Comparative study between acoustical nature and molecular interactions of copolymer and terpolymer

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ABSTRACT

The copolymer has been synthesized by condensation of p-hydroxy benzoic acid and formaldehyde in 2M HCl. The terpolymer has been synthesized by condensation of p-hydroxy benzoic acid, urea and formaldehyde in 2M HCl. Density (ρs), ultrasonic velocity (Us) and viscosity (ηs) of terpolymer and copolymer have been measured in DMF at five different temperatures.The experimental data have been used to calculate the acoustical parameters namely acoustic impedance (z), adiabatic compressibility (βs), intermolecular free length (Lf). The results are discussed in the light of solute-solvent interaction and structural effects on the solvent in solution.

Key words: Terpolymer, copolymer, acoustic impedance, adiabatic compressibility, intermolecular free length, ultrasonic velocity.
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INTRODUCTION

The understanding of intermolecular interactions between polar and non-polar component molecules can be best made by ultrasonic investigations and they find applications in several industrial and technological processes [1-2]. Muhuri and co-workers [3] have evaluated the apparent molar volume and apparent molar compressibility of tetralkyl ammonium borates in 1,2-dimethyloxyethane using sound velocity measurements and the presence of solute-solute and solute-solvent interactions were predicted in the system.Jayakumar et.al [4] have studied the molecular association and absorption on the electrolytic solutions of copper sulphate($CuSO_4.5H_2O$) and Nickel sulphate($NiSO_4.7H_2O$) in water.They concluded the existence of solute-solvent interactions betwee the components of the system.Amalendu Pal et.al [5]have made an attempt to study the speed of sound and isentropic compressibility of mixtures containing polyethers and ethyl acetate at 298.15 K and they discussed the dipole-dipole

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interactions between the components of the mixtures. Ultrasonic technique is extensively used in consumer, medical, engineering process industries, biology, biochemistry, dentistry, geography, polymers, etc. Extensive uses of polymers in technology have promoted ultrasonic studies to understand structures of polymers and furnish knowledge on solvophilic or solvophobic nature of polymers. It provides a wealth of information about molecular interactions, nature and strength of interactions. It offers a rapid nondestructive method for characterizing materials. Ultrasonic techniques are powerful and effective tool for investigation of polymer solutions properties and behavior of polymer chains in an ultrasonic field. In the present investigation, free intermolecular length acoustic impedance, adiabatic compressibility, free length of copolymer derived from p-hydroxy benzoic acid and formaldehyde and terpolymer derived from p-hydroxy benzoic acid, urea and formaldehyde in DMF has been evaluated at different temperatures over range of concentration using experimentally determined values of viscosity, density and ultrasonic velocity.

MATERIALS AND METHODS

The chemicals used in the present work were of analytical reagent (AR) with minimum assay of 99.9% were obtained from Sd fine chemicals. All reagents were used after purification. The compounds were synthesized in the laboratory [6-7]. The densities of the solutions were measured at different temperatures by the hydrostatic plunger method. A monopan balance of least count 0.0001g was used to record change in plunger weight dipped in solutions. The viscosities of the solutions were measured by using the Ostwald viscometers. The viscometer was suspended in an experimental bath having a glass window to observe the miniscus of the liquid.To determine the flow time the viscometer was cleaned thoroughly with doubly distilled DMF, dried and then filled with a fixed amount of DMF and mounted inside the thermostat vertically.It was kept in an experimental bath for (15 to 20) min to acquire the thermal equilibrium. The liquid was then allowed to flow down through the capillary.The stop watch was started as soon the liquid meniscus touched the upper fiducial mark, the stop-watch having an uncertainity of $\pm$ 0.1s.To measure the flow for given solution, the viscometer was rinsed with given solution and same amount of the solution was introduced in the viscometer and time of flow was measured between same two marks on the capillary. On average, three readings were taken. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F – 81S) at 2 MHz with accuracy of $\pm$ 0.03%.

Theory
Using the measured data, the following acoustical parameters have been calculated

$Z = U_s \times \rho_s$ … … …... (1)
$\beta_s = 1/ (U_s^2 d_s)$ ………….. (2)
$L_f = K \times \sqrt{\beta_s}$ … … …. ..(3)

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RESULTS AND DISCUSSION

The experimental data of ultrasonic velocity (Us), density (ρs), viscosity (ηs), adibatic compressibility, free length and acoustic impedance of copolymer and terpolymer in DMF is given in table-I and II.

Table-I (Data of concentration density, viscosity, velocity, adiabatic compressibility, free length & acoustic impedance for copolymer.)

Conc./ (%)	Temp /(K)	$\rho s/(Kgm^{-3})$	$\eta s/(NSm^{-2})$	$U/(ms^{-1})$	$\beta s/(X10^{-7}m^2N^{-1})$	$Lf/(A^0)$	$Z/(Kg\ m^{-2}s^{-1})$
0.7	283	928.59	0.8623	1490.7	4.84	41.898	1384.2
	288	925.77	0.7863	1477.9	4.95	42.325	1368.1
	293	919.6	0.7423	1443.0	5.22	43.494	1326.9
	298	900.5	0.6729	1433.1	5.41	44.256	1290.5
	303	895.18	0.6115	1386.6	5.81	45.876	1241.2
0.9	283	933.43	0.8731	1506.6	4.72	41.348	1406.3
	288	933.33	0.8049	1478.8	4.90	42.127	1380.2
	293	923.77	0.7540	1473.6	4.99	42.494	1361.2
	298	902.88	0.6785	1455.5	5.23	43.517	1314.1
	303	896.1	0.6203	1443.0	5.36	44.06	1293.0
1.1	283	964.31	0.9280	1509.2	4.55	40.629	1453.9
	288	945.54	0.8237	1489.9	4.76	41.543	1408.7
	293	949.57	0.7897	1477.7	4.82	41.797	1403.1
	298	907.97	0.6864	1468.3	5.11	43.017	1333.1
	303	896.81	0.6348	1447.0	5.33	43.921	1297.6
1.3	283	968.02`	0.9443	1515.6	4.497`	40.361	1467.1
	288	966.27	0.8466	1499.7	4.60	40.826	1449.1
	293	956.99	0.7922	1487.3	4.72	41.365	1423.3
	298	918.55	0.6904	1471.0	5.03	42.69	1351.1
	303	906.55	0.6351	1448.2	5.26	43.648	1312.8
1.5	283	969.63	0.9940	1518.3	4.47	40.256	1472.1
	288	960.55	0.8779	1511.6	4.56	40.625	1451.9
	293	960	0.8045	1487.8	4.71	41.287	1428.2
	298	930.76	0.7279	1472.3	4.96	42.372	1370.3
	303	925.77	0.6482	1450.4	5.13	43.127	1342.7

For both the polymers ultrasonic velocity (Us), density (ρs), viscosity (ηs) increases with concentration. The ultrasonic velocity (Us) depends on intermolecular free length (Lf).The ultrasonic velocity (Us) increases with decrease in Lf. For both the polymers Lf decreases with concentrations which suggest the presence of solute-solvent interactions. This is further confirmed by viscosity values which increase with increasing concentration suggesting more association between solute and solvent molecules. The adiabatic compressibility (βs) decreases with increasing concentration, for both the polymers which further confirms the presence of solute-solvent interactions. From table II, it is evident that, adiabatic compressibility (βs) values of terpolymers solutions show decrease with the increase of solute concentration. This can be explained in terms of the electrostatic effects of terpolymers on the surrounding solvent molecules.

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Table-II (Data of concentration, density, viscosity, velocity, adiabatic compressibility free length acoustic impedance for terpolymer.

Conc. / (%)	Temp/(K)	$\rho s/(Kgm^{-3})$	$\eta s/(NSm^{-2})$	$U/(ms^{-1})$	$\beta s/(X10^{-7}m^2N^{-1})$	$Lf/(A^0)$	$Z/(Kg\ m^{-2}s^{-1})$
0.7	283	968.54	1.2989	1500.0	4.58	40.770	1452.8
	288	966.54	1.2453	1485.6	4.69	41.208	1435.8
	293	949.57	1.1304	1468.9	4.81	41.740	1415.3
	298	949.57	1.1007	1451.6	5.00	42.548	1378.3
	303	947.07	0.9652	1424.6	5.20	43.412	1349.1
0.9	283	983.12	1.2999	1518.6	4.41	39.971	1492.9
	288	981.45	1.2565	1495.4	4.56	40.626	1467.6
	293	974.53	1.2815	1492.9	4.59	40.754	1460.8
	298	974.53	1.1007	1471.4	4.74	41.434	1433.9
	303	966.46	1.0447	1432.1	5.05	42.749	1384.0
1.1	283	984.12	1.3156	1545.6	4.25	39.253	1521.0
	288	983.62	1.2989	1516.4	4.42	40.019	1491.5
	293	976.54	1.1304	1509.6	4.48	40.281	1478.8
	298	976.54	1.0275	1481.8	4.66	41.101	1447.0
	303	968.94	1.1208	1457.8	4.86	41.942	1412.5
1.3	283	986.48	1.3898	1548.9	4.22	39.122	1527.9
	288	985.45	1.3154	1535.6	4.30	39.482	1513.2
	293	977.14	1.1310	1522.8	4.40	39.922	1492.5
	298	977.14	1.0275	1494	4.59	40.753	1459.8
	303	969.84	1.1447	1468	4.78	41.631	1423.7
1.5	283	991.25	1.412	1599.5	3.94	37.793	1585.5
	288	989.52	1.318	1540.1	4.26	39.285	1523.9
	293	987.24	1.131	1538.4	4.28	39.355	1520.2
	298	987.24	1.186	1520.4	4.38	39.840	1501.0
	303	984.32	1.165	1483.0	4.62	40.905	1459.7

It has been proposed by Kalyansundaram et.al[8] that solvent molecules are entrapped in voids formed during uncoiling of polymer chains in solution and there exists electrostatic attraction between these molecules and polymer chain. From the data; it is evident that Z increases with increase in concentration of polymer. This is in agreement with the theoretical requirements as Us and ρs both increase with increase of concentration of solute in solution. The increase of Z values with solute concentration can be attributed to the effective solute-solvent interactions. The viscosity also increases with increasing concentration of solute in solution. This indicates the solute-solvent interaction which is a measure of cohesiveness or rigidity present in between either ions or ion-solvent or solvent-solvent molecules present in a solvent or solution. In both the polymers all the parameters shows the same variations but in case of terpolymer the values are higher which suggest that as compared to copolymer the solute-solvent interaction is stronger

in terpolymer. This may be due to the presence of third monomer urea which makes the structure of polymer more rigid thereby increasing the interactions.

Experimental results reveal that ultrasonic velocity decreases with the temperature. Decrease in ultrasonic velocity cause solute-solvent interactions to break due to which intermolecular free length also increases as observed. It is also observed that the value of βs increases with the temperature. This may be due to the presence of solvent molecules around the ions. This may also imply that the increase in number of free ions, showing the occurrence of ionic dissociation due to weak ion-ion interactions.

The acoustic impedance Z decreases with increase in temperature. This also suggests that as the temperature increases the interaction decreases or in other words with increase in temperature there occurs destruction of structure due to thermal fluctuations. In both the polymers the trends are same but in case of terpolymer all the parameters show higher value which shows that the solute-solvent interactions is more in terpolymer as compared to co-polymer this may be due to the more number of monomer units which causes more crowding hence more interaction.

CONCLUSION

From the present investigation, it is eventually concluded that existence of solute-solvent interactions in both the polymers but it is more significant in terpolymer as compared to copolymer due to more number of monomeric units.

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