

Interaction of Polyacrylamide with Cetyltrimethyl Ammonium Bromide in Aqueous Solution at Various Temperatures

T.J. PATIL and H.A. PATIL*

Department of Chemistry

Jai Hind College, Deopur, Dhule-424 002, India

The interaction of cetyltrimethyl ammonium bromide (CTAB) with polyacrylamide (PAA) has been studied by means of surface tension, conductance measurements in aqueous solutions. The critical aggregation concentration (CAC) of cetyltrimethyl ammonium bromide solution from surface tension and conductance data has been found to be 0.91 mM at 303 K. The Critical aggregation concentration (CAC), and polymer saturation point (PSP) are found to decrease with increase in temperature. The thermodynamic parameters were determined at PSP; the $\Delta G_{\text{PSP}}^{\circ}$ values become more negative with increase in temperature.

Key Words: Polyacrylamide, Cetyltrimethyl ammonium bromide, Surface tension, Conductance, Critical aggregation concentration, Polymer saturation point.

INTRODUCTION

The physico-chemical studies of polymer-surfactant solution have created much interest regarding their industrial importance¹⁻⁹. The surface and thermodynamic properties of P-S solutions provide valuable information with reference to mode of interaction between different molecules^{10, 11}. The P-S interaction has been studied by various methods^{7, 12, 13}. All these studies indicate that polymers interact with surfactants by inducing micellization of surfactants on the polymer chain and after polymer gets saturated with micelles, the excess of surfactant forms free micelles¹⁴.

Usually, it has been found that the neutral polymers interact with anionic surfactants and show little or no tendency to interact with cationic or non-ionic surfactants¹⁵. However, neutral polymers with some hydrophobicity and surface activity show significant interaction with cationic surfactants¹⁶. In this paper, the results of P-S system containing polyacrylamide and cationic surfactant cetyl trimethylammonium bromide (CTAB) are presented. The surface, conductance and thermodynamic properties associated with this P-S system have been computed.

EXPERIMENTAL

Polyacrylamide was purchased from Sigma, USA and cetyl trimethyl ammonium bromide (Trizma Chemicals, India) was recrystallized from acetone-methanol mixture and then dried before use. Doubly distilled water with specific conductance $2-4 \mu\text{S cm}^{-1}$ at 303 K was used in all preparations. CMC and PSP of polymer surfactant system was obtained by surface tension measurement using a du-Nony tensiometer¹⁷ at 303, 308, 313 and 318 K. The concentration of surfactant solution was varied by adding aliquots of 30 mM concentrated stock solution to known volume of polymer solution with the help of Hamilton microsyringe. The conductance measurements were carried out by Equiptronics EQ-664 conductivity bridge having a dip type cell with a cell constant 0.7542 cm^{-1} .

RESULTS AND DISCUSSION

Surface tension and conductance data show two break points. The PSP values for polyacrylamide-CTAB system by these two methods are given in Table-1.

TABLE-1
POLYMER SATURATION POINT (PSP) VALUES BY SURFACE
TENSION AND CONDUCTANCE MEASUREMENT

Polymer concentration % (w/v)	Surface tension PSP (mM)				Conductance PSP (mM)			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.01	1.93	1.35	1.15	0.75	1.92	1.35	1.12	0.73
0.02	2.35	1.90	1.42	1.02	2.30	1.92	1.40	1.05
0.03	2.38	2.18	1.50	1.08	2.40	2.22	1.58	1.10
0.04	2.44	2.20	1.78	1.15	2.45	2.25	1.75	1.18

From the above data, it is indicated that both these methods give nearly equal values. The PSP values decrease with increase in the temperature, showing saturation of polymer at lower concentrations. This is due to the micelles present as a necklace¹² in the polymer chain observed for PEO + SDS solution reported by Cabane and Duplessix¹⁹, CMC increases with increase in polymer concentration since more binding sites are available and more surfactant is required for micellization. The PSP values increase with increase in polymer concentration. Fig. 1 shows the plot of surface tension (γ) against log of surfactant concentration at various temperatures. Fig. 2 shows plot of specific conductance against surfactant concentration shows three linear regions. Polymer-surfactant binding begins at CAC¹² with further increase in surfactant concentration; a second transition, *i.e.*, PSP is obtained²⁰.

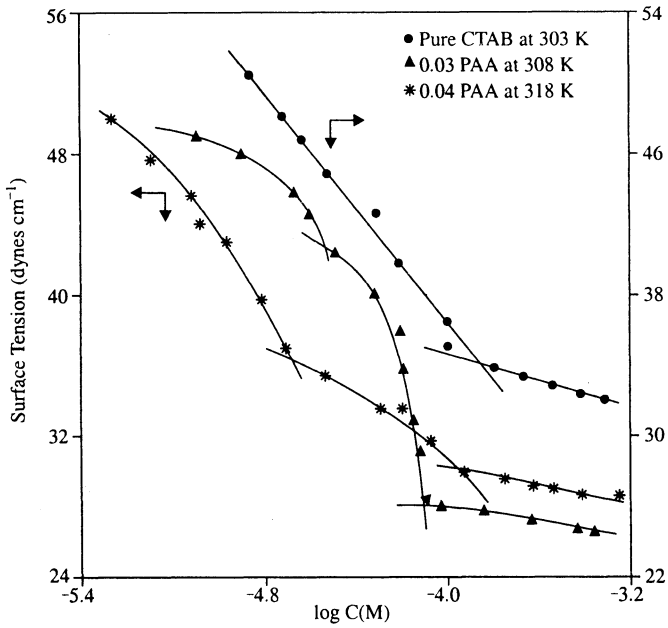


Fig. 1. Plot of Surface Tension (γ)-log C(M)

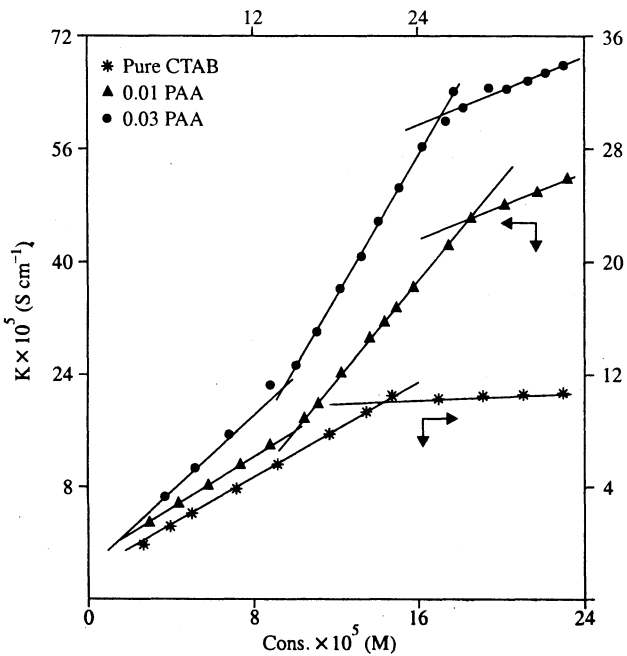


Fig. 2. Plot of specific Conductance-conc. (M) at 303 K

The thermodynamic parameters associated with micellization are calculated at CAC and PSP. The free energy of micellization at PSP, $\Delta G_{\text{PSP}}^{\circ}$ for ionic systems²¹,

$$\Delta G_{\text{PSP}}^{\circ} = (2 - \alpha) RT \ln C_{\text{PSP}}$$

where C_{PSP} is taken in the mole fraction scale. α is degree of ionization of the micelle and it is usually obtained from the slopes of specific conductivity-concentration plots above and below the CMC. Conductometric determination of ' α ' is based on the methods of slopes²². Several workers¹⁵ have found α values 0.85 and 0.65 for PVP-SDS and PEO-SDS systems. For given polymer-CTAB system, α values around 0.55 to 0.80 have been obtained. The evaluated values at 303 K for polymer-CTAB system are shown in Table-2.

TABLE-2
STANDARD FREE ENERGY, ENTROPY AND ENTHALPY AT PSP FOR POLYACRYLAMIDE-CTAB SOLUTION

Polymer concentration % (w/v)	$-\Delta G_{\text{PSP}}^{\circ}$ (kJ mol ⁻¹)	$\Delta H_{\text{PSP}}^{\circ}$ (kJ mol ⁻¹)	$\Delta S_{\text{PSP}}^{\circ}$ (kJ mol ⁻¹ K ⁻¹)	α 303 K
0.01	36.6	-3.9	109	0.80
0.02	36.4	-5.8	101	0.74
0.03	36.3	-6.4	110	0.68
0.04	36.0	3.2	140	0.55

The $\Delta G_{\text{PSP}}^{\circ}$ values are found to be more negative with increase in temperature indicating spontaneous micelle formation.

A linear $\Delta G_{\text{PSP}}^{\circ}$ vs. T plot (correction coefficient 0.878–0.889) was used to obtain $\Delta H_{\text{PSP}}^{\circ}$ and $\Delta S_{\text{PSP}}^{\circ}$ values. The $\Delta S_{\text{PSP}}^{\circ}$ values for ionic surfactant systems are negative but at higher concentration (0.04% polymer concentration) the values become positive, indicating interaction seems to be endothermic; the nonionic nature of the polymer may be the reason for this positive enthalpy at high polyacrylamide concentration.

Conclusions

Polycrylamide-CTAB in aqueous solution was studied at various temperatures by surface tension and conductance measurement. Both the methods show two critical concentrations CAC and PSP values. For this P-S system the PSP values decrease with increase in temperature. The knowledge of the energies of the process plays an important role in determining the nature of interaction. From the present study, it was observed that CTAB interacts with polyacrylamide and the interaction is mildly exothermic; however at higher polymer concentration the interaction seems to be endothermic due to non-ionic nature of polyacrylamide.

ACKNOWLEDGEMENT

The authors wish to acknowledge UGC, New Delhi for awarding Teacher Fellowship. The authors are also thankful to Dr. K.B. Patil, Principal, and Dr. A.A. Patil, Head, Chemistry Department, Jai Hind College, Dhule.

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. M.N. Jones, H.A. Skinner and E. Tipping, *Biochem J.*, **135**, 231 (1973).
4. M. Saraste, *Anal. Chem.*, **92**, 444 (1979).
5. S. Satio, Nonionic Surfactants, in: M.J. Shick (Ed.), Physical Chemistry, Marcel-Dekker Inc., New York, Ch. 15, p. 881 (1989).
6. E.D. Goddard, in: E.D. Goddard and K.P. Ananthpadmanabhan (Eds.), Interaction of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, FL, p. 123 (1993).
7. E.D. Goddard, *Colloids Surf.*, **19**, 255 (1986).
8. D.M. Bloor, H.K.O. Makibete and E. Wyn-Jones, *J. Colloid Interface Sci.*, **178**, 334 (1996).
9. M.L. Fishman and F.R. Eirich, *J. Phys. Chem.*, **79**, 2740 (1975).
10. I. Satake and J. Yang, *J. Biopolymers*, **15**, 2263 (1976).
11. K. Anand and O.P. Yadav, *Indian J. Chem.*, **33A**, 857 (1994).
12. B. Cabane and R. Duplessix, *J. Phys. (Paris)*, **48**, 651 (1987).
13. K. Chari, B. Antalek, M.Y. Lin and S.K. Sinha, *J. Chem. Phys.*, **7**, 100 (1994).
14. R. Zana, J. Lang and P. Lianos, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **23**, 39 (1982).
15. H. Haffman and G. Huber, *Colloids Surf.*, **40**, 181 (1989).
16. R. Zana, W. Binana-Limbeli, N. Kamenka and B.J. Lindman, *J. Phys. Chem.*, **96**, 5461 (1992).
17. S.P. Maulik and S. Ghosh, *J. Mol. Liq.*, **72**, 145 (1997).
18. P. Datta and S.P. Maulik, *Indian J. Biochem. Biophys.*, **35**, 1 (1998).
19. B. Chabane and R. Duplessix, *J. Phys. (Paris)*, **43**, 1529 (1982).
20. E. Minatti and D. Zanette, *Colloids Surf.*, **113**, 237 (1996).
21. R.E. Verral, Z. Milioto and R. Zana, *J. Phys. Chem.*, **92**, 3939 (1988).
22. H.G. Evans, *J. Chem. Soc.*, 579 (1956).

(Received: 1 September 2004; Accepted: 31 January 2005)

AJC-4075