Study on the Effect of Alkali Metal Chlorides in Aqueous Solutions of Sodium Carboxymethyl Cellulose using Ultrasound

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Measurement of ultrasonic velocity, density and viscosity were carried out for the aqueous solutions of sodium carboxymethyl cellulose with various concentrations of sodium chloride, lithium chloride and potassium chloride at different temperatures. The experimental data were used to estimate the ultrasonic parameters like adiabatic compressibility, free length, rao's constant, acoustic impedance, *etc.* In particular, the ionic hydration numbers for the electrolyte were estimated when the electrolyte is in polymer solutions. The results are interpreted in terms of polymer-solvent, polymer-polymer and polymer-ion interactions.

Key Words: Ultrasonic velocity, Polymer-electrolyte, Hydration number.

INTRODUCTION

The study of the effect of organic and inorganic salt species on polymers in solutions becomes more important in the scientific and technological point of view. Mixtures of polymers and salts in aqueous solution have been utilized in several complex colloidal systems to achieve physico-chemical properties including emulsification, colloidal stability of flocculation, structuring and suspending properties and rheology control. As a result, polymer-salt systems have several industrial applications in diversed areas ranging from latest paint technology, food products, cosmetics and pharmaceutical applications to crop disease formulations[1].

Molecular interactions between small solute molecules and long chain polymers have been studied by many researchers[2-5] with one of the primary objectives of measuring the binding of affinity constants of solutes to synthetic and natural macromolecules and to correlate the constants with chemical structures of the species involved. Another important goal is to elucidate the change in polymer conformation in solution due to the interactions with small solute molecules.

Though the interaction between polymer and electrolyte (additive) is studied using different techniques like equilibrium dialysis, solubility measurements and cloud-point measurement, ultrasonic method is preferred in the present study. Sodium

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carboxymethylcellulose (Na-CMC), a semi-synthetic water-soluble polymer and the alkali metal chlorides such as, sodium chloride, potassium chloride and lithium chloride have been chosen due to its wide industrial applications.

EXPERIMENTAL

Sodium carboxymethyl cellulose (approx. MW $\approx$ 90000) was obtained from Sigma Aldrich Company. Alkali metal chlorides (AR grade) were obtained from BDH.

The stock solution was prepared by adding a known weight of polymer to a fixed volume of double distilled water and then stirring under reflux using a magnetic stirrer until a clear solution was obtained. Due to its high viscous nature, low concentrated stock solution (say 0.5 %) was chosen for a study. This stock solution was used to prepare solutions of desired concentration of electrolytes under study, namely sodium chloride, lithium chloride and potassium chloride.

The ultrasonic velocity was measured using a pulse echo interferometer (10 MHz). Densities and viscosities were measured using specific gravity bottle and Ostwald's viscometer respectively. In order to study the influence of heat on molecular interactions, the experiments were carried out at three different temperatures 303, 313 and 323 K.

RESULTS AND DISCUSSION

Using the measured values of ultrasonic velocity, density and viscosity of the solutions for electrolytic concentrations 0.0 to 1.0 molarities at temperatures 303, 313 and 323 K, the related ultrasonic parameters are calculated as detailed below.

The adiabatic compressibility (β_{ad}) is calculated using the relation $\beta_{ad} = (U^2\rho)^{-1}$, where ρ is the density of the solution and U is the ultrasonic velocity of the solution. The intermolecular free length (L_f) is calculated using the formula $L_f = K_T (\beta_{ad})^{1/2}$ where K_T is a temperature dependent constant. The values of K_T for different temperatures are available in the literature[6]. The Rao's number (R) is calculated using the relation $R = U^{1/3}V$, where V is the molar volume of the solution. Ionic hydration number of electrolyte in ternary solutions is calculated using the formula given by Maisano *et al.*[7] as $H_n = (V_2\beta_2-V\beta) /n_3V_1\beta_0$, where H_n is the ionic hydration number of electrolyte in polymer-salt solutions, V is the molar volume of solution and is given as $V = (n_1m_1 + n_2m_2 + n_3m_3)/\rho$, V_2 is the volume of polymer-solvent system and is given as $V_2 = (n_1m_1 + n_2m_2)/\rho_2$ and V_1 is the molar volume of polymer solvent. m_1, m_2 and m_3 are the molecular weight of pure solvent, polymer (repeat unit) and salt, respectively. ρ and ρ_2 are the densities of the three component system and of the polymer-solvent system respectively. β_0 and β_2 are the compressibilities of pure solvent and polymer-solvent solutions and n_3 is the number of moles of salt in ternary solutions.

The measured values of velocity, density, viscosity and other related parameters at temperatures 303, 313 and 323 K for electrolyte concentrations are shown in Tables 1-3.

TABLE-1
ULTRASONIC VELOCITY AND RELATED PARAMETERS OF
NaCl IN AQUEOUS Na-CMC SOLUTION

Temp. (K)	Conc. (mol/L)	U (m s^{-1})	ρ (kg m^{-3})	$\eta \times 10^3$ (Nsm^{-2})	$\beta_{ad} \times 10^{10}$ (N^{-1} m^2)	L_f (Å)	$Z \times 10^4$ (kg m^{-2} s^{-1})	$R \times 10^3$	$H_n \times 10^2$
303	0.0	1522.1	1001.48	6.0594	4.3099	0.4152	152.44	215.01	–
	0.2	1530.8	1008.46	2.7257	4.2315	0.4144	154.38	208.58	8.3913
	0.4	1532.4	1015.81	2.5819	4.1921	0.4095	155.66	208.83	6.2178
	0.6	1535.8	1023.63	2.3587	4.1417	0.4070	157.21	208.95	6.0734
	0.8	1540.1	1025.59	2.1747	4.1109	0.4055	157.95	210.34	4.7762
	1.0	1542.7	1028.38	1.9567	4.0858	0.4042	158.65	211.48	3.9480
313	0.0	1540.9	990.42	4.7738	4.2523	0.4186	152.62	218.31	–
	0.2	1558.2	998.18	2.0992	4.1261	0.4148	155.54	211.97	14.6117
	0.4	1558.6	1005.11	1.9914	4.0955	0.4108	156.55	212.17	8.7869
	0.6	1564.1	1013.34	1.7138	4.0338	0.4077	158.49	212.35	8.3481
	0.8	1568.9	1016.11	1.5869	3.9982	0.4059	159.41	213.61	6.7392
	1.0	1570.8	1018.14	1.5479	3.9806	0.4050	159.93	214.89	5.2920
323	0.0	1563.5	983.67	3.9003	4.1586	0.4200	153.79	220.87	–
	0.2	1576.1	991.03	1.5820	4.0620	0.4151	156.19	214.32	11.0767
	0.4	1582.7	998.22	1.5026	3.9992	0.4119	157.98	214.76	8.9999
	0.6	1587.4	1006.50	1.3245	3.9428	0.4090	159.77	214.86	8.3142
	0.8	1595.3	1010.74	1.2729	3.8875	0.4061	161.24	215.96	7.4796
	1.0	1596.3	1012.86	1.2058	3.8750	0.4055	161.67	217.17	5.7860

TABLE-2
ULTRASONIC VELOCITY AND RELATED PARAMETERS OF
LiCl IN AQUEOUS Na-CMC SOLUTION

Temp. (K)	Conc. (mol/L)	U (m s^{-1})	ρ (kg m^{-3})	$\eta \times 10^3$ (Nsm^{-2})	$\beta_{ad} \times 10^{10}$ (N^{-1} m^2)	L_f (Å)	$Z \times 10^4$ (kg m^{-2} s^{-1})	$R \times 10^3$	$H_n \times 10^2$
303	0.0	1522.1	1001.48	6.0594	4.3099	0.4152	152.43	215.01	–
	0.2	1533.7	1004.83	4.7586	4.2308	0.4113	153.11	208.80	8.3203
	0.4	1540.4	1009.30	4.6856	4.1755	0.4086	155.41	209.17	7.1906
	0.6	1547.1	1013.12	4.3338	4.1238	0.4061	156.37	209.67	6.5795
	0.8	1550.2	1017.30	4.2999	4.0904	0.4045	157.70	209.92	5.8604
	1.0	1552.7	1021.58	4.2805	4.0602	0.4030	158.62	210.11	5.3155
313	0.0	1540.9	990.52	4.7743	4.2519	0.4185	152.62	218.31	–
	0.2	1546.4	995.23	3.5004	4.2017	0.4161	153.90	211.39	5.9552
	0.4	1555.2	999.57	3.2723	4.1363	0.4128	155.45	211.88	5.6795
	0.6	1559.7	1003.27	2.9752	4.0973	0.4109	156.48	212.30	5.7546
	0.8	1567.4	1008.07	2.9033	4.0378	0.4079	158.00	212.06	6.1040
	1.0	1570.6	1012.41	2.8450	4.0041	0.4062	159.01	212.83	5.6167
323	0.0	1563.5	983.67	3.9003	4.1586	0.4200	153.79	220.87	–
	0.2	1570.1	989.19	2.1995	4.1007	0.4171	155.31	213.98	7.2236
	0.4	1575.4	993.15	2.1155	4.0569	0.4149	156.46	214.59	5.9554
	0.6	1581.6	997.66	1.8209	4.0070	0.4123	157.79	215.12	5.8623
	0.8	1588.2	1002.82	1.7636	3.9533	0.4095	159.26	215.52	6.0669
	1.0	1590.5	1007.52	1.7273	3.9235	0.4080	160.24	215.82	5.5350

TABLE-3
ULTRASONIC VELOCITY AND RELATED PARAMETERS OF
KCl IN AQUEOUS Na-CMC SOLUTION

Temp. (K)	Conc. (mol/L)	U (m s^{-1})	ρ (kg m^{-3})	$\eta \times 10^3$ (Nsm^{-2})	$\beta_{ad} \times 10^{10}$ (N^{-1} m^2)	L_f (Å)	$Z \times 10^4$ (kg m^{-2} s^{-1})	$R \times 10^3$	$H_n \times 10^2$
303	0.0	1522.1	1001.48	6.0594	4.3099	0.4152	152.43	215.01	–
	0.2	1528.3	1008.74	4.9739	4.2442	0.4120	154.16	209.07	7.4917
	0.4	1535.7	1019.35	4.5132	4.1569	0.4079	156.54	209.51	7.4805
	0.6	1543.6	1027.45	4.0872	4.0847	0.4042	158.59	210.47	7.3971
	0.8	1551.1	1035.64	3.8533	4.0133	0.4006	160.63	211.37	7.2831
	1.0	1551.5	1041.03	3.6732	3.9990	0.3995	161.52	212.43	5.6641
313	0.0	1540.9	990.42	4.77389	4.2523	0.4186	152.61	218.31	–
	0.2	1545.6	999.11	3.5037	4.1897	0.4155	154.42	211.88	6.0419
	0.4	1555.2	1008.35	3.1679	4.1166	0.4118	156.50	212.55	6.8941
	0.6	1565.4	1017.03	2.9581	4.0124	0.4066	159.20	213.62	7.9690
	0.8	1569.3	1024.61	2.8368	3.9630	0.4041	160.79	214.47	7.3170
	1.0	1571.3	1030.98	2.6649	3.9275	0.4023	162.01	215.48	6.2888
323	0.0	1563.5	983.67	3.9003	4.1586	0.4200	153.79	220.87	–
	0.2	1566.4	993.15	2.2596	4.1037	0.4173	155.56	214.06	5.6291
	0.4	1575.1	1002.17	2.2087	4.0219	0.4131	157.85	214.91	7.1904
	0.6	1581.9	1011.84	2.1354	3.9493	0.4093	160.06	215.47	7.4656
	0.8	1590.1	1019.12	2.0129	3.8808	0.4058	162.05	216.58	7.2211
	1.0	1593.3	1025.56	1.8970	3.8409	0.4037	163.40	217.61	6.3364

It can be seen from the Tables 1-3, that the ultrasonic velocity and density increases against the concentration of electrolytes concentration. In contrast, the adiabatic compressibility is found to decrease. This indicates the existence of molecular interactions among the species involved in the systems. This interactions may be brought either by hydration of solvents around ion and polymer[8] or through hydrogen bonding between the solute and solvent molecules[9-11].

When electrolytes are added to aqueous polymer solutions they affect the polymer structure either through direct interaction with various polar and ionized groups or indirectly due to the electrolytic effect on solvent structure and activity. This leads to an eventual modification of polymer-water coordination in polymer-electrolyte-water solutions[12].

The addition of electrolyte lowers the compressibility of the solvent due to orientation of the solvent molecules around the ions. When a strong electrolyte is added to water an electrostatic field is developed by the presence of ions and exerts an electrostrictive effect on the surrounding water molecules. This electrostatic pressure has the same effect as the application of an external pressure and the compressibility of water molecules is lowered leading to an increase in sound velocity. This conclusion is also supported by the fact that intermolecular free length (L_f) is found to decrease with increase in molar concentration of electrolytes.

The shear viscosity of all ternary system is found to be less than that of binary polymer system. This may be attributed to the effect of added electrolyte on polymer confirmation. Viscosity of polymer solution depends on the molecular size of polymer in solution[13]. In good solvents polymer molecules interact strongly with solvent molecules and the solvation is high. This leads to an increase in size of the polymer molecule and hence the polymer solution exhibit high viscosity. Upon the addition of electrolytes with polymer solutions, the electrolytes affect the conformational status of polymer by weakening of attractive or repulsive forces in the intra or intermolecular interactions involving the ionogenic groups of the polymer. Thus the addition of electrolytes in aqueous solutions of polymer reduces the solvency of the water and makes the solution as a poorer medium for the polymer. This results in the contraction of polymer chain and hence the size of polymer molecules decreases which leads to the observed reduction in viscosity of polymer-salt solutions. As temperature increases the viscosity decreases which is ascribed to the weakening of molecular interactions.

The values of molar sound velocity R and acoustic impedance Z of all the three systems at different compositions have been calculated and found to be increase linearly with electrolyte concentration. The increase of Z and R is an indication of strong interaction between the polymer and ion. A complex formation or association is expected in this polymer, similar to that observed in polyethylene oxide[14] and polyacrylic acid, polyacrylamide or carboxymethyl cellulose[15] in water, while a decrease in the value of Z with temperature at all concentrations of solute may be attributed to the weak interactions.

In order to study the influence of electrolyte in polymer solutions, recently, Maisano *et al.*[7] have estimated the ionic hydration number of electrolyte in polymer solutions. The H_n values for the polymer solutions containing electrolytes are estimated and are given in the tables. In all the three systems the ionic hydration number of electrolyte decreases with increase in concentration. When a salt is added to aqueous polymer solution eventual modification of polymer-water co-ordination may be produced due to the salt induced ionic interaction. The water surrounding the ion is polarized by the ionic field. This lowers the free energy on the other hand, the water in the polymer hydration shell is in the high free energy state because of an unfavourable entropy contribution. When an ion and polymer segment approach each other, the amount of intervening water decreases. Since polymer, being ionic in nature, the ionic field has a great influence on the polymer, so the interaction is favoured between polymer and ion, which makes the solution a poorer solvent medium for the ions of electrolyte. This results in the reduction of ionic hydration number in polymer solution[16]. In electrolyte rich-region the ionic hydration number of salt is not found to be reduced to that much when compared with that of pure solvent. This shows that the image-charge force *i.e.*, the repulsive force between polymer and ion in electrolyte-rich region is not so stronger as in polymer-rich region[17]. In other words, when the polymer concentration is lesser than that of salt,

the competitive mechanism between the water molecules of ionic hydration shell is reduced in binding to the polymer.

In the series of alkali metal chlorides studied, the variation of velocity in LiCl and KCl system is much pronounced when compared to the sodium chloride system. This clearly indicates a strong cohesion among the water molecules around the electrolytes of lithium ion and potassium ion. In the case of sodium, repulsion may occur between the sodium ion present in both the polymer and electrolyte which prevents the bonding between the solute and the aqueous polymer. In NaCl solution the variation in hydration number is drastically decreased with concentration. But in the case of KCl and LiCl solution the decrease in hydration number is very much less. This indicates that the number of water molecules around the electrolyte is very much reduced at higher concentration of NaCl. This reduction in hydration number is due to the strong repulsive force acting between the sodium ions in the aqueous Na-CMC and NaCl molecules.

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