Research Article

Molecular interactions of surfactants with polymer in aqueous solutions

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ABSTRACT

In the present study, the ultrasonic velocity for Hydroxy propyl methyl cellulose (HPMC) in Sodium Lauryl Sulphate (SLS) and in Sodium Acetate Trihydrate (SAT) have been measured in the concentration range of 0.2%-1.2% at different temperatures (303K, 313K and 323K). Using the measured values of ultrasonic velocity, density, viscosity and other related thermodynamic parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance, solvation number, relaxation time and internal pressure have been evaluated. These parameters have been utilized to study the strong solute-solvent interactions in these systems. The ultrasonic velocity shows a maxima and adiabatic compressibility in corresponding minima with a function of concentration for these blends. The trends in the variation of the solution property parameters indicate the existence of positive molecular interactions of the surfactant and polymer aqueous solutions. The results also indicate the presence of higher values of interactions between HPMC and SAT in solution compared to HPMC and SLS.

Keywords: Ultrasonic velocity, Viscosity, molecular interactions.

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INTRODUCTION

The study of molecular interaction in the complex formation of considerable importance in the elucidation of the structural properties of the molecules [1-3]. The intermolecular interactions influence the structural arrangement along with the shape of the molecules [4-6]. Water soluble polymers have been shown to interact with surfactant species to varying degrees depending on the properties of the polymers and surfactants [7]. Surfactants and water soluble polymers have very broad ranges of applications. Hydroxy propyl methyl cellulose has variety of applications in day to day life. The combined occurrence of polymers and surfactants is found in diverse products such as cosmetics, paints, detergents, food, polymer synthesis and formulations of drugs and pesticides.

Polymers are often used in pharmaceutical work i.e., to control the release rate of active substances from formulations and used as stabilizers in emulsions and suspensions etc.,Several factors may influence the behaviour of the polymers in the formulation [8].

When both the surfactant and the polymer are charged, the interactions are dominated by strong Coulombic forces [9]. Solubility of the polymer is, however, possible at lower concentration of the surfactant. Hence, as a part of our research program we have focused our attention on ultrasonic behaviour and other thermodynamical properties of Sodium Lauryl Sulphate (SLS) & Sodium Acetate Trihydrate (SAT) at different concentrations in 0.4% of Hydroxy propyl methyl cellulose (HPMC) for different temperatures.

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EXPERIMENTAL DETAILS

Materials:
HPMC was supplied by chem chemicals, Sodium acetate trihydrate (CH$_3$COONa.3H$_2$O) (500gm) molecular weight of 136.08gmol^{-1} and Sodium lauryl sulphate (NaC$_{12}$H$_{25}$SO$_4$) of anionic surfactant with molecular weight of 288.38gmol^{-1} was obtained from (Fluka AG Switzerland) conductivity water was used for the preparation of all aqueous solutions.

The various physical parameters were calculated from measured values of ultrasonic velocity (U) and density (ρ) using the standard formula,
(i)   Adiabatic compressibility $\beta = 1/U^2 \rho$
(ii)   Inter molecular free length $L_f = k \beta^{1/2}$
(iii) Internal pressure $\pi_i = bRT [k \eta/U]^{1/2} \rho^{2/3}/M^{7/6}$
       (Where,T-absolute temp, η-Viscosity,U-Ultrasonic velocity).
(iv)   Relaxation time $\tau = 4/3 \beta \eta$
(v)   Acoustic impedance $z_a = \rho U$
(vi)   Solvation number $S_n = M2/M1[1 - \left(\frac{\beta}{\beta_o}\right)][\frac{100-x}{x}]$

       Where M$_1$.M$_2$-Molecular weight of the solvent and solute
       β and β_o –an adiabatic compressibility's of solution and solvent.

Methods:
Aqueous solutions of HPMC were prepared on a w/v%. Using distilled water as a solvent 0.4% of HPMC were dissolved in 100ml of water as a solvent. Sodium lauryl sulphate (SLS) and Sodium acetate trihydrate (SAT) of different concentration were prepared by using 0.4% of HPMC as a solvent. The preparation of aqueous mixture of the polymer in the above composition was done by magnetic stirrer. Ultrasonic interferometer of fixed frequency 2MHz (Model F-81 Mittal Enterprises,New Delhi) with temperature was used to measure the velocity of the solution. A 5ml of specific gravity bottle was used to measure the density of the solution and are accurate to three decimal places. Viscosity of the solution was measured by using Ostwald Viscometer. The temperature was maintained constant by circulating water from a thermostatically controlled water bath (accuracy $\pm$ 0.1°C). The measurements were made at 303K, 313K and 323K.

RESULTS

Acoustical parameters such as adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, Internal pressure and solvation number were calculated from the measured ultrasonic velocity, density and viscosity values at temperatures 303K, 313K and 323K and tabulated in table 1 and 2 for various concentrations of SAT, SLS with 0.4% of HPMC aqueous solutions.

Fig: 1 to 8 shows the graphical representation of ultrasonic velocity, density, adiabatic compressibility, and intermolecular free length as a function of concentration. The linear and non linear behavior of the curve reveals the respective tendency of the molecular interactions.

DISCUSSION

It is seen from the fig 1 and 2 that in HPMC-SAT and HPMC-SLS systems at 303K ultrasonic velocity increases with increasing concentration respectively and with further increase in temperature from 303K to 313K and 323K ultrasonic velocity decreases for HPMC –SAT and HPMC-SLS systems respectively.

The non linear variation of ultrasonic velocity with temperature indicates the occurrence of complex formation between unlike molecules [9] through hydrogen bonding (OH-O) which   in turn produces displacement of electron and nuclei [9-11]. Also it is noted that the ultrasonic velocity decreases with increase in temperature. As the temperature is increased, available thermal energy facilitates the breaking of the bonds between the associated molecules into their monomers**.** Moreover, increase of thermal energy weakens the molecular forces which tend to decrease the ultrasonic velocity as expected [11]. The experimental results of density measurements of HPMC with SAT and SLS at different temperature is shown in fig 3 & 4.The viscosity (η) increases with concentration of

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surfactants with polymer in all the three temperatures. The solution becomes more and more viscous, as solute is added. The increase of surfactants concentration is accompanied by an increase of relaxation time. The interaction causing association between the polymer, surfactants molecules and the solvent molecules are responsible for the increase in relaxation time.

The variation of adiabatic compressibility as a function of temperature is shown in fig 5 & 6. The compressibility of solvent is higher than that of a solution and decreases with the increase in concentration of the solution. With increase in solute concentration, their electrostatic forces cause the water structure to break and the solute surrounded water molecules are more compactly packed. This hydration effect in turn, results in reading the compressibility with increase in solute concentration. In the aqueous HPMC-SAT and HPMC-SLS solutions, it is observed (table1&2) that adiabatic compressibility decreases with the increase in two systems concentration and temperature.

Table 1: Ultrasonic velocity and related acoustical parameters of Sodium Lauryl Sulphate (SLS) in aqueous Hydroxy propyl methyl cellulose (HPMC)

Temp K	Conc %	U ms^{-1}	ρ kgm^{-3}	η $x10^{-3}$ Nsm^{-2}	β $X10^{10}$ $N^{-1}m^2$	L_f Å	S_n	π_i $X10^{-6}$ Pascal	z_a $x10^6$ $kgm^{-2} s^2$	τ $X10^{-13}s$
303K	0	1521	1065	0.963	4.058	0.401	-	295.43	1.619	5.213
	0.2	1509	1015	0.975	4.326	0.415	-5.813	218.67	1.531	5.625
	0.4	1513	1018	0.992	4.291	0.413	-2.400	233.22	1.540	5.676
	0.6	1519	1022	1.025	4.240	0.410	-1.229	241.84	1.552	5.796
	0.8	1524	1027	1.053	4.192	0.408	-0.670	247.53	1.565	5.867
	1	1531	1031	1.085	4.138	0.405	-0.315	253.78	1.578	6.012
	1.2	1539	1035	1.113	4.079	0.402	-0.067	257.51	1.592	6.054
313K	0	1536	1056	0.896	4.013	0.399	-	281.93	1.622	4.795
	0.2	1518	1008	0.904	4.305	0.414	-5.973	208.94	1.530	5.188
	0.4	1527	1014	0.923	4.229	0.410	-2.055	223.41	1.548	5.208
	0.6	1534	1016	0.954	4.182	0.408	-1.027	231.23	1.558	5.319
	0.8	1546	1019	0.988	4.105	0.404	-0.374	237.19	1.575	5.409
	1	1553	1020	1.013	4.064	0.402	-0.133	241.20	1.584	5.490
	1.2	1562	1022	1.045	4.010	0.399	0.070	245.59	1.596	5.588
323K	0	1558	1042	0.942	3.953	0.396	-	259.40	1.623	4.128
	0.2	1531	986	0.887	4.326	0.415	-8.327	199.26	1.509	4.926
	0.4	1539	991	0.692	4.260	0.411	-3.258	214.48	1.525	5.024
	0.6	1545	994	0.762	4.214	0.409	-1.181	221.92	1.535	5.119
	0.8	1552	999	0.748	4.155	0.406	-1.044	229.52	1.550	5.283
	1	1561	1007	0.773	4.075	0.402	-0.500	234.87	1.571	5.336
	1.2	1571	1009	0.846	4.015	0.399	-0.212	238.90	1.585	5.417

Intermolecular free length L_f shows similar behavior as reflected by adiabatic compressibility. The decreased compressibility brings the molecules to a closer packing resulting into a decrease of inter molecular free length as shown in fig 7& 8. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. When inter molecular free length decreases, ultrasonic velocity increases and vice versa, showing an inverse behavior. The interdependence of intermolecular free length and the ultrasonic velocity has been evolved from a model for sound. propagation [12].

The decrease in the values of β and L_f with increase in ultrasonic velocity indicates that there is a significant interaction between the HPMC-SAT and HPMC-SLS solute molecules due to which structural arrangement is considerably affected [13].

When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as acoustic impedance of the medium [14]. The acoustic impedance is the parameter which depends on the concentration and temperature of the solutions. The increase of acoustic impedance is an indication of strong interaction between the surfactant and polymer aqueous solutions. The inference is confirmed by the decrease of intermolecular free length and increase of internal pressure with concentration in all two systems.

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Table 2: Ultrasonic velocity and related acoustical parameters of Sodium Acetate Trihydrate (SAT) in aqueous Hydroxy propyl methyl cellulose (HPMC)

| Temp K	Conc %	U ms^{-1}	ρ kgm^{-3}	η x10^{-3} Nsm^{-2}	β X10^{10} N^{-1}m^2	Lf Å	S$_n$	π_i X10^{-6} Pascal	z$_a$ x10^6 kgm^{-2} s^2	τ X10^{-13} s
	0	1521	1065	0.963	4.058	0.401	-	295.43	1.619	5.213
	0.2	1512	1022	0.984	4.28	0.412	-2.290	522.64	1.545	5.615
	0.4	1517	1026	1.067	4.235	0.410	-0.865	579.13	1.556	6.025
303K	0.6	1526	1029	1.084	4.173	0.407	-0.366	595.67	1.570	6.031
	0.8	1535	1032	1.103	4.112	0.404	-0.127	606.76	1.584	6.047
	1	1540	1036	1.123	4.07	0.402	-0.021	616.90	1.595	6.094
	1.2	1547	1040	1.143	4.017	0.399	0.063	625.23	1.608	6.122
	0	1536	1056	0.896	4.032	0.400	-	280.57	1.614	4.802
	0.2	1532	1012	0.913	4.210	0.409	-1.86	496.84	1.550	5.125
	0.4	1538	1016	0.934	4.160	0.407	-0.637	534.75	1.562	5.184
313K	0.6	1544	1019	0.952	4.116	0.404	-0.273	551.32	1.573	5.224
	0.8	1551	1020	0.963	4.075	0.402	-0.104	559.79	1.58	5.235
	1	1559	1022	0.984	4.025	0.400	0.011	568.68	1.593	5.281
	1.2	1566	1025	1.053	3.978	0.397	0.084	590.72	1.605	5.588
	0	1558	1042	0.783	3.953	0.396	-	259.40	1.623	4.128
	0.2	1545	990	0.904	4.231	0.410	-2.961	485.13	1.529	5.099
	0.4	1550	996	0.923	4.179	0.407	-1.137	522.40	1.543	5.142
323K	0.6	1557	1001	0.944	4.120	0.405	-0.551	540.28	1.558	5.186
	0.8	1564	1004	0.962	4.071	0.402	-0.289	551.22	1.570	5.223
	1	1576	1009	0.984	3.990	0.398	-0.072	560.97	1.590	5.237
	1.2	1581	1012	1.043	3.938	0.395	0.023	579.61	1.603	5.476
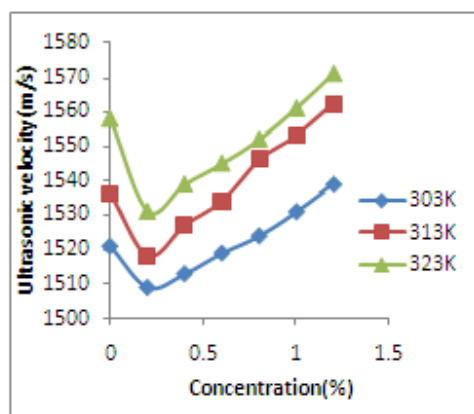
Fig 1: Ultrasonic velocity versus Concentration of HPMC with SLS aqueous solutions at different temperature
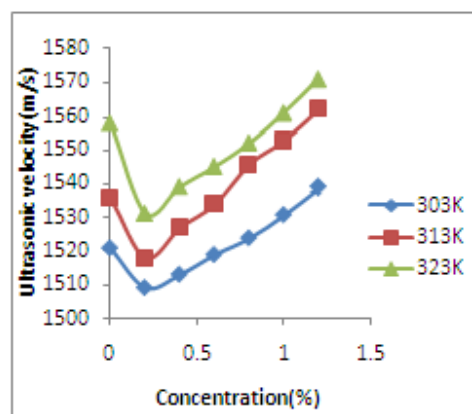

Fig 2: Ultrasonic velocity versus Concentration of HPMC with SAT aqueous solutions at different temperature
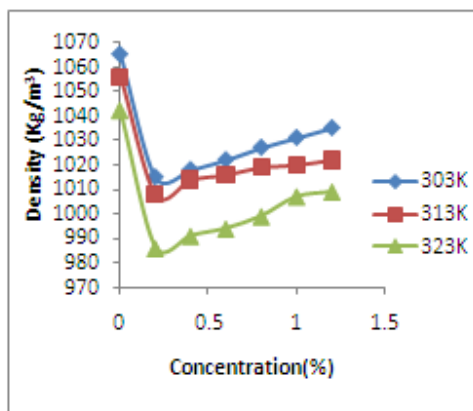
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Fig 3: Density versus Concentration of HPMC with SLS aqueous solutions at different temperature
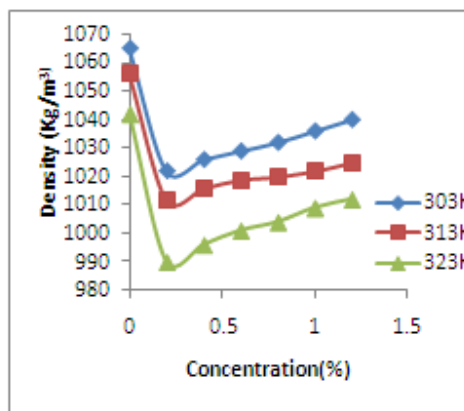

Fig 4: Density versus Concentration of HPMC with SAT aqueous solutions at different temperature
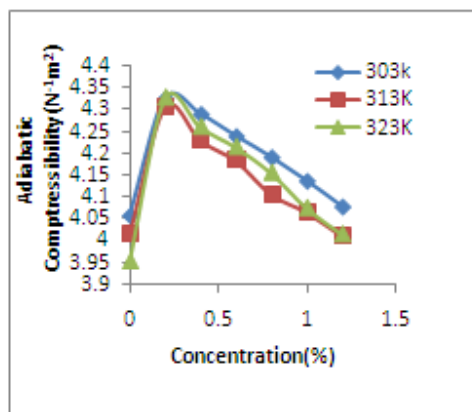

Fig 5: Adiabatic Compressibility versus Concentration of HPMC with SLS aqueous solutions at different temperature
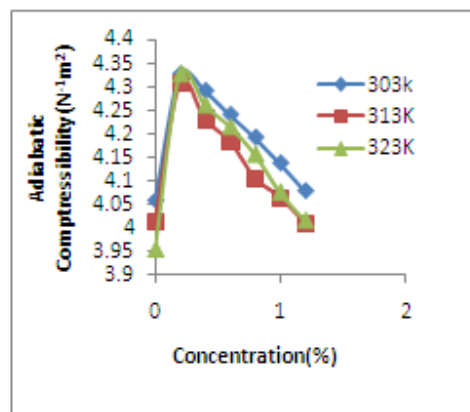

Fig 6: Adiabatic Compressibility versus Concentration of HPMC with SAT aqueous solutions at different temperature.

CONCLUSION

A systematic study of HPMC-SAT and HPMC-SLS in water has been carried out at different concentrations and at different temperatures. The ultrasonic velocity data and other acoustical parameters give valuable information to understand the solute-solvent interactions in the aqueous solutions. Hence it is concluded from the above discussion, the high values of viscosities and the torque confirms the polymer surfactant interaction process dominates in the HPMC and SAT in solutions compared to HPMC and SLS.
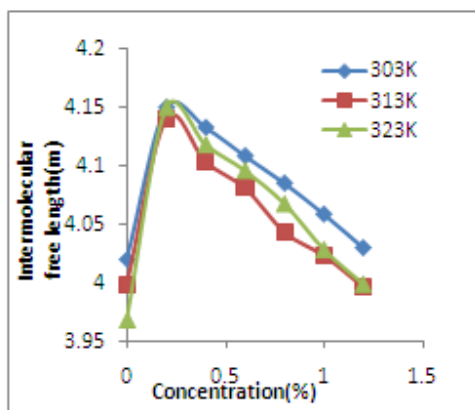
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Fig 7: Intermolecular free length versus Concentration of HPMC with SLS aqueous solutions at different temperature.
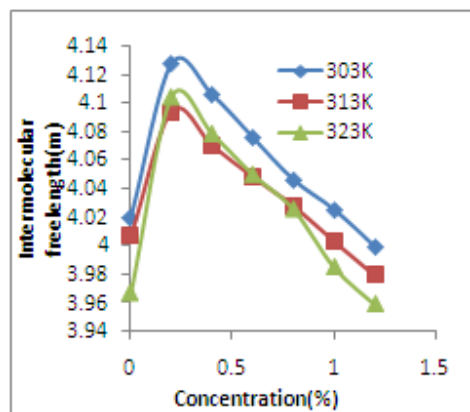

Fig 8: Intermolecular free length versus Concentration of HPMC with SAT aqueous solutions at different temperature.

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