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Acoustical Studies on Hydroxypropyl Methylcellulose in Alcohols and Methylene Chloride Mixture

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Ultrasonic velocity, viscosity and density for the solutions of hydroxypropyl methyl cellulose (HPMC) in propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol with methylene chloride (1:1) mixtures were measured at 303 K. From the experimental data observed as a function of concentration, various acoustical parameters such as, adiabatic compressibility, internal pressure, intermolecular free length, free volume and solvation number were calculated. The results are interpreted in terms of molecular interactions occurring in the solutions.

Key Words: Ultrasonic velocity, Adiabatic compressibility, Polymer-polymer interactions, Solvation number, Hydroxypropyl methyl cellulose.

INTRODUCTION

Ultrasonic studies in polymer solutions and in solid polymer have been a subject of extensive research activity in recent years[1-4]. It is also found that ultrasonic velocity together with density and viscosity studies throw more light on the polymer-solvent interactions[5-7]. Hydroxypropyl methyl cellulose (HPMC) is chosen for the present investigation because of its great importance in various industrial applications. Hydroxypropyl methyl cellulose are widely used in food, cosmetic and other daily use chemical lines.

Hydroxypropyl methyl cellulose (HPMC) are mainly used as an adhesive and coating film in tablets, increasing markedly rate of dissolution and release and strengthen water proof for tablets and also used as a mixed dispersing agent. Tablets coated with HPMC exhibit poor dissolution. Hydroxypropyl methyl cellulose (HPMC) may be dispersed or wet with organic solvents such as alcohols. Hence, it is planned to study the behaviour of the solutions of HPMC in alcohols with methylene chloride mixture. In the present paper, the authors have reported the results of density, viscosity and ultrasonic velocity studies of the solution of HPMC in methylene chloride and alcohols (propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol) 1:1 mixture at 303 K as a function of polymer concentration.

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EXPERIMENTAL

The commercially available hydroxypropyl methyl cellulose (HPMC) (*ca.* MW 13000) was obtained from Fluka Company. The alcohols and methylene chloride were obtained from BDH Company. They were used after standard purification[8,9].

The HPMC + alcohol + methylene chloride solutions were prepared by adding a known weight of polymer (HPMC) to a fixed volume of solvents *viz.*, alcohols and methylene chloride (1:1) and then stirring under reflux using a magnetic stirrer, until a clear solution was obtained. Due to its high viscous nature, the low concentration range of polymer were studied *i.e.*, 0 to 0.5 % (weight %). 0.0 % corresponds to alcohol and methylene chloride (1:1) mixture.

The ultrasonic velocity was measured using a Pulse echo interferometer (10 MHz) by the standard procedure[10]. Accuracy in the measurement of the velocity is 0.01 %. The density and viscosity of these solutions were measured using specific gravity bottle and an Ostwald's viscometer, respectively. All the measurements were carried out at 303 K.

Theory

From the measured values of density (ρ), viscosity (η) and ultrasonic velocity (U) the following acoustical parameters were calculated.

The adiabatic compressibility (β_{ad}) has been 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) has been calculated using the formula

$$L_f = K_T\,[\beta_{ad}]^{1/2}$$

where, K_T is a constant for different temperatures known as Jacobson constant[11].

The internal pressure (π_i) is calculated using the formula[12]

$$\pi_i = bRT\,[K\eta/U]^{1/2}[\rho^{2/3}/M_{eff}^{7/6}]$$

where b stands for the cubic packing factor which is assumed to be 2 for all liquids and solutions, K, the temperature independent constant (4.28×10^9), R, the gas constant (8.3143 J K^{-1} mol^{-1}), T, the absolute temperature and M_{eff} is the effective molecular weight of the solution.

The free volume (V_f) was calculated by using the relation[13],

$$V_f = [M_{eff}\,U/K\eta]^{3/2}$$

where, the symbols have their usual meaning.

The solvation number, the number of solvent molecules taking part in solvation of a repeat unit was calculated by using the Passynsky equation[14],

$$Sn = [m/m_o][1-(\beta/\beta_0)][(100-x)/x]$$

where β and β_0 are the adiabatic compressibility of polymer solution and the solvents respectively, m and m_0 are the molecular weight of the polymer repeat unit and the solvent respectively and x is the weight of the polymer in 100 g of solution.

Then these parameters are correlated with concentration (c).

RESULTS AND DISCUSSION

The solution property parameters namely, density (ρ), viscosity (η) and ultrasonic velocity (U), adiabatic compressibility, internal pressure, intermolecular free length, free volume and solvation number for HPMC in alcohols and methylene chloride (1:1) mixtures at 303 K are presented in the Table-1.

TABLE-1
VARIATION OF ULTRASONIC VELOCITY AND RELATED PARAMETERS WITH CONCENTRATION OF HRDROXYPROPYL METHYLCELLULOSE (HPMC) IN ALCOHOLS AND METHYLENE CHLORIDE (1:1) MIXTURES AT 303 K

Conc. (wt %)	U (ms^{-1})	ρ ($kg\ m^{-3}$)	$\eta \times 10^3$ (Nsm^{-2})	$\beta_{ad} \times 10^{10}$ ($N^{-1}m^2$)	L_f (Å)	$\pi_i \times 10^{-6}$ (pascal)	$V_f \times 10^8$ ($m^3\ mol^{-1}$)	$S_n \times 10$
HPMC in propan-1-ol + methylene chloride (1:1)								
0.0	1074.8	960.1	0.644	9.0160	0.600	505.06	15.330	-
0.1	1080.6	980.7	1.260	8.7320	0.591	738.46	5.653	13.04
0.2	1081.3	1000.2	2.807	8.5500	0.584	1115.71	1.703	9.26
0.3	1082.5	1016.2	3.568	8.3970	0.579	1269.33	1.191	8.19
0.4	1085.4	1030.6	7.022	8.2360	0.573	1793.79	0.433	7.74
0.5	1087.1	1041.5	10.103	8.1240	0.570	2163.32	0.252	7.07
HPMC in butan-1-ol + methylene chloride (1:1)								
0.0	1090.2	984.0	0.706	0.8550	0.584	496.49	15.626	-
0.1	1096.4	995.9	1.413	8.3520	0.578	705.44	5.575	7.58
0.2	1097.6	1012.6	2.247	8.1970	0.572	898.26	2.788	6.77
0.3	1100.0	1032.1	4.269	8.0070	0.565	1251.61	1.069	6.94
0.4	1102.8	1036.2	7.818	7.9350	0.563	1694.69	0.433	5.89
0.5	1105.7	1048.2	10.710	7.8030	0.558	1994.74	0.271	5.78
HPMC in pentan-1-ol + methylene chloride (1:1)								
0.0	1118.0	993.6	0.780	8.0520	0.567	479.29	15.461	-
0.1	1122.6	1004.4	1.575	7.9000	0.562	683.68	5.435	5.81
0.2	1124.2	1021.2	2.412	7.7480	0.556	854.35	2.877	5.80
0.3	1125.4	1039.3	4.401	7.5969	0.551	1166.18	1.170	5.79
0.4	1128.0	1051.6	8.110	7.4730	0.546	1592.69	0.469	5.52
0.5	1129.6	1056.6	11.303	7.4170	0.544	1883.45	0.286	4.84
HPMC in hexan-1-ol + methylene chloride (1:1)								
0.0	1150.8	1024.4	0.871	7.3700	0.542	479.19	14.812	-
0.1	1155.6	1042.9	1.424	7.1800	0.535	618.10	7.143	7.55
0.2	1158.3	1050.9	2.540	7.0920	0.532	828.29	3.011	5.52
0.3	1160.5	1052.8	3.809	7.0530	0.531	1013.90	1.645	4.19
0.4	1161.9	1053.3	8.441	7.0320	0.530	1507.56	0.499	3.34
0.5	1165.7	1056.9	13.386	6.9630	0.527	1898.39	0.252	3.22

From the Table-1, it has been observed that all the four systems are behaving in a similar manner for all the concentrations. It can be seen that all these parameters except adiabatic compressibility, intermolecular free length, free volume and solvation number are found to increase with increase of concentration of polymer. The adiabatic compressibility of the polymer solutions decreased with concentration and the remaining parameters intermolecular free length, free volume and solvation number also show the same dependency.

In all the 4 systems studied, the velocity is gradually increasing with concentration at room temperature. The increase in velocity with polymer concentration in alcohols with methylene chloride is due to the interaction between polymer and solvent molecules. At lower concentrations, the interaction is between the polymer and the solvent molecules. As the concentration increases, one macromolecule may influence another indirectly by way of mutual interaction. In more concentrated solutions and bulk polymers, direct segment-segment interaction will exist[15]. This vander Wall's interaction causes association between the molecules of HPMC and alcohols in the lower concentrations and in the higher concentrations, in addition to polymer-solvent interactions, polymer-polymer interaction may be responsible for the increase in ultrasonic velocity[16].

The rapid decrease in adiabatic compressibility with increase of concentration in alcohols with methylene chloride systems clearly indicates the formation of a more number of tightly bound systems. Since the velocity increase with concentration and the density does so, the compressibility must decrease with concentration. This could be caused by more rigid liquid structure associated with hydrogen bonding of HPMC with alcohols. Such reductions in compressibilities have been found in the solutions of cellulose derivatives which are attributed to change in compressibilities of the solvent molecules concerned in solutions[17]. This implies the increase of density with concentration, which leads to a decrease in compressibility.

At lower concentrations, the number of hydrogen bonds formed may be less and at higher concentrations, it may be more due to polymer-polymer interactions. In the polymer solutions, the hydrogen bond is formed between the hydrogen of the methyl group in HPMC and the oxygen of hydroxyl group in alcohols[18]. At lower concentrations of HPMC in alcohols with methylene chloride mixtures, the molecules are not closer and thus the intermolecular free length will be high. As the concentration increases, the molecules come closer through segment-segment interaction and thereby decreasing the intermolecular free length[19].

As it is known that the internal pressure is increased in hydrogen bonded systems[20], the internal pressure increases with increase of concentration for all the four systems. This increased internal pressure and decreased intermolecular free length confirms the formation of hydrogen bonding between polymer and alcohols and the interaction between polymers at higher concentrations. Thus an increase in internal pressure and decrease in free volume suggest that there is a strong cohesive force between the molecules[21].

The solvation numbers decreased with increase in polymer concentration indicating the increased polymer-polymer interaction with concentration. Higher solvation numbers obtained at lower concentrations of HPMC may be due to the presence of interactions between the polymer and the solvent molecules. The lower solvation number values obtained at higher concentrations may be due to the lesser interaction with the solvent caused by the larger size of the repeat unit and also due to the higher molecular weight of the sample used. This observation is again in line with the previous results[22].

Thus, on the basis of experimental findings it is concluded that, as the concentration of HPMC increases, in all the four systems, the motion of HPMC molecule is affected by the mutual interaction between the macromolecules and solvent molecules in one hand and the interaction between one macromolecule with another. The first type of mutual interaction is termed as hydrodynamic screening, which is significant in determining the viscous flow properties of dilute polymer solutions. In more concentrated solutions direct segment-segment interaction may exist. Thus, in low concentrations HPMC and solvent interaction dominates whereas in higher concentrations HPMC-HPMC interaction exists.

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