Original Article

ACOUSTICAL STUDIES OF COPOLYMER OF P-HYDROXY BENZOIC ACID AND FORMALDEHYDE IN N, N-DIMETHYL FORMAMIDE AND DIMETHYL SULFOXIDE BY ULTRASONIC VELOCITY MEASUREMENTS

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ABSTRACT

The density (ρ), viscosity (η) and ultrasonic speeds (U) of copolymer of p-hydroxy benzoic acid and formaldehyde in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) solutions have been investigated to understand the effect of substituent's on intermolecular interactions at 283K, 288K, 293K, 298K, and 303K. Various acoustical parameters such as adiabatic compressibility (β), intermolecular free length (Lf), acoustical impedance (Z), internal pressure (π), relaxation time (τ) and relative association (RA) were determined and correlated with concentration (C). A good correlation between a given parameter and concentration is observed at all temperatures and solvent systems studied. The results have been used to discuss the nature and strength of intermolecular interactions in the system.

Keywords: Molecular interaction, Acoustical parameters, Solute-solvent and Solute-Solvent interactions, Internal pressure.

INTRODUCTION

Ultrasonic speeds and related acoustical properties of organic liquids; and non-aqueous electrolytic solutions are extensively useful especially in process industries[1]. Ultrasonic studies furnish information regarding molecular interactions, nature and strength of interactions. The interactions help in better understanding the nature of solute and solvent i. e. Whether the solute modifies or distorts the structure of the solvent. The measurement of ultrasonic speed enables the thermodynamic parameters which are highly sensitive to molecular interactions in liquid mixtures and pure liquid [2, 3].

Ultrasonic measurement is non-destructive technique to characterize the organic compounds and polymers. Although the relationships between material properties and acoustical parameters have been studied for a long time, ultrasonic devices are not used frequently for material characterization. With the development of high frequency digital and computer techniques it was possible to overcome some of the limitations in applying ultrasonic methods to material characterization and process monitoring. When propagated in polymeric materials acoustic waves are influenced by the polymeric structure as well as by molecular relaxation processes. It is possible to estimate the viscoelastic properties of polymeric materials from the velocity and allied parameters. Also the information about the structure of polymers and molecular interaction occurring in the solution can also be obtained. Literature survey on ultrasonic studies of copolymer of p-hydroxy benzoic acid and formaldehyde revealed that no work has been reported. Thus, in the present paper we have used this technique for the better understanding of the molecular interactions in polymer solutions. The experimental data is used for the evaluation of various thermodynamic and acoustical parameters by which molecular interaction in solutions is interpreted.

Ultrasonic studies in copolymer solution have drawn the attention of several researchers in recent years. Many attempts have been made to study intermolecular interaction between polymer and solvents. The molecular interaction between copolymer of p-hydroxy benzoic acid and formaldehyde in solvents, such as dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) has been investigated in the present work[4]. Dimethyl formamide (DMF) is vers a tile solvent, used in the separation of saturated and unsaturated hydrocarbons and serves as a solvent of many polymers and dimethyl sulfoxide (DMSO) is a commercially dipolar aprotic solvent which is also a naturally occurring substance.

In the present paper, we repeat the experimental measurement of the ultrasonic velocity, density and viscosity for copolymer of p-hydroxy benzoic acid and formaldehyde and solvent such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) over a wide range of composition at 283K, 288K, 293K, 298K and 303 K. Analysis of the results and their correlation with molecular interaction has also been made using copolymer solution models [5, 6].

MATERIALS AND METHODS

Materials

The solutes used in the present investigation were synthesized by refluxing 1:2 proportion of p-hydroxy benzoic acid and formaldehyde in 2M hydrochloric acid (as catalyst) for about 4-5 hrs in oil bath at 140ºC. The resultant compound was dissolved in concentrated sodium hydroxide and reprecipitated from 50% hydrochloric acid solution. The sample of copolymer of p-hydroxy benzoic acid and formaldehyde was used without purification. Dimethyl formamide (DMF) and dimethylesulfoxide (DMSO) used were of analytical grade. The ultrasonic velocity of the solution of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) in copolymer of p-hydroxy benzoic acid and formaldehyde of different concentration measured at 283K, 288K, 293K, 298K and 303 K [7, 8].

Methods

Density measurements were made by Plunger methods, based on Archimedes principle using bottom loading balance (kRoy, max 100 gm). The accuracy in density measurement was found to be + 0.0001 gm. The viscosity was measurement made by Ostwald's viscometer with an accuracy 0.001 Ns m-2. Ultrasonic sound velocity measurement were made by variable path single crystal interferometer (Mittal Enterprises, Model F – 81S) at 2 MHz with accuracy of + 0.03%. Electronically digitally operated (Plasto craft Industries) low temperature bath model, LTB – 10 was used to circulate water. The temperature was maintained with an accuracy of 0.1°C.

RESULTS AND DISCUSSION

Measured values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (Lf) at 283K, 288K, 293K, 298K and 303K for copolymer of p-hydroxy benzoic acid and formaldehyde in DMF and DMSO as a solvent[9]are given table 1 (Fig. 1 and 2) and 2 (Fig. 3 and Fig. 4).

The coefficient of viscosity decreases with temperature as well as concentration up to 1.1% concentration. This may be due to solute – solvent interactions between the molecules. The decrease in viscosity is due to steric effect and may be explained that, as the concentration increases, steric effect or steric crowding is more so that the intermolecular interaction between the copolymer of p-hydroxy benzoic acid and formaldehyde decreases with DMF and DMSO solvent as shown in Table 1 and 2.

With liquids containing molecules held by hydrogen bonds, energy changes markedly with temperature. The viscosity activation energy for these substances consists not only of the fraction i. e. about one-third of the energy of vaporization, which is due to the breaking of what, may be termed "physical" bonds, but also of the energy of these hydrogen bonds which must be broken when the liquid flows. As the temperature is increased the number of hydrogen bonds in the liquid probably diminishes, because of thermal movements of the molecules and the energy of activation will decrease. The larger the number of hydroxy groups in the molecule, the more complexes will be the network of hydrogen bonds and the greater the resistance to flow; the energy required to produce a hole will be large, since work must be done in breaking down part of this system of bonds. In carboxylic acids the hydrogen bonds probably do not extend throughout the whole system, but are probably restricted by the combination of the molecules in pairs; it is significant, therefore that at the same temperature the viscosity of an organic acid is less than that of the corresponding alcohol [10]. The linear increase of density (ρ), viscosity (η), ultrasonic velocity (U) with concentration (C) confirmed increase of cohesive forces because of strong molecular interactions, while decrease of these parameters with temperatures (T) supported decrease of cohesive forces. The increase in temperature has two opposite effects namely structure formation (intermolecular association) and structure destruction. The structure forming tendency is mainly due to solute-solvent interactions, while destruction of structure formed previously is due to thermal fluctuations [11, 12].

In DMSO, due to presence of two oxygen atoms, the copolymer will try to interact via hydrogen bonding. Due to this, there will be more interaction and more compressibility of copolymer of p-hydroxyl benzoic acid and formaldehyde in DMSO as well as DMF and also with temperatures which reflect in increases in adiabatic compressibility with concentration as show in table 1 and 2. In case of DMF, there is presence of unshared electron pair on N-atom, which is accepted by proton. The same trend is observed with intermolecular free length. Increased in intermolecular free length leads to increase adiabatic compressibility, so adiabatic compressibility and free length varies in same manner. And this behavior is observed in both mixtures in Table 1 and 2 [13].

The relative association (RA) is influenced by two factors; the breaking up of the solvent molecules on addition of electrolyte to it and the solvation of ions that is simultaneously present. The former results in the decrease and the later in increase of relative association [14]. In the present case relative association decreases which is due to the breaking up of the solvent molecules on the addition of solute which also indicates prominent polymer-solvent interaction. Copolymer of p-hydroxy benzoic acid and formaldehyde in DMSO shows much variation as compared to the copolymer of p-hydroxy benzoic acid and formaldehyde in DMF solution. So when comparison is made between these two solutions of copolymers the polymer-solvent interaction is much prominent in DMF. This may be due to the fact that hydrogen from competing with lone pair of nitrogen and oxygen of DMF for H- bonding [15].

Table 1: Density, viscosity, ultrasonic velocity, adiabatic compressibility, free length and relative association of p-hydroxy benzoic acid and formaldehyde with DMF solvent

	Temp.(^{o}K)	DMF				
		Concentration (%)				
		0.7	0.9	1.1	1.3	1.5
ρ Kg m^{-3}	283k	0.96341	0.93343	0.96963	0.96802	0.92859
	288k	0.96055	0.92877	0.93433	0.93554	0.9362
	293k	0.94957	0.96	0.9196	0.95699	0.9237
	298k	0.93076	0.91855	0.9005	0.90288	0.8961S
	303k	0.92577	0.89681	0.89518	0.90797	0.9065
η 10^{3}Ns m^{-2}	283k	0.99404	0.92809	0.87313	0.94432	0.8623
	288k	0.87799	0.82372	0.78637	0.84666	0.80495
	293k	0.80459	0.79223	0.74239	0.78974	0.75404
	298k	0.72794	0.68646	0.67297	0.69045	0.67856
	303k	0.64829	0.62035	0.61158	0.63517	0.63483
U ms^{-1}	283k	1525.61	1530.31	1503.81	1500.7	1512.60
	288k	1511.63	1499.72	1489.92	1478.8	1477.90
	293k	1487.84	1443.05	1477.76	1487.36	1473.60
	298k	1471.04	1433.12	1455.52	1468.32	1472.32
	303k	1447.08	1386.61	1443.04	1450.4	1448.16
β 10[10]Pas^{-1}	283k	4.46E-07	4.57E-07	4.56E-07	4.59E-07	4.71E-07
	288k	4.56E-07	4.79E-07	4.82E-07	4.89E-07	4.89E-07
	293k	4.76E-07	5E-07	4.98E-07	4.72E-07	4.99E-07
	298k	4.96E-07	5.3E-07	5.24E-07	5.14E-07	5.08E-07
	303k	5.16E-07	5.8E-07	5.36E-07	5.3E-07	5.26E-07
L_f 10[10]m	283k	40.19289	40.70784	40.64456	40.76237	41.29138
	288k	40.62549	41.64252	41.79152	42.07798	42.08718
	293k	41.5122	42.56753	42.47096	42.48222	42.49462
	298k	42.40842	43.81891	43.5748	43.13797	42.90002
	303k	43.22663	44.05123	44.08206	43.83585	43.64988
RA	283k	0.967734	0.967158	0.966411	0.966036	0.965882
	288k	0.976534	0.972519	0.980481	0.984201	0.985169
	293k	1.003686	1.002534	0.995655	0.986734	0.979551
	298k	0.982331	0.980012	0.972436	0.972165	0.976759
	303k	0.969456	0.968834	0.967237	0.966591	0.964533

Table 2: Density, viscosity, ultrasonic velocity, adiabatic compressibility, free length and relative association of p-hydroxy benzoic acid and formaldehyde with DMSO solvent

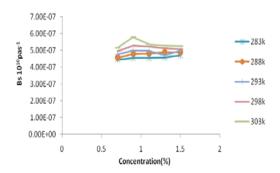|	Temp. (ºK)	DMSO Concentration (%)				
		0.7	0.9	1.1	1.3	1.5
ρ Kg m^{-3}	283k	1.11988	1.11222	1.12794	1.13014	1.13014
	288k	1.11698	1.11292	1.1228	1.12408	1.12075
	293k	1.10475	1.10294	1.10787	1.11073	1.10711
	298k	1.03607	1.08458	1.08458	1.70374	1.07889
	303k	1. s02686	1.08282	1.11222	1.08474	1.06736
η 10^{3}Ns m^{-2}	283k	2.52108	2.85855	2.61329	1.99264	1.76
	288k	2.325	2.31654	2.30663	2.2889	2.32269
	293k	1.7	1.9589	2.0869	1.99264	2.18477
	298k	1.62962	1.6965	1.81902	1.70374	1.8711
	303k	1.53464	1.5258	1.64087	1.50071	1.69543
U ms^{-1}	283k	1527.68	1545.28	1536.32	1530.08	1546.72
	288k	1529.12	1531.52	1532.16	1533.44	1533.44
	293k	1520.16	1521.60	1530.64	1530.08	1520.81
	298k	1501.11	1493.44	1501.60	1502.10	1509.12
	303k	1492.08	1488.96	1477.36	1488.96	1481.44
β 10[10]Pas^{-1}	283k	3.83E-07	3.77E-07	3.76E-07	3.78E-07	3.69E-07
	288k	3.83E-07	3.83E-07	3.79E-07	3.78E-07	3.79E-07
	293k	3.92E-07	3.92E-07	3.85E-07	3.85E-07	3.91E-07
	298k	4.28E-07	4.13E-07	4.09E-07	4.08E-07	4.07E-07
	303k	4.37E-07	4.17E-07	4.12E-07	4.16E-07	4.19E-07
L_f 10[10]m	283k	37.22865	36.93116	36.88678	36.75344	36.6030
	288k	37.24185	37.25125	37.07151	37.01946	37.7744
	293k	37.66814	37.66336	37.35752	37.32305	37.6121
	298k	38.88234	38.69697	38.48668	38.44373	38.3957
	303k	38.89773	38.84493	38.62903	38.81053	38.9585
RA	283k	0.996527	0.998999	1.001514	1.001898	1.00254
	288k	0.992446	0.994534	0.996957	0.997816	1.00301
	293k	1.000213	1.000543	1.000744	1.003449	1.00362
	298k	1.004533	1.003399	1.001578	1.001021	1.00812
	303k	1.043544	1.037466	1.035454	1.030565	1.02441

Fig. 1: Adiabatic compressibility Vs concentration with different temperature in DMF
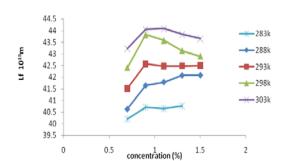

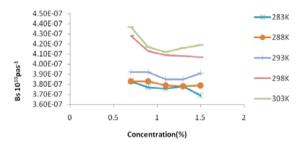Fig. 2: Free length Vs concentration with different temperature in DMF

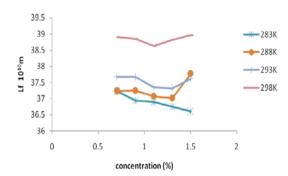Fig. 3: Adiabatic compressibility Vs concentration with different temperature in DMSO

Fig. 4: Free length Vs concentration with different temperature in DMSO

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