

Ultrasonic and Viscometric Studies of the Behaviour of Cetyltrimethyl Ammonium Bromide in Aqueous Polyacrylamide at Different Temperatures

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Polymer-surfactant interaction between aqueous cetyltrimethyl-ammonium bromide and water soluble polyacrylamide has been investigated over wide range of cetyltrimethyl ammonium bromide concentration at 303 K by using ultrasonic measurement at 2 MHz frequency and also by viscometric study. Ultrasonic results show clear and well defined break at 0.90 mM as a critical aggregation concentration and at 0.190 mM as polymer saturation point. Intrinsic viscosity of polymer-surfactant solution was determined in presence of various amounts of surfactants. It was observed that values increase as the temperature of the system increases, indicating increase in solvent power and solubility of polyacrylamide.

Key Words: Cetyltrimethyl ammonium bromide, Polyacrylamide, Critical aggregation concentration, Polymer saturation point, Ultrasonic velocity, Intrinsic viscosity, Polymer-surfactant interaction, Critical micelle concentration.

INTRODUCTION

Polymer-surfactant interaction has been studied by various methods¹⁻⁹. All these methods indicate that polymers interact with surfactants by inducing micellization of surfactant on the polymer chain and after getting saturated with micelles, the excess of surfactants form free micelles¹⁰. The polymer surfactant interactions consider the effect of polymer molecule on surfactant self-assembly through micelle formation. At lower concentration individual surfactant molecules get attached to the polymer segment. The phenomenon of aggregation of surfactant in presence of polymer can be characterized by Chu and Thomas¹¹; further addition of surfactant leads to polymer saturation point (PSP) or critical micelle concentration (CMC) of the surfactant in presence of the polymer.

In this paper, the results of ultrasonic velocity measurement along with the derived parameters at 303 K and viscosity data of the polymer-surfactant system containing water-soluble polymer polyacrylamide (PAA) and cetyl-trimethyl ammonium bromide (CTAB) at 303 and 313 K are reported.

EXPERIMENTAL

The water-soluble polymer polyacrylamide was the product of Sigma U.S.A. (m.w. = 5,00,000). It was dialyzed to remove low molecular weight fractions and other associated electrolytic impurities. Cetyltrimethyl ammonium bromide was obtained from Trizma Chemicals, India and was recrystallized from acetone-methanol mixture and dried before use. Triply distilled water from all glass apparatus was used to prepare stock solutions and further dilutions. Solutions of different concentrations were prepared by appropriate dilutions of the stock solutions of polyacrylamide 1.0% (w/v) and CTAB (30 mM). For PAA-CTAB system the concentration of PAA was kept constant at 0.001% (w/v) while that of CTAB (30 mM) was varied continuously.

Sound Velocities: Ultrasound velocities of pure CTAB solutions and those of the polymer-surfactant mixtures were measured at 2 MHz and at 303 K using an ultrasonic interferometer (M/s Mittal Enterprises, New Delhi, M-81 model) by the procedure described elsewhere¹². The test solution in the interferometric cell was maintained at 303 K by a thermostatic bath-pump system with an accuracy of bath ± 0.02 K. The distance between the crystal and the reflector was slowly varied by micrometer screw. The estimated accuracy in sound velocity was $\pm 0.2\%$. Different acoustical parameters were calculated using standard equations¹³.

Densities: Densities of pure CTAB solution and PAA-CTAB mixture were determined by using a bicapillary pycnometer. The pycnometer was calibrated at 298 K with double distilled water.

Viscosity: Viscosities were measured at 303, 308 and 313 K using a calibrated Ubbelohde viscometer placed in a well-stirred water bath.

All the measurements were carried out such as to avoid various types of possible degradation of the polymer in the solution¹⁴.

RESULTS AND DISCUSSION

The ultrasonic velocity as a function of [CTAB] in aqueous solutions at 303 and 313 K (Fig. 1) exhibit a clear and well defined break at 0.92 mM. Since ultrasonic waves are high frequency mechanical waves, their velocity in the medium depends¹⁵ inversely on the density and the compressibility of the medium. In the present work, the densities of CTAB solution do not undergo appreciable changes under the experimental conditions; hence the ultrasound velocity in aqueous solution of CTAB should be determined primarily by the compressibility of the medium. As long as CTAB exists as free monomer in very dilute solutions and which forms compact micelles, *i.e.*, at the CMC, the sound velocity initially increases, acquires a maximum value at its CMC and then starts decreasing as the concentration of CTAB is increased. If this is possible and true then the break at 0.92 mM in the plot of velocity vs. concentration of CTAB at 303 K should correspond to the CMC of CTAB which is close to the value reported¹⁶ as 0.90 mM for CTAB at 303 K. This observation suggests that ultrasound velocity measurement can be relied upon to yield meaningful information about the micellar aggregation in aqueous solution.

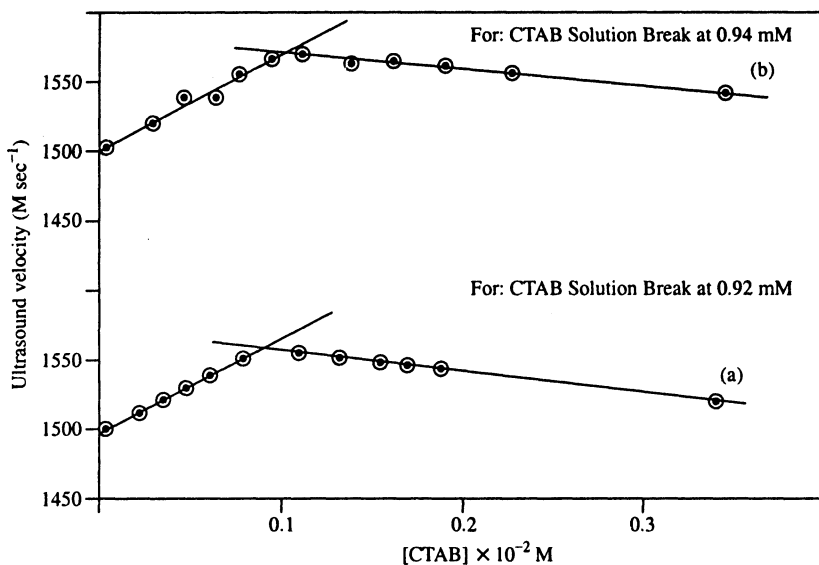


Fig. 1. Plot of ultrasound velocity vs. concentration (a) for CTAB at 303 K, (b) for CTAB at 313 K;

The ultrasound velocities and derived parameters for polyacrylamide CTAB (PAA-CTAB) system at 303 K are given in Table-1.

TABLE-I
ULTRASOUND VELOCITIES AND DERIVED PARAMETERS FOR PAA-CTAB
SYSTEM AT 303 K

Mole fraction χ_1	u (M sec ⁻¹)	d (kg m ⁻³)	β (m ² N ⁻¹ × 10 ⁻¹⁰)	Z (kg m ⁻² s ⁻² × 10 ⁻⁵)	L_f (Å)	V_m (mL mol ⁻¹)	R [m ³ mol ⁻¹ (N/m ²) ^{-1/3} × 10 ⁴]
0.8205	1582	1108.4	3.6045	17.5349	7.1924	370.17	0.4312
0.6958	1565	1109.6	3.6796	17.3652	7.3422	313.636	0.3640
0.6045	1557	1110.2	3.7155	17.2858	7.4139	272.378	0.3156
0.5335	1545	1111.9	3.7677	17.1788	7.5181	240.058	0.2774
0.4778	1507	1112.0	3.9598	16.7578	7.9014	215.009	0.2464
0.3788	1505	1112.3	3.9612	16.7401	7.9201	170.481	0.1953
0.3139	1492	1112.9	4.0345	16.6045	8.0544	141.252	0.1613
0.2680	1487	1113.2	4.0626	16.5533	8.1065	120.537	0.1375
0.2337	1480	1113.7	4.0993	16.4828	8.1797	105.171	0.1198
0.1862	1475	1114.4	4.1245	16.4374	8.2300	83.809	0.0953
0.1547	1467	1114.8	4.1681	16.3541	8.3170	69.661	0.0791
0.1234	1465	1115.3	4.1776	16.3391	8.3360	55.608	0.0631

u = ultrasonic velocity, d = density, β = adiabatic compressibility, Z = acoustic impedance, L_f = intermolecular free length, V_m = molar volume and R = molar sound velocity at 303 K for polyacrylamide-CTAB system.

Fig. 2 shows the variation of ultrasound velocity as a function of [CTAB] for PAA-CTAB system. For this measurement concentration of polyacrylamide is

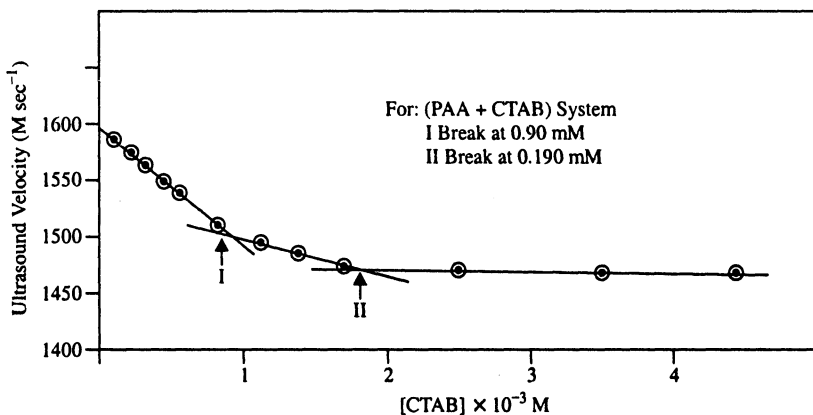


Fig. 2. Plot of ultrasound velocity vs. concentration of CTAB at 303 K

fixed at 0.001% (w/v) while the [CTAB] varied continuously; it is interesting to note that the ultrasound velocity as a function of [CTAB] exhibits two clear and well defined break points at the detergent concentrations 0.90 and 0.190 mM. The first break at 0.90 mM can be considered as critical aggregation concentration (CAC) since it is close to the reported^{17,18} value of CAC (0.91 mM) by surface tension method; at this concentration the polymer-surfactant binding starts, which is similar to micellization. With further increase in surfactant concentration, a second transition point known as polymer saturation point (PSP) or the CMC of polymer-surfactant complex is obtained¹⁹. At the PSP, *i.e.*, at 0.192 mM the micelles are present as a necklace⁸ in the polymer chain where the neutral polymer molecules decrease the ion-ion repulsion.

Viscosities of polymer-surfactant solutions were also determined. The water-soluble polymers are most widely used to control the rheological properties of an extensive range of aqueous based formulations. Table-2 gives the intrinsic viscosity (η) of the polyacrylamide in presence of various surfactant concentrations. All the (η) values for a given polymer-surfactant system were computed by well known procedures²⁰.

TABLE-2
INTRINSIC VISCOSITY (η) FOR PAA-CTAB SYSTEM AT DIFFERENT TEMPERATURES

[CTAB] % (w/v)	Intrinsic viscosity (η) (dL /g)			
	303 K	308 K	313 K	318 K
0.75	1.85	1.87	1.88	1.91
1.00	1.82	1.83	1.91	1.95
1.50	1.80	1.87	1.87	1.92

From the viscosity data, it is indicated that intrinsic viscosity (η) values increase with increase in temperature for a given concentration of surfactant; this behaviour of CTAB is just like a salt; it is further indicated that as temperature increases, solvent power and the solubility of the polymer increases, resulting in uncoiling of the polymer chains, providing interaction possibility leading to an increase in viscosity; but as temperature increases further, the kinetic energy helps in the lowering of rotational barrier and thereby enhancing the degree of rotation about the skeletal bond, allowing the molecular chains to assume more compact coiled configuration²¹, which leads to decrease in intrinsic viscosity (η) values.

Conclusions

The ultrasonic velocity measurement for a given polymer-surfactant system is a more reliable technique in order to understand critical aggregation concentration (CAC) and polymer saturation point (PSP). In the present work, these points are indicated by two clear and well defined breaks. The viscosity measurement shows strong interaction between polymer and surfactant over a wide range of surfactant concentrations. The water soluble polymer polyacrylamide is thus surface active on which the surfactant can bind effectively.

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