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# THERMODYNAMICS OF SOLUBILIZATION OF TRITON–X–100 IN PURE AND MIXED SYSTEM WITH POLYACRYLAMIDE

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## ABSTRACT

The solvation and desolvation phenomenon of nonionic surfactant Triton X–100 (TX–100) have been studied by measuring the cloud points (CP) at different [TX–100] concentrotions in pure and mixed system with polyacrylamide (PAA). It has been found that the low [PAA] did not have much effect on CP of TX–100. Considering the CP as threshold temperature of solubility, the theromodynamics of solubilization (std. Free energy, std. enthalpy and std. entropy) of the pure surfactant and surfactant/polymer mixture have been evaluated. An attempt has been made to provide evidence for probable interaction between the surfactant and polymer.

**Key words:** Triton–X–100, Polyacrylamide, Cloud point, Polymer/Surfactant interaction

## INTRODUCTION

The physico–chemical studies of polymer/surfactant solution have created much interest regarding their industrial importance[1–9]. Ionic surfactants hardly show the property of clouding while many non–ionic surfactants and water soluble polymers cannot withstand at elevated temperature and become perceptible even with the naked eye known as "clouding". The cloud point (CP) is an important property of non–ionic surfactant, 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[10] by formation of giant molecular aggregates in the state of separate phase[11–14]. Water soluble polymers also exhibit clouding by similar mechanism. The phenomenon is reversible and the CP stands for the transition from water soluble state to oil soluble state[15]. The CP values for a polymet–surfactant mixture may be a guide to its hydrophilic or hydrophobic character. This information is useful in pharmaceutical preparations, biomedical formulations, enhanced oil recovery processes etc., where nonionic surfactants and polymers are used in combination.

The clouding of ionic/nonionic surfactants and polymers alone and mixture has been studied by many workers[16–24].

The aqueous solution is not only composed of highly dispersed surfactant and polymer molecules but also of surfactant aggregates as well as complexes of polymer and surfactant. The stability is aqueous solution alone and in polymer–surfactant combination with respect to temperature need to be known with regard to their multifold applications mentioned above. This can be understood from the knowledge of their cloud points.

In this paper, the results of our study on the clouding phenomenon of TX–100 in absence and presence of polyacrylamide at different concentrations have been reported. The thermodynamic parameters of clouding (considering CP as a phase separation point) has been evaluated in the light of probable interaction between nonionic surfactant and polymers.

## MATERIALS AND METHODS

Nonionic surfactant Triton X–100 was obtained from Fluka Chemie and it was used as received. Polyacrylamide was the product of sigma USA (Mol. Wt. $5 \times 10^5$). It was dialysed to remove low molecular weight fractions and other associated electrolytic impurities. Doubly distilled water with sp.conductance 2–4 $\mu S\ cm^{-1}$ at 303 K was used in preparation of solutions of different concentrations. The cloud point (CP) was determined by controlled heating in well stirred surfactant and surfactant–polymer system, until it clouded or got turbid. The sample was then allowed to cool slowly under stirring condition and the temperature of the disappearance of turbidity was considered as the CP. Heating and cooling was regulated to about 1°C per minute around the cloud point. The reproducibility of the measurement was found to be within ± 0.2°C.

## RESULTS AND DISCUSSION

### Cloud points (CP) of pure TX–100

The cloud points of TX–100 at different concentrations in (Wt%) are given in Table 1. The CP of TX–100 are substantially constant over a wide range of concentration, the values of CP increase mildly with increase in concentration of surfactant. In fact, CP of TX–100 has been reported[11] to change very slowly.

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

| Wt% | Molraity x $10^2$ | Mole fraction x $10^4$ | CP/°C |
|---|---|---|---|
| 2 | 3.096 | 5.565 | 64.3 |
| 4 | 6.192 | 11.124 | 65.0 |
| 6 | 9.288 | 16.677 | 66.0 |
| 8 | 12.380 | 22.216 | 66.5 |
| 10 | 15.480 | 27.834 | 67.0 |

## Triton X–100 – polyacrylamide system

The influence of polymer on the cloud point of TX–100 at varied concentrations has been also studied. The results are presented in Table 2. It has been found that the low concentration of PAA, less than 0.005 (wt%), did not have much effect on the CP of TX–100, it remained around 64°C. The values of CP in Table 2 show that CP declines with increase in [PAA] effectively. This is mainly due to the removal of water by the polymer, which helps the surfactant micelles to come nearer to each other resulting into lowering of CP.

**Table 2. Influence of PAA on CP of Triton X–100**

| [Triton X–100] Wt% | CP/°C at [PAA] (Wt%) | | | | |
|---|---|---|---|---|---|
| | 0.005 | 0.01 | 0.02 | 0.03 | 0.04 |
| 2 | 63.5 | 63.0 | 62.5 | 62.0 | 61.0 |
| 4 | 63.0 | 62.5 | 62.0 | 61.5 | 60.0 |
| 6 | 62.3 | 61.8 | 61.0 | 60.2 | 59.5 |
| 8 | 62.0 | 61.5 | 60.0 | 59.0 | 58.5 |
| 10 | 60.5 | 60.0 | 59.0 | 58.4 | 57.0 |

## Thermodynamics of clouding process

Cloud points are the characteristics of nonionic surfactants. It is the manifestation of the solvation/desolvation phenomenon in nonionics[12,25]. The desolvation of hydrophilic groups of the surfactant leads to the formation of cloud in the surfactant solution. Kjellander *et al.*[12] stated that the appearance of cloud point is entropy dominated. At the CP, the water molecules get totally detached from the micelles. The overall entropy is very high and hence, the free energy change is more negative and the appearance of cloud point is facile.

Considering the cloud point as the phase separation point, i.e. the solubility limit of solute, the thermodynamic parameters such as standard free energy ($\Delta G^o_{Cl}$), enthalpy ($\Delta H^o_{Cl}$), and entropy ($\Delta S^o_{Cl}$) for the clouding process have been calculated using phase separation model[26]. The following relation can be written as –

$$\Delta G^o_{Cl} = - RT \ln X_S \qquad ...(1)$$

Where $X_S$ is the mole fractional solubility of the solute.

Standard entropy ($\Delta S^o_{Cl}$) for the clouding process have been calculated using following relationship –

$$\Delta S^o_{Cl} = (\Delta H^o_{Cl} - \Delta G^o_{Cl}) / T \qquad ...(2)$$

The standard enthalpy ($\Delta H^o_{Cl}$) for clouding process can be calculated from the solubilization curve given by[26]

$$-\Delta H^o_{Cl} = RT^2 \left(d \ln X_S / dT\right)_P \qquad \ldots(3)$$

$$\ln X_S = (\Delta H^o_{Cl} / R)(1/T) + C \qquad \ldots(4)$$

The value of $\Delta H^o_{Cl}$ for TX–100 have been determined from the slope of linear plot ln $X_S$ V/s. (1/T) (Fig. 1) are given in Table 3. The negative values of $\Delta H^o_{Cl}$ indicate the process of clouding is exothermic in nature.

The dependence of CP on [PAA] is depicted in Fig. 2 and the values of CP are presented in Table 2, which indicate initial flat portion followed by mild decline in CP values. Fall in CP depends on [TX–100].

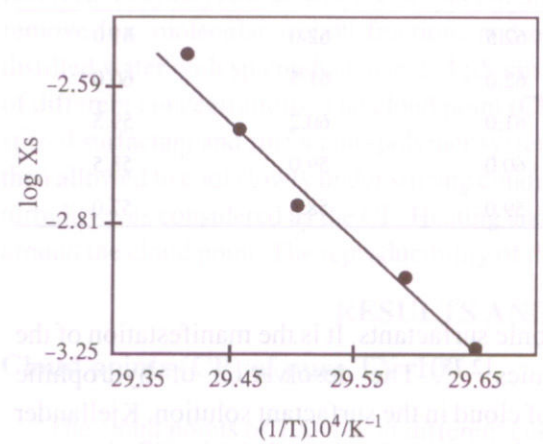


**Fig. 1. : log Xs V/s (1/T) Plot for TX–100 to derive enthalpy of clouding ($\Delta H^o_{Cl}$)**

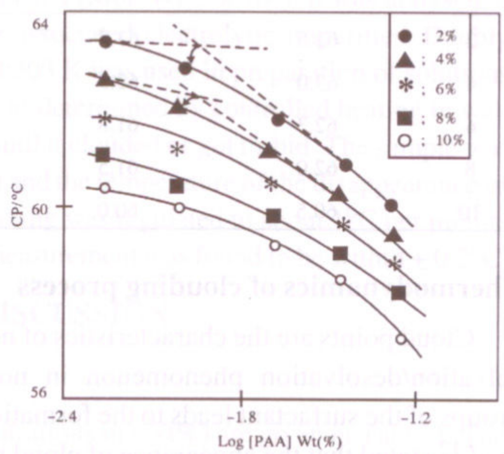


**Fig. 2. : CP V/s Log [PAA] plot at different [TX–100] in Wt (%)**

**Table 3. Thermodynamic Parameter of Solubilization of TX–100**

| $\Delta G^o_{Cl}$ KJmole$^{-1}$ | $-\Delta H^o_{Cl}$ KJmole$^{-1}$ | $-\Delta S^o_{Cl}$ Jmole$^{-1}$ K$^{-1}$ |
|---|---|---|
| 21.0 | | 593 |
| 19.1 | | 586 |
| 18.0 | 179 | 581 |
| 17.2 | | 578 |
| 16.2 | | 575 |

**Table 4. Thermodynamic parameters of TX–100 in presence of PAA**

| Wt% [PAA] | $\Delta G^o_{Cl}$ KJmole$^{-1}$ | $-\Delta H^o_{Cl}$ KJmole$^{-1}$ | $-\Delta S^o_{Cl}$ Jmole$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 0.005 | 22.8 | 280 | 898 |
| 0.01 | 20.9 | 278 | 884 |
| 0.02 | 18.9 | 270 | 835 |
| 0.03 | 18.2 | 265 | 834 |
| 0.04 | 16.9 | 260 | 814 |

Thermodynamic parameters for polymer/surfactant system are evaluated on the basis of phase separation model and are given in Table 4. In the evaluation of $\Delta H^o_{Cl}$ for TX–100/PAA system from the plot of ln $X_S$ V/s (1/T) shows two stages of the temperature limits. The $X_S$ for this system is calculated by considering both [TX–100] and [PAA] since both are amenable to concluding, but the number of moles of polymer is insignificant compared to that of TX–100 due to the high molecular weight and consequently the overall $X_S$ is essentially that of TX–100. It has been found that addition of polyacrylamide decreases the CP of TX–100 due to the fact that the additive compete for the water molecules with the micelles and the surfactant becomes less hydrated and thereby lowers the cloud point. $\Delta H^o_{Cl} > T\Delta S^o_{Cl}$ indicate that the process of clouding is guided by both; the enthalpy and entropy. As shown in Table 4, $\Delta H^o_{Cl} < \Delta G^o_{Cl}$ indicate overall clouding process is exothermic.

The present work would be a supportive evidence about the probable interaction between nonionic surfactant and neutral water soluble polymer leading to phase separation at or near the cloud point.

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## REFERENCES

1. M. N. Jones, J. Colloid Interface Sci., **23**, 36 (1967).
2. H. Arai, M. Murata and K. Shinoda. J. Colloid Interface Sci., **37**, 223 (1971).
3. E. D. Goddard, Colloids Surf., **19**, 255 (1986).
4. M. L. Fishman and F. R. Eirich, J. Phys. Chem., **79**, 2740 (1975).
5. D. M. Bloor and Wyn. E. Jones, J. Chem. Soc. FaradayII, **78**, 657 (1982).

6. C. Tonder, J. Phys. Chem., **89**, 5110 (1985).

7. E. D. Goddard, Interaction of Surfactants with Polymers and Proteins. Edited by E. D. Goddard and K. P. Ananthpadmanabhan, CRC Press, Baca Raton, PL (1993) p. 123.

8. B. Cabane and R. Duplessix, J. Phys. (Paris), **48**, 651 (1987).

9. K. Chari, B. Antalek, M. Y. Lin and S. K. Sinha., J. Chem. Phys., **7**, 100 (1994).

10. D. Myers, Surfactant Science and Technology, 2[nd] Edn. VCH, N. York (1963).

11. K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, Colloidal Surfactant, Some Physicochemical properties Academic Press, New York (1963).

12. R. Kjellander and E. Florin, J. Chem. Soc. Faraday Trans. I, **17**, 2053 (1981).

13. D. Blankchtein, G. M. Thurston and G. B. Benedeck, J. Chem. Phy., **85**, 7268 (1986).

14. L. A. M. Rupert, J. Colloid Interface Sci., **153**, 92 (1992).

15. K. V. Schubert, R. Strey and M. Kahlweit, J. Colloid Interface Sci., **141**, 21 (1991).

16. S. P. Maulik and Soumen Ghosh, J. Mol. Liqs., **72**, 145 (1997).

17. IO. D. Robb, An Anionic Surfactants – Physical Chemistry of Surfactant Action, Edited by E. H. Lucassen Rehynders Marcel Dekker, New York (1981).

18. Wang and G. Olofsson, J. Phys. Chem., **99**, 5588 (1995).

19. S. Saito, J. Colloid Interface Sci., **24**, 227 (1967).

20. M. L. Fishman and F. R. Erich, J. Phys. Chem., **75**, 3135 (1971).

21. M. L. Smith and N. Muller, J. Colloid Interface Sci., **43**, 491 (1973).

22. Bailey Jr. and J. V. Koleske, Poly (Ethyleneoxide); Academic Press, New York (1976).

23. M. J. Schwuger, J. Colloid Interface Sci., **43**, 41 (1973).

24. P. Molyneux, Water Soluble Synthetic Polymers : Properties and Behaviour CRC Press, Boca Raton FL Vol II Chap.2 (1984).

25. L. Marszall, Langmuir, **4**, 80 (1988).

26. D. Attwood, A. T. Florence, Surfactant System Champman and Hall, Landon, (1983) p. 99.

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