Research Article **Polymer Sciences**

International Journal of Pharma and Bio Sciences **ISSN 0975-6299**

THERMODYNAMIC PROPERTIES OF CELLULOSE IN AQUEOUS ELECTROLYTE SOLUTIONS AT DIFFERENT TEMPERATURE

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ABSTRACT

Ultrasonic velocity, density and viscosity have been measured in the aqueous solutions of Hydroxy Propyl Methyl Cellulose (HPMC) with Sodium Chloride (NaCl), Calcium Chloride ($CaCl_2$) and Potassium Chloride (KCl) with a view to understand the nature of interaction between the cellulose and electrolytes at different temperatures (303K,313K and 323K). The acoustical parameters such as adiabatic compressibility (β), intermolecular free (length (L_f), internal pressure (π_i), acoustic impedance (z_a) and solvation number (S_n) are calculated. These parameters provide valuable information in understanding the solute-solvent interaction in a polymer cellulose (HPMC) and electrolyte solutions. The velocity decreases suddenly in addition of electrolyte and then increases on further increase of electrolyte concentration at all three temperatures.

KEYWORDS: Molecular interaction, Electrolyte, Adiabatic compressibility, Intermolecular free length

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INTRODUCTION

Cellulose is an outstanding polymer because of its comparatively rigid chains. The use of cellulose material has grown in significance. In recent years, there has been a tremendous interest in the preparation of polymer and electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because of its great potential in variety of important applications. Mixture of polymer and salts in aqueous solution has been utilized in several complex colloidal systems to achieve specific physiochemical properties. When electrolytes are added to polymer solutions, they affect the polymer structure either through direct interaction with various polar and ionized groups or indirectly due to electrolyte effect on solvent structure and activity. Electrolytes dissolving in water have been classified as structure makers or structure breakers depending on the charge density [1]. Ultrasonic investigation in aqueous solutions of electrolytes with Hydroxy Propyl Methyl Cellulose (HPMC) provides useful tool in understanding physiochemical properties of the interacting components. A number of researchers have studied the acoustical behaviour of electrolyte solutions containing metal ions [2-4]. The ultrasonic velocity measurements have been successfully employed to detect and assess the weak and strong molecular interaction present in the system.

MATERIALS AND METHODS

All the chemicals used in this present research work are Analytical Reagent (AR) of minimum assay of 99.9% obtained from Sd Fine chemicals, India. The solutions were prepared in double distilled water. The concentration of HPMC in aqueous NaCl, $CaCl_2$ and KCl were changed by weight percentage. All the solutions are left for 1hour and complete solubility is found. The ultrasonic velocities in prepared solutions have been measured by using an ultrasonic interferometer (Mittal Enterprises, New Delhi) working at $2MH_Z$. The accuracy of sound velocity is $0.1 ms^{-1}$. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 kgm^{-3}$. An Ostwald's viscometer of 10 ml capacity was used for the viscosity measurement. An electronic digitally operated constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental liquid at the desired temperature is ±0.01K. Thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i), acoustic impedance (z) and Solvation number (S_n), were calculated from empirical Jacobson's relations [5-7].

(i) Adiabatic compressibility $\beta = 1/U^2 \rho$

(ii) Intermolecular 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) Acoustic impedance $z_a = \rho U$

(v) 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 of solution and solvent.

RESULTS AND DISCUSSION

Ultrasonic investigations have been carried out on aqueous solutions of HPMC with NaCl, $CaCl_2$ and KCl at 303K, 313K and 323K are presented in table [1-3]. The ultrasonic velocity decreases suddenly when the electrolyte is added to the aqueous solution. The decrease of velocity and increase of compressibility in addition of electrolyte is an indicative for the influence of metal ions on the Hydroxy Propyl Methyl Cellulose (HPMC) sheath which weakens the intermolecular force. HPMC being ionic in nature, the ionic field has a great influence on the cellulose. Hence the interaction is favoured between cellulose polymer and ion which makes the solution a poorer solvent medium for the ions of electrolyte. This results in the sudden decrease of velocity on addition of electrolyte to cellulose solutions. The increase in adiabatic compressibility (β) clearly indicates a break in the cellulose water bonding which reduces the number of water molecules and decrease in β is due to the increase in electrostriction compression of solvent around the molecules as shown in fig 1-3. The variation of ultrasonic velocity (U) with temperature indicates the significant interaction in the systems studied. The variation in ultrasonic velocity depends on the intermolecular free length (L_f) on mixing which is predominant factor in determining the variation of ultrasonic velocity in the solutions [8]. The intermolecular free length has an inverse behaviour of ultrasonic velocity. The increase in ultrasonic velocity (table1, 2& 3) value in 0.4% of HPMC with aqueous NaCl, $CaCl_2$ and KCl solutions may be attributed to overall increase of cohesion brought about by the solute-solute, solute-solvent and solvent-solvent interaction in the solution. It also increases in the order of electrolytes as $CaCl_2$ > NaCl > KCl. The Na^+, K^+, Ca^+ and Cl^- ions in the electrolytes interact electro statically with the addition of water and the dipoles are strongly aligned to the cation /anion as well as to the polymer cellulose. The ultrasonic velocity increases with increase in concentration and temperature. The increase in the ultrasonic velocity and decrease in the adiabatic compressibility with increase of concentration of polymer is an indication that the intermolecular forces increases with addition of polymer in aqueous electrolytic solution. The interaction may either result from hydration of solvent molecules like sodium, calcium and potassium ion polymer or hydrogen bonding between the solute and the solvent molecule [9-10]. Intermolecular free length in binary mixtures can be used to access the attraction between the component molecules. Increase in concentration leads to decrease in gap between the two system and it is referred as intermolecular free length as shown in fig 4-6. The decrease in L_f with increase of solute concentration in solution indicates that there is a significant interaction between solute and co-solvent suggesting the structure promoting behaviour on addition of electrolytes. From the experimental data the internal pressure of electrolytic solution at different concentration gives correlation of the physical chemical behaviour. The internal pressure (π_i) reflects the, total interaction in a solution. It is a measure of cohesive force in solution and is considered as a rational basis to understand thermodynamics of electrolytic solutions. The internal pressure is coloumbic interaction between ions with net charges leading to a long range attraction. The acoustic impedance (z_a) increases with increasing concentration of salt solutions suggesting that the ion-solvent interaction increases. It is clearly observed in table (1 to 3) the solvation number (S_n) increases with increase in concentration of NaCl, $CaCl_2$ & KCl where as the solvation number decreases as temperature increases. This suggests significantly strong interaction in both the systems. The increase in (S_n) supports structure maker (SM) tendency of electrolyte [11]. But decrease in the value of [S_n] at high temperature favours presence of solute-solvent interaction. Interaction of $CaCl_2$ with aqueous HPMC is stronger as compared to interaction of NaCl, KCl with HPMC due to divalent nature of $CaCl_2$.

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Table 1
Ultrasonic velocity and related acoustical parameters of Sodium Chloride (NaCl) 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}
303K	0	1569	1057	0.908	3.843	0.391	-	0.888	1.658
	0.2	1542	1021	1.954	4.119	0.404	-1.304	6.134	1.574
	0.4	1547	1029	1.728	4.060	0.402	-0.485	6.174	1.591
	0.6	1552	1033	1.630	4.018	0.400	-0.256	6.137	1.603
	0.8	1556	1039	1.472	3.975	0.397	-0.142	5.914	1.616
	1	1559	1042	1.274	3.948	0.396	-0.090	5.545	1.624
	1.2	1561	1047	1.123	3.919	0.395	-0.054	5.243	1.634
313K	0	1577	1047	0.873	3.843	0.391	-	0.863	1.651
	0.2	1561	1015	1.852	4.043	0.401	-0.959	1.871	1.584
	0.4	1569	1018	1.675	3.990	0.398	-0.335	1.896	1.597
	0.6	1575	1022	1.526	3.944	0.396	-0.152	1.852	1.609
	0.8	1579	1026	1.362	3.909	0.394	-0.074	1.772	1.620
	1	1583	1031	1.178	3.870	0.392	-0.026	1.662	1.632
	1.2	1587	1037	1.096	3.828	0.390	0.007	1.615	1.645
323K	0	1583	1042	0.779	3.829	0.390	-	0.811	1.649
	0.2	1577	999	1.766	4.025	0.400	-0.928	5.688.	1.575
	0.4	1581	1004	1.548	3.984	0.398	-0.348	5.691	1.587
	0.6	1588	1007	1.413	3.937	0.395	-0.159	5.558	1.599
	0.8	1592	1011	1.245	3.902	0.394	-0.079	5.284	1.609
	1	1595	1017	1.058	3.865	0.392	-0.030	4.919	1.622
	1.2	1599	1022	0.952	3.826	0.390	0.001	4.697	1.634

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Table 2
Ultrasonic velocity and related acoustical parameters of Calcium Chloride ($CaCl_2$) 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
303K	0	1569	1057	0.908	3.843	0.391	-	0.888	1.658
	0.2	1553	1035	1.992	4.006	0.399	-1.925	2.138	1.607
	0.4	1556	1039	1.832	3.975	0.397	-0.739	2.182	1.616
	0.6	1559	1043	1.755	3.944	0.396	-0.371	2.185	1.626
	0.8	1564	1048	1.597	3.900	0.394	-0.156	2.110	1.639
	1	1569	1057	1.421	3.843	0.391	0	2.012	1.658
	1.2	1572	1065	1.252	3.799	0.388	0.077	1.904	1.674
313K	0	1577	1047	0.873	3.840	0.391	-	0.863	1.651
	0.2	1564	1028	1.852	3.976	0.397	-1.616	2.045	1.607
	0.4	1579	1032	1.683	3.886	0.393	-0.260	2.067	1.629
	0.6	1581	1036	1.526	3.861	0.392	-0.079	2.014	1.637
	0.8	1584	1041	1.383	3.828	0.390	0.030	1.943	1.648
	1	1587	1047	1.247	3.792	0.388	0.102	5.889	1.661
	1.2	1592	1052	1.137	3.750	0.386	0	1.789	1.674
323K	0	1583	1042	0.779	3.829	0.390	-	0.256	1.649
	0.2	1579	1012	1.724	3.963	0.397	-1.591	1.943	1.597
	0.4	1582	1015	1.572	3.936	0.395	-0.603	1.974	1.605
	0.6	1585	1019	1.348	3.906	0.394	-0.283	1.870	1.615
	0.8	1589	1026	1.261	3.860	0.392	-0.084	1.834	1.630
	1	1593	1032	1.187	3.818	0.389	0.022	1.796	1.643
	1.2	1605	1040	1.023	3.732	0.385	0.172	1.677	1.669

Table 3
Ultrasonic velocity and related acoustical parameters of Potassium Chloride (KCl) 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}
303K	0	1569	1057	0.908	3.843	0.391	-	0.888	1.658
	0.2	1534	1016	1.834	4.182	0.408	-0.710	4.476	1.558
	0.4	1539	1019	1.678	4.143	0.406	-0.229	4.564	1.568
	0.6	1543	1023	1.469	4.105	0.404	-0.083	4.372	1.578
	0.8	1546	1026	1.273	4.077	0.402	-0.025	4.120	1.586
	1	1550	1029	1.132	4.045	0.401	0.013	3.915	1.594
	1.2	1554	1032	1.095	4.012	0.399	0.038	3.869	1.603
313K	0	1577	1047	0.873	3.840	0.391	-	0.863	1.651
	0.2	1552	1009	1.783	4.114	0.404	-0.473	4.368	1.565
	0.4	1556	1013	1.561	4.077	0.402	-0.122	4.361	1.576
	0.6	1559	1016	1.434	4.049	0.401	-0.031	4.278	1.583
	0.8	1562	1019	1.220	4.022	0.400	0.012	3.994	1.591
	1	1565	1021	1.123	3.998	0.399	0.034	3.859	1.597
	1.2	1569	1023	1.003	3.970	0.397	0.052	3.664	1.605
323K	0	1583	1042	0.779	3.829	0.390	-	0.811	1.649
	0.2	1561	991	1.641	4.141	0.406	-1.794	4.128	1.546
	0.4	1564	996	1.452	4.104	0.404	-0.743	4.148	1.557
	0.6	1566	1003	1.310	4.065	0.402	-0.413	4.045	1.570
	0.8	1569	1008	1.113	4.029	0.400	-0.257	3.779	1.581
	1	1571	1011	1.031	4.007	0.399	-0.179	3.667	1.588
	1.2	1573	1015	0.917	3.981	0.398	-0.125	1.100	1.596

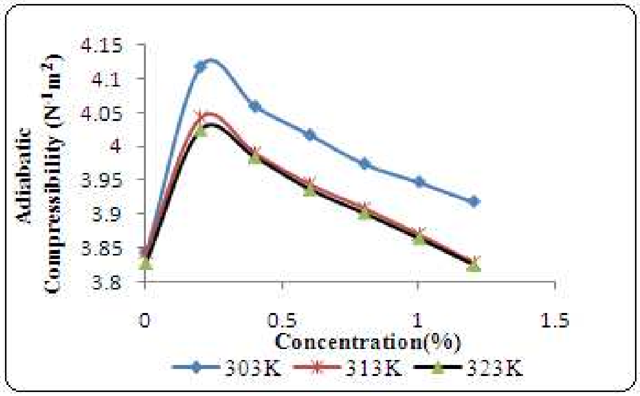

Figure.1
Variation of Adiabatic compressibility with concentration of NaCl salt solution in HPMC at different temperature

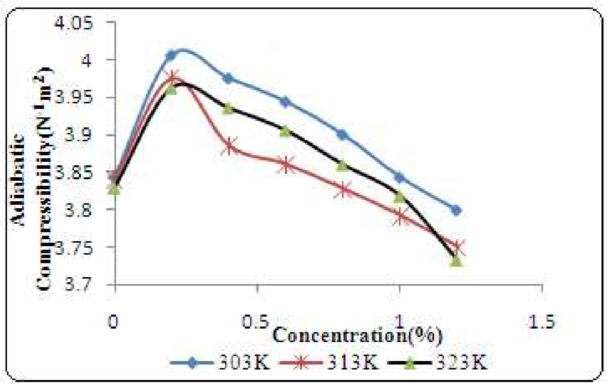

Figure.2
Variation of Adiabatic compressibility with concentration of $CaCl_2$ salt solution in HPMC at different temperature

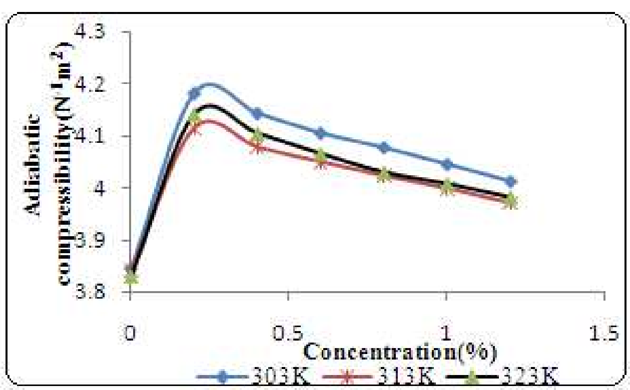

Figure.3
Variation of Adiabatic compressibility with concentration of KCl salt solution in HPMC at different temperature

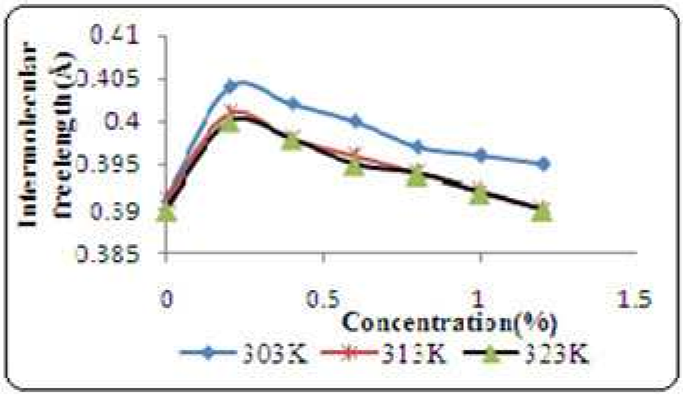

Figure.4
Variation of Intermolecular free length with concentration of NaCl salt solution in HPMC at different temperature

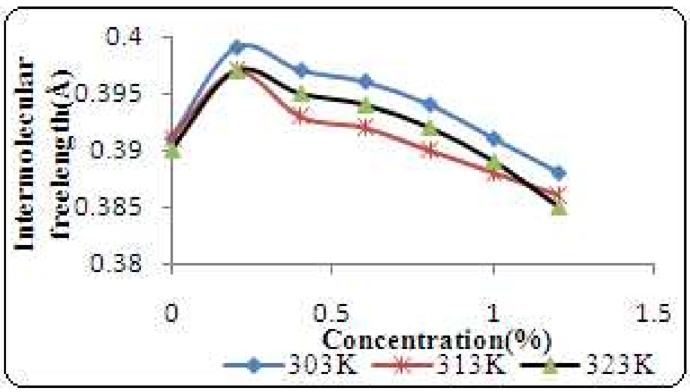

Figure.5
Variation of Intermolecular free length with concentration of $CaCl_2$ salt solution in HPMC at different temperature

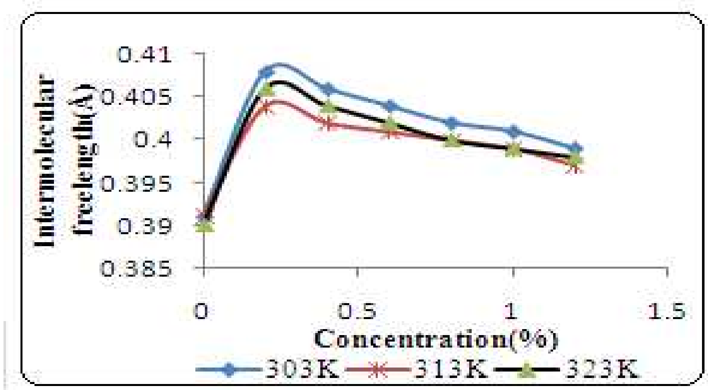

Figure.6
Variation of Intermolecular free length with concentration of KCl salt solution in HPMC at different temperature

CONCLUSION

Ultrasonic velocity, density and viscosity have been measured for NaCl, $CaCl_2$ and KCl in aqueous HPMC solutions at 303K, 313K and 323K. The variation of thermodynamic properties of NaCl, $CaCl_2$ and KCl at various concentrations and temperature in co-solvent of water and HPMC shows the variation is non-linear. Consequently ultrasonic velocity of the system increases depending on the structural properties of the solute. It is clear that the solute causing electrostriction leads to decrease in the compressibility of the solution. Hydrophobic solutes often show the negative compressibility due to ordering that it is induced by them in water structure. The solute that increases the ultrasonic velocity is structure maker. The non-linearity confirms the presence of solute-solvent, ion-ion, dipole-dipole, ion-solvent interactions. The observed molecular interaction, complex formation, hydrogen bond formation are responsible for the hetero-molecular interaction in the liquid system. The mixture of HPMC and electrolytes were widely used in industrial applications like food, pharmaceuticals, cosmetics, paint, textiles, paper, constructions, adhesives, coatings, water treatment, etc. From the above discussion it is concluded that interaction is strong between HPMC and electrolyte in the order of $CaCl_2$> NaCl> KCl.

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