31768

G.Ramachandran et al./ Elixir Org. Chem. 81 (2015) 31768-31772

Available online at www.elixirpublishers.com (Elixir International Journal)

Organic Chemistry



Elixir Org. Chem. 81 (2015) 31768-31772

Ultrasonic Studies in Binary Mixture of Polyvinyl Alcohol (PVA) – Water System

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ARTICLE INFO
Article history:
Received: 9 February 2015
Received in revised form:
15 March 2015;

Accepted: 7 April 2015;

ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the binary liquid mixture of polyvinyl alcohol+ water has been measured as a function of the composition of 303,308,313and318 K. The experimental data have been used to calculate some parameters namely, acoustic impedance (z), adiabatic compressibility (κ), intermolecular free length (L_f), and relative association (R_A). The results are discussed and interpreted in terms of structural and specific interactions that predominated by intermolecular hydrogen bonding.

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Keywords

Intermolecular Hydrogen bond, PVA, Ultrasonic velocity, Relative association.

Introduction

In recent years the measurement of ultrasonic velocity has got great importance in understanding the nature of molecular interaction in pure liquid and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to provide quantitative information about physical nature and strength of molecular interaction in liquid mixtures. Ultrasonic study is an analytical tool to analysis various acoustic parameter like free volume, using above parameter easily predict the ion-ion interaction, hydrogen bond, dipole-dipole interaction. In my present work interaction of PVA-Water at different temperature. **Experimental Details**

Water was purified by double distillation method. All the binary mixtures were prepared by weight and were kept in air tight bottles. The weightings were done on A Shzimadzu electronic balance with precision of \pm 0.1mg. The ultrasonic speeds in pure liquids and their binary mixtures were measured by using ultrasonic interferometer of Mittal F-5 model, single crystal variable path interferometer at 2MHZ with accuracy $\pm 0.05\%$. The densities of pure liquids and their binary mixtures were measured by using a single -capillary pykonometer at 303.15±0.015k,308.15±0.015k,313.15±0.015kand318.15±0.015 k.The measured densities were reproducible within±0.1g/cm. The temperature of test liquids and their mixtures were maintained at 303.15±0.015k, 308.15±0.015k , 313.15±0.015k and 318.15±0.015k in an electronically controlled thermostatic water bath. Viscosities of the PVA-Water solution were measured by Oswald's viscometer at different temperature 303.15±0.015k,308.15±0.015k,313.15±0.015kand318.15±0.015

k.The acoustical parameters are calculated from U, $\rho,$ and η using following relation.

1. Ultrasonic Velocity (U)

The relation used to determine the ultrasonic velocity is given by, $U=f\lambda\ ms^{-1}$

Where, f - Frequency of ultrasonic waves

 λ - Wave length

2. Adiabatic Compressibility (κ)

Adiabatic compressibility which is defined as

$$\kappa = (1/U^2 \rho) kg^4 ms^2$$

Where, U – Ultrasonic velocity

 ρ – Density of the solution.

3. Acoustic impedance (Z)

The acoustic impedance is computed by the formula

$Z = U_{\rho} kgm^{-2}s^{-1}$

Where, U –Ultrasonic velocity

 ρ –Density of the solution

4. Free Length (L_f)

Jacobson¹⁵ introduced the concept of the free length in liquids. He suggested the following relation to calculate the intermolecular free length.

$$L_f = (K/U \rho^{1/2}) m$$

Where U - Ultrasonic velocity of liquid

ρ - Density of liquid

K - Jacobson temperature dependent constant defined as

 $\mathbf{K} = (93.875 + 0.345T) \times 10^{-8}$

Where V_m is the molar volume and

 $U_a = 1600 \text{ms}^{-1}$

5. Relative Association (R_A)

 $\mathbf{R}_{A=(}\rho/\rho_{0)}$ Where ρ is the density of solute,

P0 Is the density of solvent.

Result and Discussions

Density

The general trend is that the density of solution, increases with in concentration, and normally a straight –line graph is expected for an ideal solution. Any deviation from the linear behavior is explained on the basis of intermolecular interaction. Initially in the concentration region the density decreases, reaches a minimum value at 0.1% Polyvinyl Alcohol (PVA) at all temperatures. There is a change at 0.5% concentration at all temperatures except 45°C.

The initial sharp decrease can be attributed to the increases in volume of the solution with the addition of the solute, because of the disruption of the solvent/solvent interaction. This is followed by the solvent/solute interaction reaching a maximum at concentration of 0.5%. The solvent/ solute interaction is decreased with increase in concentration. At 1% concentration it is minimum for all temperature except 45°C, refer the table - I and shown in the Graph-I. After this, the solute /solute interaction leading to the inclusion of small water molecules into the voids or cavities formed by the solute/solute network take places. This leads to decreases in volume with a corresponding increase in density.

Graph I. Concentration Vs Density



Viscosity

The variation of viscosity follows the general trend of increase in viscosity with increase in concentration. Though a rectilinear graph is expected, curve type plot is obtained as the temperature is increased. The decrease in viscosity especially at low concentration can be attributed to the disruption at PVA/water clusters formed by strong hydrogen bonding. The increase in viscosity can be attributed to the formation of intermolecular hydrogen bonding between polyvinyl alcohol molecules, refer the table - II and shown in the Graph-II. The rate of increase in viscosity is increased with the disruption intermolecular hydrogen bonding present in PVA molecules. The disruption of intermolecular hydrogen bonding takes place even at low concentrations at higher temperature.

Graph II. Concentration Vs Ultrasonic Velocity



Velocity

Ultrasonic velocity is expected to increase in concentration and decrease with increase in temperature for an ideal solution. In the system understudy, there is a sharp decrease in ultrasonic velocity, reaches a minimum at 0.1% of PVA for all temperatures. This can be explained by the disruption of solvent network formed by intermolecular interaction, with the result intermolecular free length increases. This leads to decrease in ultrasonic velocity. At temperature 35°C or 40°C there is sharp increase velocity with concentration, reaches a maximum at 0.5%. This can be seen in the density Vs Concentration graph at all temperatures. This trend can be attributed to replacement of solvent/solvent interaction by solute/solvent interaction. Further increase in concentration leads to a decrease in ultrasonic velocity at temperatures higher than 30°C.An exactly a similar trend is noticed for density and Acoustic Impedance (Z), while opposite trend is observed for intermolecular free length (Lf) and Adiabatic-compressibility(β). This is especially between the concentrations range of 0.5% - 1% and temperature of 35-45°C, solute/solvent interaction leads to aggregation of solvent molecules around the hydrophilic molecules.

Graph III. Concentration Vs Viscosity



Adiabatic Compressibility

Adiabatic Compressibility is a measure of the free spaces present in the solvent network. The trend of behavior of Adiabatic compressibility is very similar to the (Lf) intermolecular free length. Generally as concentration increases the Adiabatic Compressibility value decrease. There is an initial increase in β values at very low concentration range. This is reflected in the initial increase in free length and decrease in density. The decomposition of solvent/solvent interaction results in the increase of β value. Further addition of solute, decreases β because of the formation of solvent/solute polymeric network. The β reaches a minimum value of 0.5% in the case of temperatures 35°C to 40°C. Further increase in concentration leads to the decomposition of solvent/solute interaction, leading to the increase in β maximum occurs at 1% concentration. Beyond this β value decreases, due to the formation of solute/solvent /solute network.

Generally β value increases with increase temperature. For the system under study no linear relationship seems to exist. For the concentration of 0.1% deviations is observed. There seems to be a decrease in β with increasing temperature. This indicates that at this concentration, formation of new intermolecular bonds predominates the breaking of the already existing intermolecular interaction.

Graph. IV Concentration Vs Adiabatic compressibility



Acoustic Impedance (Z)

The Change of Acoustic Impedance with concentration and temperature of solutions is expected in the same direction as the ultrasonic velocity, while it is in a direction opposite to that of (Lf) intermolecular free length. At 30° C there is an initial decrease and then a slow increase is observed. Initial decrease of Acoustic Impedance in the concentration range 0.05% to 0.1% is observed at all temperatures. The initial depression in the curve is explained on the basis of increase in intermolecular free length.

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Table 1. Concentration vs Density							
Concentration→	0.010/	0.050/	0.10/	0.50/	10/		
Temperature↓	0.01%	0.05%	0.1%	0.5%	1%		
303 K	1189	1181	1180	1181	1182		
308 K	1179	1179	1178	1180	1186		
313 K	1178	1179	1176	1179	1183		
318 K	1176	1176	1175	1176	1181		

Table 1. Concentration Vs Density

Table II. Concentration Vs Ultrasonic Velocity

Concentration→	0.010/	0.059/	0.10/	0.59/	10/
Temperature↓	0.01%	/0 0.05 70	0.170	0.5%	1 70
303 K	1443	1302	1147	1121	1185
308 K	1376	1324	1231	1460	1247
313 K	1308	1152	1226	1226	932
318 K	1416	1374	1211	1211	1113

Table III. Concentration Vs Viscosity

Concentration→	0.01%	0.01% 0.05% 0.1%	0.10/	0.5%	1%
Temperature↓			0.1%		
303 K	0.9546	0.9965	1.0437	1.5480	2.5870
308 K	1.0706	1.0217	1.0340	1.5800	2.4590
313 K	1.0182	1.0450	1.0595	1.0595	2.4900
318 K	0.9645	1.0512	1.0530	1.0117	2.4224

Table IV. Concentration Vs Adiabatic compressibility

Concentration→	0.01	0.059/	0.19/	0.59/	10/
Temperature↓	%	%	0.1 70	0.570	1 70
303 K	4.0664	4.9949	6.4410	6.7381	1.5150
308 K	4.4790	4.8384	5.6019	3.9756	5.4540
313 K	4.9617	6.3911	5.6570	5.6429	9.7728
318 K	4.5790	4.5042	4.7326	5.7980	3.7080

Table V. Concentration Vs Free Length

Concentration→	0.01%	0.01% 0.05% 0	0.1%	0.5%	1%
Temperature↓		0.03 /0	0.1 /0		
303 K	6.112	7.179	8.1545	8.336	7.879
308 K	7.080	7.542	8.1188	6.833	8.007
313 K	6.943	9.208	8.674	8.652	6.004
318 K	8.586	9.590	8.400	9.297	3.250

Table VI. Concentration Vs Acoustic impedance

Concentration→	0.010/	0.050/	0.10/	0.50/	10/
Temperature↓	0.01%	0.05%	0.170	0.5%	1 70
303 K	1.704	1.537	1.353	1.323	1.400
308 K	1.537	1.560	1.450	1.722	1.470
313 K	1.540	1.357	1.441	1.445	1.097
318 K	1.542	1.496	1.575	1.424	2.423

Table VII.Concentration Vs Relative Association

Concentration→	0.01%	0.05%	0.1%	0.5%	1%
Temperature↓	0.01 /0	0.0570	0.1 /0	0.570	1 /0
303 K	1.835	2.330	2.300	2.360	2.230
308 K	1.775	1.845	1.982	1.674	1.958
313 K	2.040	2.302	2.158	2.164	2.843
318 K	1.736	1.786	1.829	2.027	4.082

This is due to the disruption of the existing intermolecular network in the structure of solvent by the addition of PVA. The formation of solute/solvent interaction is maximum at 0.5% concentration at 35°C and 45°C. The further decrease in the 'Z' values with increase of PVA Concentration can be attributed to the formation intermolecular interaction between PVA molecules till 1% concentration is reached. Beyond this concentration 'Z' does not show any significant change with increase in concentration.





Intermolecular Free Length (Lf)

Normal trend is that the intermolecular free lengths decreases with increases in concentration solution and it increase with increase in temperature. For the system understudy, initially at low concentration region from 0.01-0.05% the Lf value increase. The increase is very sharp. It reaches a maximum value at 0.5% concentration at 30°C. The concentration at which maximum occurs is shifted to 0.5% from 0.05% as the temperature is increased from 30-45°C. The initial sudden increase may be due to break down of the solvent network. The solvent/solvent intermolecular interaction is reduced by the addition of PVA. The intermolecular free length (Lf) increase correspondingly the density decrease. As the concentration increases the solvent/solvent interaction is replaced by solvent/solute and solute/solute interaction.





Relative association (R_A)

It is a measure of the solvent/solvent interaction leading to intermolecular association normally when a solute is added because of solute/solvent interaction or to accommodate comparatively bigger solute molecules, breaking up of solvent molecular clusters takes place. This results in the increase of RA. This is due to the salvation of PVA molecules. This takes place for all temperatures as concentration 0.5% is reached. Afterwards the RA value reaches a maximum at 0.1%. When the concentration is increased further solute/solvent interaction is replaced by solute/solute interaction.

Graph VII. Concentration Vs Relative Association



Conclusion

The system consisting of PVA/H₂O is a binary system with some special features. PVA is a polymeric molecule, which is hydrophilic. Number of hydroxyl groups in PVA can take part in intra molecular hydrogen bonding, intermolecular hydrogen bonding and (PVA/H₂O) intermolecular Hydrogen bonding between unlike molecules. In aqueous solution, in addition to these intermolecular hydrogen bonds between water molecules also exist. Because of intra molecular Hydrogen Bonding, PVA molecule is expected to have some rigidity in conformation. When PVA is added to water (at very low concentration region). 1.Intra molecular Hydrogen bonding in PVA molecules may be broken leading to conformational flexibility.

2. This may lead to intermolecular interaction with the solvent.

3. The intermolecular Hydrogen bonding present in water may be broken.

This leads to sharp changes in the properties of the system, which is observed at 0.1% concentration and almost at all temperatures. Further increase in concentration leads to replacement intermolecular interaction between solvent molecules by the solvent/solute molecular interaction. This is observed between 0.1%-0.5% concentrations. Beyond this concentration, solvation of solute molecules, caused by the replacement of intra molecular Hydrogen Bonding in PVA and formation PVA/H₂O intermolecular Hydrogen Bonding takes place (between 0.5%-1%). Depending upon the temperature, inter solute interaction also plays an important role in deciding the properties of the binary system. It is observed from the results that 1% concentration of PVA and 40C temperature are very important conditions at which the ultrasonic velocity, Acoustic Impedance, are maximum and the intermolecular free length, adiabatic compressibility are minimum. This indicates that under this condition the interaction between the added solute (PVA) and the solvent (water) are very weak and are loosely held. This condition is much favorable in dying process, where the polymer/solvent interaction should be minimum.

Acknowledgement

I thank the Department of Chemistry and Environmental Sciences, AMET University, Chennai, India for the constant support and encouragement to do the article for publication.

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