Molecular Interactions Studies in Some Terpolymers Using Ultrasonic Techniques

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Abstract: ***The experimental data of ultrasonic velocity, density, viscosity have been obtained for some Terpolymers in, DMF and DMSO over the concentration range of, (0.2 to 1.0) mol.Kg^{-1}. The derived parameters such as adiabatic compressibility (βs), free length (Lf), Relative Association (RA), Acoustic Impedance (Z) have been calculated from Viscosity, velocity and density measurements. The variations of these properties with concentration , Temperature give the information about solute-solvent interactions.***

Keywords: Adiabatic Compressibility, intermolecular free length Relative Association. Acoustic Impedance.

1. Introduction

The study of intermolecular interaction plays an important role in the development of molecular Sciences. The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been studied by the ultrasonic method [1]. A large number of studies have been made on the molecular interaction in liquid mixtures by various physical methods like Ultraviolent [2], Infrared [3]. Nuclear Magnetic resonance, Dielectric constant [4], Raman effect [5] and ultrasonic method [6]. For interpreting solute-solvent, ion-solvent interaction in aqueous and non-aqueous medium was helpful from Ultrasonic velocity measurements in recent year [7]. In recent years, there has been considerably greater interest in theoretical and experimental investigation of the excess thermodynamic properties of polymers and their mixtures[8]. For decades together, ultrasonic techniques have been excellent tools for non destructive testing and imaging. Although the relationship between material properties and acoustical parameters has been studied for a long time[9], 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 for material characterization and process monitoring. Ultrasonic investigation has been the subject of exhaustive research and finds extensive applications in characterizing physico-chemical behaviour and solute-solvent interaction in pure liquids[10], liquid mixtures[11] and electrolytic solutions[12] at various temperatures[13].

2. Materials and Methods

The solutes used in the present investigation were synthesized by standard methods.[14]. The solvent DMF and DMSO used was of analytical grade. It was obtained from E. Merck Chemical Company. Solvent was used after purification by distillation. Double distilled water was used for preparing the different percentage of DMF-water system. A thoroughly cleaned and dried Ostwald viscometer filled with the experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. Once the thermal equilibrium was attained, the flow times of the liquid were recorded with an accurate stopwatch (±0.01s). The viscosities were calibrated with double distilled water and with DMF. Care was taken to reduce evaporation during the measurements. The present value for the liquids agrees with the literature value within a deviation of ±0.01 poise. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F–81) at 2MHz with the accuracy of ±0.03 %. Ultrasonic and thermodynamic parameters have been measured at 10°C (283K).The polymers are as follow:

S.No	Terpolymers	Structure
1	8- hydroxyquinoline,thiourea and formaldehyde	
2	8-hydroxyquinoline,urea and formaldehyde	

3. Theory and Formulae

The relative viscosity of each solution is determined by the following empirical formula–

$\eta_r = d \text{ x } t \text{ x } \eta_0 / d_0 \text{ x } t_0$ .... (3)

Where, "η_r" is relative viscosity of solute solution; "d"is density of solution; "d_0" is density of solvent; "t" is flow time of solution and "t_0" is flow time of solvent. "η_0" is the viscocity of solvent.

"βo" is adiabatic compressibility of pure solvent and "β" is adiabatic compressibility of solution, calculated using the equations:

$\beta s = 100 / (U^2 d)$ .... (a)

And $\beta o = 100 / Uo^2\ do$ .... (b)

where, "U" is the ultrasonic velocity in the solution in m/s; "β" is in bar^{-1} and

The Intermolecular free length (Lf), Specific acoustic impedance (Z) and Relative Association(RA)[15] are calculated by using the following equations:

Lf=K x √β ….. … … (9)

Z=U x d … … … (10)

RA=(d x Uo) / (do x U) … … … (11)

4. Results and Discussion

Table 1: Values of Velocity (U), Viscosity (η), Adiabatic Compressibility (β), Intermolecular Free Length (Lf), Relative Association (R_A), Specific Acoustic Impedance (Zs) at 316 K (43 °C) in N,N, Dimethyl Formamide.

S. No	Conc (%)	D (Kg/m^3)	U (ms^{-1})	η X10^3	βX10^{-9}	L_F (A°)	R_A	Z
HUF								
1	1.0	918.3	1075.4	0.9490	9.4160	1.8468	1.1705	987540
2	0.8	949.1	968.2	0.9403	1.1240	2.0177	1.0884	918919
3	0.6	924.9	837.0	0.9323	1.54331	2.364409	1.0460	774141.3
4	0.4	948.8	802.0	0.9181	1.63861	2.436317	1.0222	760937.6
5	0.2	913.8	661.8	0.9088	2.49859	3.008452	0.9553	604752.8
HTF								
1	1.0	957.0	907.5	0.9570	1.2688	2.143843	1.0904	868477.5
2	0.8	949.1	903.4	0.9491	1.2910	2.162516	1.0674	857416.9
3	0.6	948.8	798.6	0.9488	1.6526	2.446689	1.0109	757711.7
4	0.4	924.9	787.6	0.9249	1.7429	2.51271	1.0461	728451.2
5	0.2	918.3	787.4	0.9183	1.7564	2.522364	1.0109	723069.4

Table 2: Values of Velocity (U), Viscosity (η), Adiabatic Compressibility (β), Intermolecular Free Length (Lf), Relative Association (R_A), Specific Acoustic Impedance (Zs) at 316 K (43 °C) in Dimethyl Sulphoxide.

Sr. no.	Conc (%)	U (**ms^{-1}**)	**d (g/cm^3)**	η **(Nsm^{-2})**	R_A	β x 10^{-9} **(m^2N^{-1})**	L_f	Z **($kgm^{-2}s^{-1}$)**
HUF								
1	1.0	953.8	1076.6	0.9221	0.9503	1.0210	60.816	1026861
2	0.8	902.7	1081.1	0.92597	0.972	1.1351	64.124	975909
3	0.6	815.6	1076.3	0.92188	1.001	1.3967	71.129	877830.3
4	0.4	801.8	1081.5	0.92631	1.0111	1.4383	72.090	867146.7
5	0.2	635.4	1088.0	0.93192	1.0038	2.2765	69.068	691315.2
HTF								
1	1.0	667	1076.6	0.92208	1.0706	2.0878	86.967	718092.2
2	0.8	736	1080.4	0.92535	1.0397	1.7087	78.674	795174.4
3	0.6	766.6	1096.8	0.93939	1.0413	1.5514	74.967	840806.9
4	0.4	670.4	1076.7	0.92217	1.0689	2.0665	86.521	721819.7
5	0.2	656	1083.7	0.9282	1.0837	2.1443	88.133	710907.2

Table 3: Values of Velocity (U), Adiabatic Compressibility (β), Relative Association (R_A), at different Temperature in N,N, Dimethyl Formamide.

S.No	Conc (%)	U (ms^{-1})	D (g/cm^3)	R_A	β x 10^{-9} (m^2N^{-1})
23 ^{0}C					
1	1.0	920.5	948.8	1.2226	1.2439
2	0.8	868.3	949.6	1.0901	1.3968
3	0.6	825.0	947.8	1.1617	1.5502
4	0.4	721.0	952.5	1.1615	2.0196
5	0.2	513.0	924.9	0.9644	4.1084
43 ^{0}C					
1	1.0	1075.4	918.3	1.1705	9.416
2	0.8	968.2	949.1	1.0884	1.124
3	0.6	837.0	924.9	1.0460	1.543
4	0.4	802.0	948.8	1.0222	1.638
5	0.2	661.8	913.8	0.9553	2.498
63 ^{0}C					
1	1.0	1102.2	912.3	0.9670	0.9022
2	0.8	997.2	924.4	0.9447	1.0879
3	0.6	909.9	914.6	0.9257	1.3206
4	0.4	823.0	915.0	0.9052	1.6135
5	0.2	773.7	916.1	0.8441	1.8235

Ultrasonic Velocity (U)

The ultrasonic velocity, 'U' depends on the wavelength 'λ' of the sound wave. Since the frequency (2 MHz) is constant, λ increases with the increase in the concentration as depicted in Table-I. the ultrasonic velocity in medium depends inversely on density and adiabatic compressibility of the medium. For both the Terpolymers ,data reveals increase in ultrasonic velocity (U) increases with increse in the concentration of solute. This suggests presence of solute-solvent interactions[16,17]. The increase suggests a structure-making capacity of polymers in solution. Moreover, the increase in ultrasonic velocity indicates the possibility of H-bond formation between solute and solvent. There is also an indication of greater association among the molecules.

Perusal of data given in Table-3 shows that ultra sonic velocity increases with increases in temperature. The similar findings were observed by earlier author[18-22]. The solute occupy the interstitial space of solvent and tend to break the an given ordered state of solvent due to its self association

.But With increse in temperature their occurs a structural rearrangement as a result of solvation leading to a comparatively more ordered state.

Viscosity (η):

Viscosity of a solvent or solution is a measure of cohesiveness or rigidity present in between either solute-solute or solute-solvent or solvent-solvent molecules in a solution. As density and viscosity of any solution or solvent are directly related to each other, the measured values show similar trend. From the computed data given in Table-I, for both the terpolymers viscosity increases with concentration of solute. This may be due to the formation of cage like structure during solute-solvent interactions. Again the increase suggests the H-bond forming tendency of the solute. The solutes are of structure-maker type. Both the terpolymers contains two bulky rings therefore viscosity is high and it increses with the concentration.

Adiabatic Compressibility (βs):

When an ion is added to a solvent, it attracts certain solvent molecules towards itself by wrenching the molecule species from the bulk of the solvent. Hence, less number of solvent molecules will be made available for the next incoming species. This is known as compression. Every solvent has a limit for compression and is known as limiting compressibility.

From the Table-1 it can be seen that for both the Terpolymers, adiabatic compressibility decreases with increase in concentration of solute. This may be due to the aggregation of solvent molecules around the ions supporting solute-solvent interaction. The results are in accordance with the findings of earlier authors [23,24]. As concentration increases, a larger portion of the solvent molecules are electro restricted and the amount of bulk solvent decreases causing the compressibility to decrease. Decrease in adiabatic compressibility indicates the formation of large number of tightly bound systems.

Tabli-3 reflects that with increase in temperature β value decreses this may be due to the penetration of solute molecules in to the molecular free space. This electrorestiction effect causes a decreases in the solution volume. thus resulting in a more compact and less compressible medium.

5. Relative Association

Relative Association (RA)
Relative association is influenced by two important factors:
1) Breaking up of the associated solvent molecules on addition of solute into it.
2) The solvation of solute molecules that is simultaneously present [25].
The variation of RA values with increase in concentration is shown in Table–1. It depicts that relative association (RA) increases with increase in concentration. This increase indicates salvation of solute molecules. A similar increase in the value of RA has been found in case of sucrose solution by Syal *et al.*[26]. But with rise in temperature RA decreses. The interaction tends to be weaker due to the presence of weak intermolecular forces and thermal dispersive forces with elevation of temperature . This is in accordance with earlier findings[27]

Intermolecular Free Length (Lf):

Intermolecular free length (Lf) depends on the intermolecular attractive and repulsive forces. The attractive force depends on the distance between the centres of attraction of the molecules whereas the repulsive force depends on the distance between the surfaces of the molecule. Out of these two, distance between the surfaces of the molecule has a clear physical significance. As concentration increases, number of ions or particles increase in a given volume leading to decrease in the gap (intermolecular free length) between two species. Also, the decreased compressibility brings the molecules to a closer packing resulting in decrease in intermolecular free length. Similar type of trend was also observed by Vasantharans *et al.*[28]. Again for both the terpolymers decrease in the intermolecular free length with the increase in ultrasonic velocity has been observed. The variation of intermolecular free length with concentration is shown in Table–1.

Acoustic Impedance (Zs):

Acoustic impedance is the product of ultrasonic velocity and density. As density and velocity both increase with increase in concentration for the the Zs value also increases as shown in table–I which indicates the interaction between the solute and solvent molecules. A similar type of behaviour has been obtained for tetraalkylammonium and alkali metal salts in methanol-chlorobenzene mixtures by Syal *et al.*[29].

With a view to understand solvophilicity and solvophibility of HTF and HUF in solutions the study was made in DMSO too. The computed data shows that Ultrasonic velocity is higher in DMF as compared to DMSO. This indicates that Polymer-solvent interactions are more in DMF as compared to DMSO.It is more likely that –H and –CH3 group of DMF interacts stongly with –OH group of HTF and HUF to form H-bond and it is less probable with lone pairs of electrons of –CO and amide -O_2 of DMF with Phenyl ring due to stearic hindrance. In present case powerful structure forming tendency is observed in DMF. It is reflected in the Table–2 that the change in structure of solvent or solution as a result of H-bond formation or disruption or hydrophobic (structure-breaking) or hydrophilic (structure-forming) character of solute can be related to increase or decrease of viscosity. Solutes can occupy the intestinal spaces in solvent or get solvated forming new weaker bonds. A keen observation to the data reveals that viscosity values for both the terpolymers are higher in DMF-Water which indicates the greater association of solute and solvent molecules.

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