

Ultrasonic Studies on the Micellar Behaviour of Non-Ionic Surfactant in Aqueous Polyelectrolyte at 303 and 313 K

T.J. PATIL

Department of Chemistry, Z.B. Patil College Deopur, Dhule-424 002, India

Tel: (91)9423916046; E-mail: tjpatil123@rediffmail.com

Ultrasonic velocities (U) and densities (ρ) have been measured for the aqueous solution of non-ionic surfactant Triton-X-100 (TX-100) in presence of polyelectrolyte polymethacrylic acid (PMAAc) at 303 and 313 K, to understand polymer-surfactant interaction (P-S) in aqueous medium. Various acoustic parameters such as adiabatic compressibility (β_{ad}), intermolecular free length (L_f), molar sound velocity (R), specific acoustic impedance (Z), molar volume (V_m) and surface tension (γ) are evaluated using standard relations. The trends in acoustical parameters of present polymer-surfactant system suggests the aggregation of surfactant micelles on to the polymer chain at critical micelle concentration (CMC) forming polymer-surfactant complex, supporting the well accepted morphology of Pearl Necklace Model.

Key Words: Polymer-surfactant interaction, Acoustic parameters, Critical micelle concentration.

INTRODUCTION

Polymer surfactant interactions have been studied by various methods¹⁻⁵. Non-ionic surfactants play an important role in many chemical reactions by forming micelles in aqueous medium due to the presence of polar head group and non-polar long chain hydrocarbon. Triton-X-100 is used in biological study because it does not denature the integral protein and it is found to be biodegradable. Polymer interacts with surfactant by inducing micelization of surfactant on the polymer chain after getting saturated with micelles, the excess of surfactant form free micelles⁶. The polymer-surfactant interaction consider the effect of polymer molecule on surfactant self assembly through micelle formation. The phenomenon of aggregation of surfactant in presence of polymer can be characterized by further addition of surfactant leads to polymer saturation point (PSP) or the CMC of surfactant in presence of polymer^{7,8}.

In present studies, the data of ultrasonic velocity, density of the polymer-surfactant system containing water soluble polymer polymethacrylic acid (PMAAc) and non-ionic surfactant Triton-X-100 (TX-100) at 303 and 313 K have been reported.

EXPERIMENTAL

Non-ionic surfactant Triton-X-100 (TX-100) was obtained from Fluka Chemie and was used as received. Polymethacrylic acid (PMAAc) was the product of SIGMA (USA), (m.w. 300000). It was dialyzed to remove low molecular weight fraction and other associated electrolytic impurities. Doubly distilled water with sp. conductance $2-4 \mu\text{S cm}^{-1}$ at 303 K was used in all preparation of test solutions. Solutions of various concentrations were prepared by appropriate dilution of stock solutions of polymer (0.01 % w/v) and surfactant (30 mM). For the present study polymer concentration was kept constant and that of surfactant concentration was varied continuously.

Sound velocities: The ultrasonic velocities of pure surfactant and polymer-surfactant mixtures were measured at 2 MHz using ultrasonic interferometer M-81 (M/s Mittal Enterprises, New Delhi, India) by procedure described elsewhere⁹. The test solution in interferometric cell was maintained at required temperature by circulating thermostatic water with an accuracy of ± 0.1 K. The estimated accuracy of sound velocity was ± 0.2 %.

Densities: Densities of the solutions have been determined using bicapillary pycnometer. The accuracy of density measurement was ± 0.001 Kg/m³.

All the measurements were carried out such as to avoid various types of possible degradation of the polymer solution¹⁰.

Theoretical formulations: The various acoustical parameters such as adiabatic compressibility (β_{ad}), intermolecular free length (L_f), molar sound velocity (R), sp. acoustic impedance (Z), molar volume (V_m) and surface tension (γ) are evaluated using following standard relations;

$$\beta_{ad} = \rho^{-1} U^{-2}$$

$$L_f = K (\beta_{ad})^{1/2}$$

$$R = (M/\rho) U^{1/3}$$

$$Z = \rho U$$

$$V_m = M/\rho$$

$$\gamma = (U^{3/2}) (6.3 \times 10^{-4}) \times \rho$$

where U is ultrasound velocity, ρ is density, K is Jacobson's temperature dependent constant $[(93.875 + 0.375T)10^{-8}]$, M is the effective molecular weight which can be calculated using the relation,

$$M = X_1 M_1 + X_2 M_2$$

In above relation M_1 and M_2 are the molecular weights, X_1 and X_2 are the mole fractions of component 1 and 2.

RESULTS AND DISCUSSION

In the present investigation, critical micelle concentration (CMC) of surfactant is determined by ultrasonic method. The plot of sound velocity vs. concentration of TX-100 (Fig. 1) exhibit a clear and well-defined 'break' at 0.25 and 0.84 mM at 303 and 313 K, respectively. As ultrasonic waves are high frequency mechanical waves, their velocity in the medium depends¹¹ inversely on the density and the compressibility of the medium. In the present study, the densities of TX-100 do not undergo appreciable change at experimental conditions. Hence the sound velocity in aqueous solution of the surfactant should be determined primarily by the compressibility of the medium. As long as TX-100 exists as free monomer in very dilute solution and if these monomers form compact micelles *i.e.* at the CMC, the sound velocity initially increased, acquires maximum value at its CMC and then starts decreasing as the concentration of TX-100 increased. If this is possible and true then the 'break' found at 0.25 and 0.84 mM at 303 and 313 K, respectively, are close to the reported values¹². This observation suggests that the ultrasound velocity measurement can be relied upon to yield meaningful information about the micelle aggregation in aqueous solution.

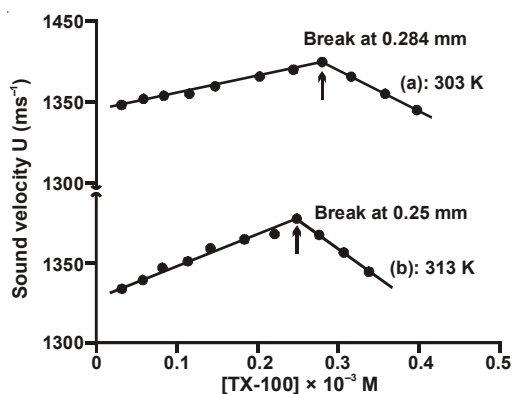


Fig. 1. Plot of sound velocity vs. [TX-100] at (a: 303 K) and (b: 313 K)

The sound velocities and the derived parameters for PMAAc-TX-100 system are presented in Tables 1 and 2.

The plots of surface tension (γ) vs. concentration of TX-100 (Figs. 2 and 3) shows at characteristic concentration of surfactant, the surface tension is maximum indicating that there are strong molecular interactions between surfactant molecules and the added polyelectrolyte in aqueous medium at different temperatures.

TABLE-1
ULTRASOUND VELOCITIES AND DERIVED PARAMETERS FOR
PMAAc-TX-100 SYSTEM AT 303 K

[TX-100] M × 10 ⁻³	U (ms ⁻¹)	ρ (kg m ⁻³)	β _{ad} (m ² N ⁻¹ × 10 ⁻¹⁰)	Z (kg m ⁻² s ⁻² × 10 ⁶)	L _f (Å)	Vm (mL mol ⁻¹)	R [m ₃ mol ⁻¹ (N/m ²) ^{-1/3} × 10 ⁴]	γ (N/m) 10 ⁴
0.5988	1123	1115.3	7.1096	1.2525	1.6825	225.42	2343.01	2.644
1.1952	1157	1116.8	6.6889	1.2921	1.6319	193.76	2034.09	2.769
1.7893	1184	1117.3	6.3845	1.3229	1.5944	170.79	1806.79	2.868
2.3809	1223	1118.3	5.9784	1.3677	1.5428	151.36	1618.64	3.013
2.9703	1245	1119.5	5.7628	1.3938	1.5148	136.39	1467.28	3.098
3.5573	1274	1120.6	5.4981	1.4276	1.4795	124.10	1345.37	3.210
4.1420	1298	1121.4	5.2928	1.4556	1.4517	113.84	1241.77	3.303
4.7244	1320	1122.1	5.1147	1.4812	1.4270	105.18	1153.82	3.390
5.3045	1343	1122.9	4.9375	1.5080	1.4021	97.72	1078.14	3.481
5.8823	1394	1123.7	4.5795	1.5664	1.3503	91.26	1019.46	6.303
6.4579	1422	1124.3	4.3986	1.5987	1.3234	85.59	962.46	3.798
7.0312	1455	1125.3	4.1973	1.6375	1.2927	80.56	912.82	3.934

TABLE-2
ULTRASOUND VELOCITIES AND DERIVED PARAMETERS FOR
PMAAc-TX-100 SYSTEM AT 313 K

[TX-100] M × 10 ⁻³	U (ms ⁻¹)	ρ (kg m ⁻³)	β _{ad} (m ² N ⁻¹ × 10 ⁻¹⁰)	Z (kg m ⁻² s ⁻² × 10 ⁶)	L _f (Å)	Vm (mL mol ⁻¹)	R [m ₃ mol ⁻¹ (N/m ²) ^{-1/3} × 10 ⁴]	γ (N/m) 10 ⁴
0.5988	1102	1115.5	7.3819	1.1293	1.7443	225.38	2327.95	2.569
1.1952	1138	1116.7	6.9148	1.2708	1.6882	193.78	2023.06	2.701
1.7893	1174	1117.3	6.4937	1.3117	1.6360	170.79	1801.66	2.831
2.3809	1201	1118.6	6.1978	1.3434	1.5983	151.32	1608.38	2.933
2.9703	1228	1119.4	5.9240	1.3746	1.5626	136.40	1460.71	3.034
3.5573	1251	1120.3	5.7036	1.4015	1.5332	124.13	1337.50	3.123
4.1420	1285	1121.6	5.3995	1.4412	1.4918	113.82	1237.45	3.252
4.7244	1316	1122.8	5.1426	1.4776	1.4559	105.11	1151.79	3.377
5.3045	1334	1123.4	5.0021	1.4986	1.4359	97.68	1075.26	3.448
5.8823	1367	1124.9	4.7572	1.5377	1.4003	91.16	1011.69	6.183
6.4579	1393	1125.4	4.5772	1.5677	1.3735	85.51	954.97	3.686
7.0312	1412	1126.1	4.4540	1.5900	1.3549	80.51	903.24	4.213

The variation of sound velocity with concentration of surfactant is given by relation¹³.

$$dU/dC = -(U/2) [(1/\rho) (d\rho/dC) + (1/\beta_{ad}) (d\beta_{ad}/dC)]$$

According to Eyring and Kincaid model for sound wave propagation; the sound velocity increased as L_f decreased as a result of mixing of components. This is further supported by expected decrease in β_{ad} with increased concentration of surfactant, signifies the probable interaction between the solute and solvent¹⁴.

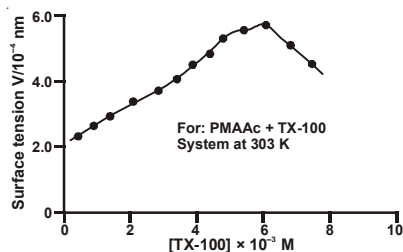


Fig. 2. Plot of surface tension vs. [TX-100] at 303 K

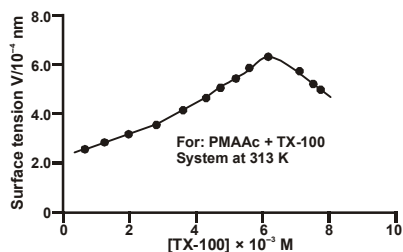


Fig. 2. Plot of surface tension vs. [TX-100] at 313 K

Conclusion

The trends in acoustical parameters of PMAAc-TX-100 systems suggests strong interaction between polymer and surfactant due to aggregation of surfactant micelles on to the polymer chain at CMC resulting in to polymer saturation point. This observation may support the well-accepted morphology of Pearl Necklace Model. In this scenario, a necklace is formed where the surfactant micelles acts as 'beads' and polymer chain behaves as a 'string'. It is evident that in this model the micelle size must be small as compared to characterized size of polymer which corresponds to high molecular weight.

ACKNOWLEDGEMENTS

The author thankful to UGC (WRO) PUNE, for sanction of Minor Research Project No.47-150/06 and also thanks Hon'ble Chairman, Jai Hind Educational Trust Dhule. Principal, Z.B.Patil College, Deopur, Dhule and Head, Department of Chemistry.

REFERENCES

1. E.D. Goddard, *Coll. Surf.*, **19**, 255 (1986).
2. C. Tonder, *J. Phys. Chem.*, **89**, 5110 (1985).
3. K.N. Mehrotra and S. Gupta, *Acoustica*, **84**, 167 (1998).
4. J. Miller and A.J. Parker, *J. Am. Chem. Soc.*, **89**, 117 (1961).
5. M.M. Chauhan and R.K. Shukla, *J. Pure Appl. Ultrasonics*, **18**, 118 (1996).
6. R. Zana, W. Binana-Limbeli, N. Kamenka and B.J. Lindman, *J. Phys. Chem.*, **96**, 5461 (1992).
7. D. Chu and J.K. Thomas, *J. Am. Chem. Soc.*, **108**, 6270 (1986).
8. P.P. Singh, K. Anand and O.P. Yadav, *Indian J. Chem.*, **29A**, 445 (1990).
9. T.J. Patil and H.A. Patil, *Asian J. Chem.*, **17**, 1979 (2005).
10. V.R. Gowarikar, N.V. Vishwanathan and J. Shreedhar, *Polymer Science*, Wiley Eastern, New Delhi, India, pp. 263-290 (1986).
11. S.P. Moulik, Md.E. Haque, P.K. Jana and A.R. Das, *J. Phys. Chem.*, **100**, 701 (1996).
12. B. Janezuk, J.M. Bruque, M.L. Gonzalez-Martin and C. Dorado-Calazaz, *Langmuir*, **11**, 4515 (1995).
13. P.S. Nikam, V.M. Kapade and M. Hassan, *Indian J. Pure Appl. Phys.*, **38**, 170 (2000).
14. B. Sundarson and A. Shrinivasarao, *Polym. J.*, **26**, 1286 (1994).

(Received: 3 May 2007;

Accepted: 6 March 2008)

AJC-6397