-spontaneous. The positive ΔG^0_c values were found to decrease with increasing concentration of polymers in all the cases, which indicates that the process tends to move toward spontaneity with the increase of polymer concentration. The effect of added polymer in decreasing the positive values of standard Gibb's

Table 5—Thermodynamic parameters of 7.63×10^{-2} mol L^{-1} Tween-80 in (polymer + water) system

$c_{Polymer}$ (% *w*/*v*)	$\triangle G^0_c$ (kJ mol^{-1})	$\triangle H^0_c \times10^2$ (kJ mol^{-1})	$\triangle S^0_c \times10^2$ (J mol^{-1} K^{-1})	$\triangle G^0_{c,t}$ (kJ mol^{-1})	$\triangle H^0_{c,t} \times10^2$ (kJ mol^{-1})
			PVP-Water		
0.11	44.05	0.25	-0.53	17.07	-5.39
0.31	40.64	1.37	2.68	13.66	-4.27
0.5	39.03	2.32	5.39	12.05	-3.32
0.81	37.46	3.52	8.82	10.48	-2.12
1.02	36.75	3.75	9.47	9.77	-1.89
1.25	36.1	4.04	10.33	9.12	-1.60
1.31	35.94	4.26	10.96	8.96	-1.38
			PVA-Water		
0.1	47.18	-8.23	-24.12	8.96	-13.87
0.26	44.18	-6.44	-19.16	20.2	-12.08
0.5	42.11	-5.50	-16.54	17.2	-11.14
0.75	40.75	-4.27	-13.11	15.13	-9.91
1.04	39.77	-3.71	-11.53	13.77	-9.35
1.25	39.07	-2.45	-8.01	12.79	-8.09
1.5	38.44	-1.66	-5.77	12.09	-7.30
			PEG-Water		
0.61	24.28	-1.54	-4.92	-2.7	-7.18
1.01	22.76	-1.45	-4.63	-4.22	-7.09
1.25	22.1	-0.82	-2.89	-4.88	-6.46
1.51	21.46	-0.64	-2.38	-5.52	-6.28
2.02	20.59	1.65	4.02	-6.39	-3.99
2.5	19.88	3.40	8.92	-7.1	-2.24
4.25	11. 44	3.74	10.12	-15.54	-1.90

[a]Uncertainty: ΔG^0_c: ±0.05-0.2 kJ mol^{-1}; $\triangle H^0_c$: ±0.03-0.1×10^2 kJ mol^{-1}; $\triangle S^0_c$: ±0.03-0.05×10^2 J mol^{-1} K^{-1}.

energy (ΔG^0_c) of Tween-80 was found to follow the order: polyethylene glycol (PEG) > polyvinyl pyrrolidone (PVP) > polyvinyl alcohol (PVA**)**. For 7.63–15.27×10^{-2} mol L^{-1} Tween-80 solutions containing varying concentrations of PVP, the values of ΔH^0_c and ΔS^0_c are found to be positive and the positive values increased with increase of the concentration of PVP. In presence of PVA, the values of ΔH^0_c and ΔS^0_c are found to be negative and the negative values tend to decrease with increase in the concentration of PVA. In the case of PEG solution, the values of ΔH^0_c and ΔS^0_c of the clouding of Tween-80 solution are found to be negative at lower PEG concentration, the sign changes from negative to positive and the positive values tend to increase with increase of the concentration of PEG.

For 22.90×10^{-2} mol L^{-1} Tween-80 in (PVP+water) system, the values of ΔH^0_c and ΔS^0_c of the clouding of Tween-80 solution are negative and the negative values decrease with increase of PVP concentrations. In the case of PVA solution, the values of ΔH^0_c and ΔS^0_c of the clouding are found to be negative at lower PVA concentration, the sign changes from negative to positive and the positive values tend to increase with increase in the concentration of PVA. For PEG solution, the values of ΔH^0_c and ΔS^0_c are found to be negative and the negative values increase, though to a small extent, with increase of PEG concentrations. Negative values of ΔH^0_c and ΔS^0_c were also observed for the clouding phenomenon of non-ionic surfactant systems in pure water and in presence of NaCl[34] as well as in presence of polymer[17]. Kabir-ud-Din *et al.*[35] also observed negative values of ΔH^0_c and ΔS^0_c for promethazine hydrochloride (PMT)-Tween-80 system. The large negative values of ΔH^0_c are indicative of a highly exothermic process. The overall system is in a disordered state at the cloud point. However, for 7.63×10^{-2} mol L^{-1} Tween-80 surfactant solutions, interactions are mainly hydrophobic in nature in presence of PVP while both hydrophobic and exothermic interactions are expected to be present in

Table 6—Thermodynamic parameters of 22.90×10^{-2} mol L^{-1} Tween-80 in (polymer+water) system[a]

$c_{Polymer}$ (% *w*/*v*)	$\triangle G^0_c$ (kJ mol^{-1})	$\triangle H^0_c \times10^2$ (kJ mol^{-1})	$\triangle S^0_c \times10^2$ (J mol^{-1} K^{-1})	$\triangle G^0_{c,t}$ (kJ mol^{-1})	$\triangle H^0_{c,t} \times10^2$ (kJ mol^{-1})
			PVP-Water		
0.11	43.9	-5.94	-17.69	20.43	-7.18
0.31	40.6	-5.11	-15.35	17.13	-6.35
0.5	38.93	-3.52	-10.94	15.46	-4.76
0.81	37.41	-2.62	-8.39	13.94	-3.86
1.02	36.69	-2.29	-7.47	13.22	-3.53
1.25	35.99	-1.64	-5.64	12.52	-2.88
1.31	35.85	-1.48	-5.18	12.38	-2.72
			PVA-water		
0.1	47.1	-3.69	-11.56	23.63	-4.93
0.26	44.15	-2.43	-8.02	20.68	-3.67
0.5	41.97	-0.85	-3.55	18.5	-2.09
0.75	40.71	-0.58	-2.78	17.24	-1.82
1.04	39.65	0.54	0.40	16.18	-0.70
1.25	39	1.22	2.35	15.53	-0.02
1.5	38.36	2.07	4.76	14.89	0.83
			PEG-water		
0.61	24.18	-9.36	-26.69	0.71	-10.60
1.01	22.63	-9.39	-26.78	-0.84	-10.63
1.25	21.98	-9.41	-26.81	-1.49	-10.65
1.51	21.37	-9.45	-26.97	-2.1	-10.69
2.02	20.48	-9.48	-27.06	-2.99	-10.72
2.5	19.84	-9.48	-27.06	-3.63	-10.72
4.25	11.39	-9.53	-27.03	-12.08	-10.77

[a]Uncertainty: ΔG^0_c: ±0.05-0.2 kJ mol^{-1}; ΔH^0_c: $\pm0.03\text{-}0.1\times10^2$ kJ mol^{-1}; ΔS^0_c: $\pm0.01\text{-}0.05\times10^2$ J mol^{-1} K^{-1}.

PVA and PEG polymers. For 22.90×10^{-2} mol L^{-1} Tween-80 surfactant solutions containing PVP and PEG polymers, the values of ΔH^0_c and ΔS^0_c indicate that the binding interactions are mainly exothermic or electrostatic in nature, though both hydrophobic and exothermic interactions may be present in PVA solution.

The net enthalpy change is the sum of the change in enthalpies arising from hydrophobic interactions, electrostatic interactions and hydration of polar head groups. A negative ΔH^0_c may occur when hydration of water molecules around the hydrophilic head group become more important than that of the destruction of the water structure around the hydrophobic alkyl chains of surfactant monomers[36,37]. The positive values of ΔH^0_c can be attributed to disruption of the water structure around the hydrophobic alkyl tails of non-ionic surfactant molecules[38]. The negative values of ΔH^0_m also signify the importance of London-dispersion interactions as an attractive force of micellization between drug-surfactant systems[39], whereas the positive ΔH^0_m values indicate breaking of the structured water around the hydrophobic parts of the molecules[40].

The transfer free energies (ΔG^0_c) and transfer enthalpies (ΔH^0_c) of clouding from water to the aqueous solutions of additives was obtained from the following relation[41]:

$$\Delta G^0_{c,t} = \Delta G^0_c \text{ (aq. of additive)} - \Delta G^0_c \text{ (aq.)} \quad \ldots (6)$$

$$\Delta H^0_{c,t} = \Delta H^0_c \text{ (aq. of additive)} - \Delta H^0_c \text{ (aq.)} \quad \ldots (7)$$

The transfer free energies (ΔG^0_c) are positive in nature and the values decrease with increase of additive concentration except (Tween-80+PEG) system containing 22.90×10^{-2} mol L^{-1} Tween-80 while with increase of PEG concentration the values are negative and increase. The transfer enthalpies of clouding of Tween-80 in presence of additives like salts and polymers used in this study are found to be negative with some exceptions in the

Table 7—Values of $\Delta H^{0,*}_c$, T_c and R^2 for Tween-80 solution in different media

$c_{\text{Tween-80}} \times 10^{-2}$ (mol L^{-1})	Medium	$\Delta H^{0,*}_c$ (kJ mol^{-1})	T_c (K)	R^2
(7.63-61.07)	water	3465.96	295.50	0.99999
7.63	NaCl+water	26.93	279.35	0.99999
7.63	$NaNO_3$+water	33.78	285.65	0.99994
7.63	Na_2SO_4+water	36.16	344.21	0.99999
15.27	NaCl+water	26.60	278.72	0.99999
15.27	$NaNO_3$+water	30.60	351.63	1
15.27	Na_2SO_4+water	39.10	332.39	0.99997
7.63	PVP+water	43.60	349.42	0.99999
7.63	PVA+water	41.31	357.89	0.99999
7.63	PEG+water	20.10	353.09	0.99974
22.90	PVP+water	37.09	356.74	0.99999
22.90	PVA+water	39.46	352.91	0.99999
22.90	PEG+water	3.52	352.14	0.83423

presence of salts. Negative transfer of enthalpies of micellization were reported for the transfer of NaCl and amino acids from water to an aqueous urea solution[42,43].

The enthalpy-entropy compensation, a linear relationship between ΔH^0_m and ΔS^0_m with R^2 value in the range of 0.994–0.999 was observed in all the cases according to the following regression equation[44],

$$\Delta H^0_m = \Delta H^{0,*}_m + T_c \Delta S^0_m \quad \ldots (8)$$

where the slope, T_c is the compensation temperature, which describes the solvation part of micellization process and is the basis of comparison for differing examples of compensation behavior, while the intercept $\Delta H^{0,*}_m$, is the intrinsic enthalpy gain. The values of ΔH^{0*}_m and T_c for the studied systems in pure water, in the presence of salts and polymers are shown in Table 7. The T_c values of (Tween-80+salts) systems in water are found to be comparable to those of biological fluids[45], whereas the values in presence of polymers used herein are higher in magnitude as compared to in biological fluids. The T_c values of (Tween-80+additives) systems in water are found to be in the range of 278.71–357.89 K. The values of ΔH^{0*}_m are highly positive and the decrease in positive values of Tween-80 solutions due to addition of solutes is the indicative of the increase in stability of the system.

Conclusions

In this study, the cloud point (CP) of non-ionic surfactant, Tween-80, has been determined in aqueous medium and in presence of aqueous solutions of salts and water soluble polymers. The CP is found to be dependent upon the varying environment of non-ionic surfactant solutions. The addition of salts lowers the cloud point of Tween-80 and SO_4^{2-} is the most efficient cloud point depressor as compared to the other monovalent ions, Cl^- and NO_3^-. The standard free energy (ΔG_c^0) change and the values of enthalpy (ΔH_c^0) and entropy (ΔS_c^0) are found to decrease with increase of concentration of Tween-80. The overall clouding process is exothermic and the process of clouding is guided by enthalpy only.

Supplementary Data

Supplementary Data associated with this article, viz., Figs S1-S4 and Tables S1-S4 are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(07)793-802_SupplData.pdf.

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