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Ultrasonic Studies on the Molecular Interaction of Ethyl Cellulose in *n*-Alkanols

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Ultrasonic velocity, viscosity and density for the solutions of ethyl cellulose in propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol mixtures were measured at 303, 313 and 323 K. From the experimental data, the various acoustical parameters such as adiabatic compressibility (β_{ad}), Rao number (R), free length (L_f), internal pressure (π_i) and solvation number (S_n) have been computed. The trends in acoustical parameters indicate that there are molecular interactions between the components.

Key Words: Ultrasonic velocity, Molecular interactions, adiabatic compressibility, Ethyl cellulose.

INTRODUCTION

The structures of the polymer solutions were studied from the same standpoint as structure of liquids and liquid mixtures of low molecular substances. In general, when two liquids are mixed together, the structure of each of the two liquids will change. The components change structurally in both aqueous and non-aqueous solution. The phenomena of a preferential interaction between unlike molecules (solvation) or similar ones (association) are observed, depending on the degree of affinity between the components. Thus solvates and associates are elements of the structure of solution[1]. When the polymer dissolves, the structure of both the components may change and the phenomena of solvation and association are observed depending on the nature of the solvent (*i.e.*) good or poor solvent.

Cellulose is an outstanding polymer because of its comparatively rigid chains. Many industrial applications of relatively pure cellulose, the ability of cellulose and its derivatives to be made fluid by the action of solvents, with or without the aid of heat, is the factor, which makes the use possible. The interaction of cellulose and its derivatives with solvents, swelling agents and plasticizers has therefore been the subject of innumerable investigations[2-5]. In the present study the cellulose derivative *viz*., 'ethyl cellulose' is chosen for investigation. Ethyl cellulose as commercially produced, whose degree of substitution is to be 2.3-2.6, is soluble in organic solvents. The important application is in pharmacy as tablet binders and coating agent. Tablets made with ethyl cellulose as a binder tend to exhibit poor dissolution and drug absorptions. Hence, it is planned to study the solutions of ethyl cellulose in different alcohols.

EXPERIMENTAL

The commercially available ethyl cellulose was used as such whose molecular weight is very high (1,50,000 approx.). The alcohols obtained from SD Fine Chemicals, Mumbai were used after standard purification[6,7].

Measurements: The solutions were prepared by adding a known weight of polymer (ethyl cellulose) to a fixed volume of solvent (alcohols) and then stirring under reflux, until a clear solution was obtained. The concentration range chosen in the solution is from 0-3 % because of its high viscous nature.

The ultrasonic velocity measurements of the ethyl cellulose and alcohol solutions were made in the ultrasonic time intervalometer (Model 101, Innovative Instruments, Hyderabad) using a pulse echo overlap technique at a fixed frequency of 10 MHz and at three temperatures (303, 313 and 323 K). The temperature was maintained constant by circulating water from a thermostatically controlled (± 0.1 °C) water bath. The values of densities at different temperatures were measured using specific gravity bottle by standard procedure and the shear viscosity was measured using Ostwald's viscometer with an accuracy of ± 1 %.

Theory: Employing the measured values of velocity (U), density (ρ) and viscosity (η), some acoustical parameters can be computed through the following expression[8,9].

The adiabatic compressibility;

$$\beta_{ad} = [U_2\rho]^{-1} \quad (1)$$

Acoustic impedance;

$$Z = U\rho \quad (2)$$

Free length;

$$L_f = K_T[\beta_{ad}]^{1/2} \quad (3)$$

where, K_T is a constant for different temperatures known as Jacobson constant[10].

Rao's number;

$$R = U^{1/3}V \quad (4)$$

where V = molar volume of the solution.

Internal pressure;

$$\pi_i = bRT\ [K\eta/U]^{1/2}[\rho^{2/3}/M_{eff}^{7/6}] \quad (5)$$

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

Solvation number;

$$Sn = [M/M_0][1-(\beta_{ad}/\beta_0)][(100-x)/x] \quad (6)$$

TABLE-1
ULTRASONIC VELOCITY AND RELATED PARAMETERS FOR THE SOLUTIONS OF ETHYL CELLULOSE IN PROPAN-1-OL

Temp. (K)	Conc. (wt %)	U (ms^{-1})	ρ ($kg\ m^{-3}$)	$\eta \times 10^3$ ($Ns\ m^{-2}$)	$\beta_{ad} \times 10^{10}$ ($N^{-1}\ m^2$)	L_f (Å)	$\pi_i \times 10^{-6}$ (Pascal)	$R \times 10^3$	$Z \times 10^{-3}$ ($kg\ m^{-2}\ S^2$)	S_n
303	0.0	1200.5	802.9	1.3276	8.6409	0.5879	251.74	795.5	963.9	–
	0.5	1210.1	803.2	2.5549	8.5028	0.5832	345.98	801.1	971.9	11.26
	1.0	1212.8	803.5	3.0397	8.4607	0.5818	374.97	805.2	974.5	7.30
	1.5	1217.5	803.8	4.4235	8.3994	0.5796	439.43	809.7	978.3	6.67
	2.0	1218.4	804.9	5.5712	8.3685	0.5786	501.53	812.7	980.8	5.45
	2.5	1220.1	806.3	7.1527	8.3317	0.5773	565.46	815.5	983.7	4.92
	3.0	1221.4	806.8	7.6775	8.3082	0.5765	582.63	819.0	985.4	4.38
313	0.0	1170.7	798.2	1.1549	9.1415	0.6047	244.65	793.6	934.4	–
	0.5	1185.2	798.5	2.0514	8.9150	0.5972	322.34	809.9	941.0	12.44
	1.0	1186.5	798.9	2.4543	8.8914	0.5964	350.55	804.0	947.9	7.09
	1.5	1192.0	799.4	3.5108	8.8044	0.5935	416.18	808.6	952.8	6.92
	2.0	1193.4	800.3	4.2884	8.7735	0.5924	457.53	811.8	955.1	5.75
	2.5	1195.8	801.3	5.3289	8.7272	0.5908	507.20	815.1	958.2	5.27
	3.0	1197.2	804.5	5.7228	8.6725	0.5890	523.86	815.9	963.1	5.05
323	0.0	1154.9	785.5	0.8597	9.5459	0.6364	216.98	802.6	907.2	–
	0.5	1160.4	785.9	1.3742	9.4502	0.6333	272.24	807.5	911.9	6.99
	1.0	1161.2	786.2	1.8740	9.4328	0.6327	316.38	811.2	912.9	4.11
	1.5	1165.7	786.6	2.6414	9.3557	0.6301	372.67	815.7	916.9	4.60
	2.0	1167.2	786.9	3.1070	9.3273	0.6291	401.82	819.5	918.5	3.94
	2.5	1170.4	788.1	3.6504	9.2637	0.6270	433.03	822.9	922.3	4.05
	3.0	1172.5	793.0	3.8317	9.1723	0.6239	442.71	822.0	929.8	4.44

TABLE-2
ULTRASONIC VELOCITY AND RELATED PARAMETERS FOR THE SOLUTIONS OF ETHYL CELLULOSE IN BUTAN-1-OL

Temp. (K)	Conc. (wt %)	U (ms^{-1})	ρ ($kg\ m^{-3}$)	$\eta \times 10^3$ ($Ns\ m^{-2}$)	$\beta_{ad} \times 10^{10}$ ($N^{-1}\ m^2$)	L_f (Å)	$\pi_i \times 10^{-6}$ (Pascal)	$R \times 10^3$	$Z \times 10^{-3}$ ($kg\ m^{-2}\ S^2$)	S_n
303	0.0	1244.6	806.6	1.6739	8.0033	0.5658	218.04	988.4	1003.9	–
	0.5	1249.9	806.9	2.6352	7.9311	0.5633	272.67	990.6	1008.7	5.13
	1.0	1252.3	807.7	3.2201	7.8938	0.5619	298.67	990.3	1011.5	3.91
	1.5	1259.4	810.2	5.6348	7.7818	0.5579	392.79	1001.1	1020.3	5.24
	2.0	1264.3	811.1	6.5998	7.7132	0.5555	422.44	1005.5	1025.5	5.12
	2.5	1265.5	811.8	8.8048	7.6919	0.5547	485.45	1009.4	1027.3	4.37
	3.0	1265.6	814.4	11.4130	7.6633	0.5537	551.22	1010.5	1030.8	3.95
313	0.0	1213.4	796.0	1.2614	8.5315	0.5929	196.76	993.1	965.9	–
	0.5	1219.9	796.5	1.9404	8.4360	0.5896	242.55	995.5	971.6	6.44
	1.0	1221.5	797.3	2.3264	8.4059	0.5886	263.26	1002.5	973.9	4.21
	1.5	1227.4	799.1	3.9018	8.3060	0.5851	338.88	1006.3	980.8	5.01
	2.0	1230.7	800.0	4.6706	8.2532	0.5832	368.69	1010.4	984.5	4.61
	2.5	1231.8	800.7	6.3223	8.2315	0.5824	426.77	1014.4	986.2	3.95
	3.0	1233.2	802.3	7.9245	8.1958	0.5812	475.91	1016.8	989.4	3.66
323	0.0	1185.0	788.3	0.9400	9.0335	0.6192	175.80	995.0	934.2	–
	0.5	1188.5	789.2	1.3950	8.9705	0.6170	213.69	996.1	937.9	4.01
	1.0	1193.1	789.9	1.6379	8.8945	0.6144	229.21	1004.0	942.4	4.40
	1.5	1196.7	791.0	2.4847	8.8273	0.6120	280.72	1007.9	946.6	4.33
	2.0	1200.4	791.6	3.1777	8.7668	0.6099	315.53	1012.6	950.2	4.17
	2.5	1201.1	792.3	4.3773	8.7482	0.6093	368.52	1016.4	951.7	3.55
	3.0	1203.7	793.3	5.4737	8.7000	0.6076	410.05	1020.0	954.9	3.43

TABLE-3
ULTRASONIC VELOCITY AND RELATED PARAMETERS FOR THE SOLUTIONS OF ETHYL CELLULOSE IN PENTAN-1-OL

Temp. (K)	Conc. (wt %)	U (ms^{-1})	ρ ($kg\ m^{-3}$)	$\eta \times 10^3$ ($Ns\ m^{-2}$)	$\beta_{ad} \times 10^{10}$ ($N^{-1}\ m^2$)	L_f (Å)	$\pi_i \times 10^{-6}$ (Pascal)	$R \times 10^3$	$Z \times 10^{-3}$ ($kg\ m^{-2}\ S^2$)	S_n
303	0.0	1246.7	810.9	2.5073	7.9334	0.5633	218.58	1169.8	1011.0	–
	0.5	1256.9	814.4	3.7671	7.7721	0.5576	266.36	1172.8	1023.7	5.85
	1.0	1257.4	815.6	5.0711	7.7542	0.5569	307.79	1176.0	1025.6	5.43
	1.5	1260.0	816.7	6.8550	7.7117	0.5554	356.13	1179.9	1029.1	4.45
	2.0	1260.9	817.5	8.9287	7.6944	0.5548	404.67	1183.8	1030.8	3.59
	2.5	1263.3	817.0	11.8805	7.6687	0.5539	464.00	1190.1	1032.2	3.15
	3.0	1265.6	817.1	15.2948	7.6411	0.5529	523.63	1195.4	1034.1	2.88
313	0.0	1223.7	802.3	1.7103	8.3230	0.5857	186.91	1175.1	981.8	–
	0.5	1226.3	805.7	2.7056	8.2534	0.5832	234.37	1175.7	988.1	4.05
	1.0	1237.8	807.1	3.6694	8.0862	0.5773	270.70	1182.2	999.1	6.85
	1.5	1239.5	808.5	4.8521	8.0511	0.5760	309.97	1185.5	1002.1	5.23
	2.0	1241.2	809.1	6.4934	8.0233	0.5750	356.83	1189.9	1004.2	4.29
	2.5	1242.1	809.6	8.3110	8.0057	0.5744	401.87	1194.1	1005.6	5.42
	3.0	1244.6	810.1	10.5850	7.9686	0.5731	451.17	1199.0	1008.3	3.33
323	0.0	1201.8	796.5	1.0833	8.6935	0.6074	154.14	1176.6	957.2	–
	0.5	1204.4	800.2	1.9120	8.6212	0.6049	204.22	1176.7	963.4	4.03
	1.0	1212.7	800.6	2.6270	8.4933	0.6004	237.51	1183.7	970.9	5.54
	1.5	1214.5	804.8	3.3414	8.4244	0.5979	267.34	1183.6	978.9	4.94
	2.0	1219.2	805.8	4.5155	8.3502	0.5953	308.93	1187.9	982.3	4.69
	2.5	1219.5	805.2	5.6131	8.3410	0.5950	342.70	1193.3	982.5	3.83
	3.0	1221.7	805.7	7.0135	8.3163	0.5941	381.14	1198.1	984.3	3.40

TABLE-4
ULTRASONIC VELOCITY AND RELATED PARAMETERS FOR THE SOLUTIONS OF ETHYL CELLULOSE IN HEXAN-1-OL

Temp. (K)	Conc. (wt %)	U (ms^{-1})	ρ ($kg\ m^{-3}$)	$\eta \times 10^3$ ($Ns\ m^{-2}$)	$\beta_{ad} \times 10^{10}$ ($N^{-1}\ m^2$)	L_f (Å)	$\pi_i \times 10^{-6}$ (Pascal)	$R \times 10^3$	$Z \times 10^{-3}$ ($kg\ m^{-2}\ S^2$)	S_n
303	0.0	1313.6	817.9	3.2932	7.0847	0.5323	206.62	1368.1	1074.5	–
	0.5	1317.3	818.3	4.8883	7.0427	0.5308	250.37	1373.9	1077.9	2.49
	1.0	1324.0	818.6	6.5223	6.9681	0.5279	287.26	1380.9	1033.9	3.43
	1.5	1327.5	819.7	8.7793	6.9228	0.5262	330.55	1389.5	1088.2	3.16
	2.0	1331.1	821.0	11.6508	6.8741	0.5244	380.38	1389.5	1092.9	3.06
	2.5	1332.7	822.8	15.7401	6.8421	0.5232	440.62	1392.1	1096.6	2.80
	3.0	1333.5	824.5	19.7839	6.8211	0.5224	492.44	1394.5	1099.4	2.52
313	0.0	1280.9	810.5	2.3706	7.5199	0.5566	182.26	1369.2	1038.2	–
	0.5	1287.9	811.2	3.3428	7.4321	0.5534	215.05	1375.4	1044.7	4.89
	1.0	1289.1	811.6	4.5613	7.4145	0.5527	250.05	1380.5	1046.2	2.92
	1.5	1294.0	813.1	5.8334	7.3456	0.5502	280.38	1389.1	1052.1	3.20
	2.0	1297.1	814.2	7.4023	7.3004	0.5484	315.50	1389.2	1056.0	3.00
	2.5	1297.6	816.2	9.2155	7.2766	0.5475	350.22	1390.9	1059.1	2.64
	3.0	1301.5	818.9	12.7274	7.2089	0.5450	411.13	1392.7	1065.8	2.80
323	0.0	1252.2	804.7	1.7170	7.9257	0.5799	161.11	1368.7	1007.6	–
	0.5	1260.4	805.4	2.5575	7.8185	0.5759	195.29	1375.4	1015.1	5.83
	1.0	1263.2	805.9	3.0010	7.7776	0.5745	210.44	1380.9	1017.9	3.92
	1.5	1265.7	806.1	4.2488	7.7440	0.5733	251.31	1390.8	1020.2	3.17
	2.0	1269.5	807.9	5.2508	7.6799	0.5709	275.77	1389.8	1025.7	3.19
	2.5	1273.9	808.4	7.3616	7.6226	0.5688	324.71	1395.7	1029.8	3.13
	3.0	1274.9	810.7	8.7058	7.5882	0.5675	352.16	1397.1	1033.7	2.89

where β_{ad} 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

Using the measured values of ultrasonic velocity, density and viscosity of the solutions, adiabatic compressibility, free length, internal pressure, Rao's constant, acoustic impedance and solvation number are calculated at three different temperatures and are shown in Tables 1-4.

Ultrasonic velocity increases non-linearly with increase of concentration of ethyl cellulose in propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol systems at three different temperatures whereas the velocity decreases with increase in temperature. Adiabatic compressibility decreases non-linearly with increase of concentrations of ethyl cellulose in alcohols. Intermolecular free length also behaves in the similar manner as that of adiabatic compressibility. As temperature increases, intermolecular free length increases in all the four systems.

Internal pressure increases rapidly with increase of concentration and decreases with increase of temperature in all the four systems studied. It is found that Rao's constant and acoustic impedance varies non-linearly with concentration in all the four systems. The number of solvated molecules per repeat unit is approximately 6 for propan-1-ol, 5 for butan-1-ol and pentan-1-ol and 3 for hexan-1-ol.

The increase in velocity is due to the association between the solute and solvent molecules. The variation is not much appreciable at higher concentration when compared to lower concentrations. This behaviour may be explained as follows, in general, the cellulose and its derivative molecules are linear, consists of sufficient number of chain linkages, which is an essential prerequisite for any chain to be randomly coiled and the chains have no overall tendency to adopt any particular conformation. The conformation of chain results from the interactions of chain segments with its environments. These interactions involve the segments of the same as well as the other chain in addition to the solvent. In a good solvent, each chain segment will prefer to contact with solvent molecules rather than with the segments of its own or those of neighbouring chains. Because of this the chain will be extended. In a poor solvent, if the polymer-polymer and solvent-solvent contacts are favoured, the chain will have a contracted form[11].

It has been observed that, in all the cases, the polymer solution compressibility is less than that of the solvents, in conformity with an earlier report[12]. In solvation, the highly polar forces results in a strong localized electric field and the solvating molecules form an incompressible region[13]. This effect results in a reduction of adiabatic compressibility of the solution relative to that of pure solvent. The rapid decrease of adiabatic compressibility with increase of concentration in alcohols systems clearly indicates the formation of more number of tightly bound systems. Since the velocity increases with concentration and the density does so, the compressibility must decrease with increase in concentration. This could be caused by a more rigid liquid structure associated with hydrogen bonding of ethyl cellulose with alcohols. The hydrogen bond may be formed between the hydrogen of methyl group of the ethyl cellulose and the oxygen of hydroxyl group of alcohols. Such reduction in compressibilities have been found in solutions of polymers which is attributed to change in compressibilities of the solvent molecules concerned in solutions[14,15].

At lower concentration of ethyl cellulose in alcohols the molecules are not closer and thus inter-molecular free length is high. In the more concentrated solution the molecules come closer and segment-segment interaction will exists, thereby decreasing the intermolecular free length and hence internal pressure increases[16]. From the experimental analysis, it is observed that the number of solvent molecules solvated per polymer unit is observed to decrease with increase in the polymer concentration. This is due to the cohesion among the polymer chains and reduction in the hydrodynamic volume. Similar observation is made in the case of cellulose acetate in cyclohexane and carbon tetra chloride[17].

When the temperature increases, the hydrogen bond may broken up due to thermal agitation, thereby causing the intermolecular free length and adiabatic compressibility to increase and hence the velocity to decrease. It is expected that as the intermolecular forces are weakened due to thermal agitations, an increase in the intermolecular free length be observed. Similar behaviour has been reported in the case of poly vinylchloride in dimethyl formamide[18].

The decrease in ultrasonic velocity with increase in temperature in binary system is a general trend of associated organic liquids and can be established by estimating Rao's constant which is independent of temperature for the associated organic liquids[19]. If the variation of Rao's constant with concentrations of one of the component is non-linear, it generally indicates a strong association between molecules. As Rao's constant varies non-linearly with concentration it may be concluded that there is an association between ethyl cellulose and alcohol molecules. The increase of acoustic impedance with increasing concentration in alcohol systems predicts a strong polymer-solvent interaction.

Hence it is concluded that in all the alcohol systems the fluctuational network between isolated macromolecules and associates exists and this is somewhat less in higher aliphatic alcohol systems, when compared to that of lower ones.

REFERENCES

1. H.G. Elias, Macromolecules, Plenum Press, New York, Vol. 1 (1984).
2. D. Geetha and C. Rakkappan, *Ind. J. Phys.*, **77B**, 525 (2003).
3. M. Selvakumar, D.K. Bhatt and N.G. Renganathan, *Indian J. Chem.*, **47(A)**, 1014 (2008).
4. R.A. Pethrick, *Euro. Polym. J.*, **9**, 169 (1973).
5. W.R. Moore, *J. Polym. Sci.*, **16**, 571 (1967).
6. J.A. Riddick, W.B. Bunger and T.K. Sankaro, Organic Solvents, Techniques of Chemistry, John Wiley, New York, Vol. 2, edn. 4 (1986).
7. A.I. Vogel, Text Book of Practical Organic Chemistry, Longmann, London, edn. 5, ISBN:0582-46236-3 (1989).
8. P.S. Naidu and K.R. Prasad, *Indian J. Pure Appl. Phys.*, **42**, 51 (2004).
9. R. Kumar, S. Jayakumar and V. Kannappan, *Indian J. Pure Appl. Phys.*, **46**, 169 (2008).
10. B. Jacobson, *Acta Chem. Scand.*, **6**, 1485 (1952).
11. W. Brown, Cellulose and Cellulose Derivatives, IV, Inter. Sci. Publ. Inc., NewYork (1965).
12. W.R. Moore and M.A. Uddin, *Eur. Polym. J.*, **59**, 185 (1969).
13. A. Passynsky, *J. Polym. Sci.*, **29**, 61 (1958).
14. V.M. Kagathara, M.R. Sanariya and P.H. Parsania, *Euro. Polym. J.*, **36**, 237 (2000).
15. S. Kalyanasundaram, B. Natarajan, A.M. Stephen and A. Gopalan, *Acoustica*, **83**, 74 (1997).
16. Bell, *J. Polym. Sci.*, **43**, 1363 (1960).
17. S. Rajagopalan and S.J. Sharma, *J. Pure Appl. Ultrason.*, **24**, 1 (2002).
18. B. Sundaresan and A.S. Rao, *Polym. Int.*, **33**, 425 (1994).
19. K. Senthil and C. Rakkappan, *Asian J. Phys.*, **6**, 467 (1997).