

Molecular Association Studies on Polyvinyl Alcohol At 303k

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ABSTRACT: Ultrasonic velocity(u), density(ρ) and viscosity(η) have been measured for the aqueous solution of Polyvinyl alcohol. PVA is mixed with triply distilled water and acoustical parameters has been calculated for different concentration at 303k. From the experimental data, the acoustical and thermodynamic parameters are calculated. These acoustical parameters are used to study the nature and the strength of the molecular interactions. The stability constant values shows that the system is stable and stability is lost when the concentration of polymer is increased, thereby weakening the bond.

KEYWORDS: Acoustical parameters, Thermodynamic Parameters, Stability constant.

1. INTRODUCTION

The study of molecular interaction in binary and ternary liquid mixtures plays an important role in molecular sciences. A large number of studies have been made on inter-molecular interaction in liquid system like dielectric, ultraviolet, Raman effect, Infrared and ultrasonic method. In recent years ultrasonic has become a powerful tool in providing information about the physio-chemical properties of liquid system [1-4]. It is possible to sense the molecular structure and motion in liquid polymer system using ultrasonic waves. The study of molecular interactions in the polymer and solvent throws light on the processes involving polymer production and their uses [5]. The Polymeric material chosen is polyvinyl alcohol. It is a water-soluble synthetic polymer. It dissolves slowly in cold water but at higher temperature it goes fairly fast into solution. PVA is a good protective colloid for aqueous emulsions and is employed for this purpose in a large variety of emulsion and suspension systems. It is approved for food contact by the food department and as drug administrator. Polymers are often used in pharmaceutical work [6].

The values of ultrasonic velocity (u), density (ρ) and viscosity (η) have been determined. From the experimental data Acoustical and Thermodynamic parameters along with stability constant have been calculated for different concentrations of the, PVA component in the mixture.

II. MATERIALS AND METHODS

The chemicals used in the present work were of Analar grade supplied by Merck, Polyvinyl Alcohol (500gms) Molecular weight ranging between (85000-1,25,000) and triply distilled water is used.

METHODS

Polyvinyl alcohol are dissolved in required volume of triply distilled water and 1% ,3% and 5% solutions was prepared by dissolving 1gms, 3 gms and 5gms of PVA in 200ml of distilled water. All the chemicals were kept in air –tight bottles. Weighing was done on electronic balance with the accuracy of 0.01 gm. PVA and Water solution was mixed and prepared in different concentrations such as 0.1,0.2,0.3.....1Molality. A 10 ml specific gravity bottle was used to measure the density of the solution accurate to three decimal places. Viscosity of the solution was measured by Ostwald's Viscometer. Ultrasonic velocity is measured by ultrasonic interferometer of fixed frequency 2MHz. The

principle of ultrasonic interferometer was stated by Pierce [7]. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentrations and temperatures through molecular interaction.[8-12]

The various physical parameters were calculated from measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) using standard formula

$$\text{Adiabatic Compressibility} \quad \beta = \frac{1}{\rho u^2} \quad \text{-----> (1)}$$

$$\text{Intermolecular Free length} \quad L_f = \frac{2 \times 10^{-6}}{u \sqrt{\rho}} \quad \text{-----> (2)}$$

$$\text{Acoustic Impedance} \quad Z = \rho u \quad \text{-----> (3)}$$

$$\text{Relaxation time} \quad \tau = \frac{4\eta}{3\rho u^2} \quad \text{-----> (4)}$$

$$\text{Free volume} \quad V_f = \left(\frac{Mu}{k\eta}\right)^{3/2} \quad \text{-----> (5)}$$

$$\text{Internal Pressure} \quad \pi_i = bRT \left[\frac{k\eta}{u}\right]^{1/2} \left[\frac{\rho^{3/2}}{M^{7/6}}\right] \quad \text{-----> (6)}$$

$$\text{Stability constant} \quad K = \frac{\sqrt[2]{k(c+c')-(c+kc')}}{(c-kc')^2} \quad \text{-----> (7)}$$

III. RESULTS AND DISCUSSION

The ultrasonic velocity was measured in a range of concentration to investigate ion-solvent interactions. The experimental values of ultrasonic velocity, density and viscosity of three different concentrations are shown in table-1 respectively and variation with different concentration as shown in Fig -1,2 & 3.

By using these values for PVA Adiabatic compressibility, Inter-molecular Free Length, Acoustic impedance Relaxation time free volume and internal pressure are calculated using equation(1),(2),(3) and (4) respectively and results are shown in table 1 to 5. The variations of these parameters with different concentration are shown in fig.1 to 9 respectively. Thermodynamic parameters such as Internal Pressure and Free volume are calculated as shown in the. The stability constant of the PVA molecule are shown in the Table (5).

The variation of density with different concentration are shown in the table-1.It is observed from fig(1) that density increases with increase in concentration. Measurement of velocity gives a better understanding about molecular mechanisms responsible for absorption and relaxation. Addition of polymer reduces the effective molecular area.

(1) **Adiabatic compressibility (β)** is inversely proportional to the square of the ultrasonic velocity. The actual deviation depends on the resultant effect. In this case adiabatic compressibility decreases with increase in all three concentrations and it is shown in the fig.4.This leads to the structural arrangement of intermolecular attraction. Particularly there is a decrease in 1% solution. So that compressibility values for 1%PVA-water < 3 % PVA-water < 5%PVA-water. Hence molecular interaction is more in 1% solution.

(2) **Free Length (L_f)** Decrease in free length signifies specific strong interaction between solute and solvent molecules. Increase in concentrations leads to the gap between two interacting species and it is called as inter-molecular free length. Inter- molecular free length is a predominant factor in determining the nature of sound velocity variation in liquid mixtures. Free length decreases with increase in all three concentrations as shown in the fig(5).It signifies strong molecular interaction. The deviation of free length with increase in velocity indicates the strong interaction between solute and solvent molecule due to structural arrangement in ions is affected. 1% PVA-water <3%

PVA-water < 5% PVA-water system. Free Length signifying strong interaction in 1% PVA-water system and weak interaction in 5% PVA-water system.

(3) **Acoustic impedance (Z)**- The strength of the intermolecular attraction is used to define the acoustic impedance values in pure liquids and binary liquid mixtures. As strength of the intermolecular attraction increases there is also increase in ultrasonic velocity and also increase in adiabatic compressibility as shown in the fig.(6). This signifies strong interaction in 1% PVA - H₂O system.

(4) **Relaxation time (τ)** decreases drastically with increase in all three concentrations as shown in the fig-(7). It is minimum at lower concentration and maximum at higher concentration. It confirms the availability of intermolecular interaction

(5) **Internal Pressure (π_i)** is a significant parameter in the study of thermodynamic properties of liquids and liquid mixtures. It is a measure of the resultant attractive and repulsive forces between the interacting components in the mixture. The maximum value of internal pressure is due to formation of inter-molecular attraction between solvent and solute molecules. The minimum value of internal pressure is due to breaking of inter-molecular forces. All three concentrations as shown in fig-(8). The increase in internal pressure for 1% PVA-water system signifies may be due to strengthening of molecular forces compared to 3% PVA-water and 5% PVA-water system. Intermolecular attraction between PVA-water molecules is strong at lower concentration.

(6) **Free volume (V_f)** is defined as the average volume in which the center of the molecules can move inside the hypothetical cell due to repulsion of surrounding molecules. Free volume for 1% PVA-water system < 3% and 5% PVA-water system as shown in the fig-(9), signifying strong hydrogen bonding between PVA - H₂O in 1% solution.

(7) **Stability constant.** The stability constant is determined by Yoshida and Osawa method [10]. Marwein and Bhat [11,12] applied successfully in the evaluation of formation constant or association constant or stability constant.

The presence of polymer in large amount in water disrupts the hydrogen bond. The weakening of bonds in PVA - H₂O includes, for 1%, 3% and 5% solution. PVA - H₂O solution clearly reduces the velocity free length values which indicates molecular loosening, and disrupted or repulsive forces existing between PVA and water molecules, at higher molality. The polymer chain length increases. Polymer coils around and disrupts the bond between PVA and H₂O, loosening the chemical bond. Addition of polymer reduces the molecular area at higher concentration.

The strength of the bond in 5% PVA - H₂O < 3% PVA - H₂O < 1% PVA - H₂O < system

TABLE:1
EXPERIMENTAL VALUES OF ULTRASONIC VELOCITY, DENSITY AND VISCOSITY FOR 1%, 3% AND 5% PVA –WATER SYSTEM.

MOLALITY (M)	1%			3%			5%		
	U ms ⁻¹	ρ kgm ⁻³	η Nsm ⁻²	U ms ⁻¹	ρ kgm ⁻³	η Nsm ⁻²	U ms ⁻¹	ρ kgm ⁻³	η Nsm ⁻²
0.1	1530.24	969.8	0.001	1521	971.4	0.0011	1511.7	971.2	0.0012
0.2	1551.1	970.7	0.0013	1521.8	972.4	0.0013	1512.7	972.8	0.0017
0.3	1559.14	970.8	0.0013	1521.9	973.3	0.0018	1515.1	973.8	0.0025
0.4	1559.2	971.3	0.0014	1524.6	973.5	0.0019	1517.25	975.3	0.0032
0.5	1560.4	971.7	0.0014	1524.6	974.1	0.0024	1520.25	976.4	0.0043
0.6	1564.42	971.9	0.0018	1523.4	974.4	0.0039	1526.45	977.3	0.0069
0.7	1565	972	0.0019	1517.9	975.4	0.004	1528.4	977.9	0.011
0.8	1565.3	972.3	0.0021	1525	976	0.0044	1529.84	979	0.012
0.9	1579.3	972.6	0.002	1526.0	976.8	0.0047	1529.86	980	0.012
1	1581.5	973	0.0026	1526.5	977.2	0.0059	1533.8	981.9	0.013

TABLE:2
ADIABATIC COMPRESSIBILITY AND FREE LENGTH FOR 1%, 3% AND 5% PVA-WATER SYSTEM

MOLALITY(M)	ADIABATIC COMPRESSIBILITY x 10 ⁻¹⁰ kg ⁻¹ s ⁻² m ⁻¹			FREE LENGTH x 10 ⁻¹⁰ m		
	1%	3%	5%	1%	3%	5%
0.1	4.40	4.45	4.50	4.35	4.38	4.40
0.2	4.281	4.44	4.49	4.29	4.37	4.39
0.3	4.23	4.44	4.47	4.27	4.37	4.38
0.4	4.23	4.42	4.453	4.27	4.36	4.37
0.5	4.22	4.42	4.43	4.26	4.36	4.36
0.6	4.20	4.42	4.39	4.25	4.36	4.34
0.7	4.20	4.45	4.37	4.25	4.38	4.34
0.8	4.19	4.41	4.36	4.25	4.36	4.33
0.9	4.1	4.4	4.35	4.21	4.35	4.33
1	4.10	4.39	4.32	4.20	4.35	4.31

TABLE:3
ACOUSTIC IMPEDANCE AND RELAXATION TIME FOR 1%, 3% AND 5% PVA-WATER SYSTEM.

MOLALITY(M)	ACOUSTIC IMPEDANCE x 10 ⁶ Kg m ⁻² s ⁻¹			RELAXATION TIME x 10 ⁻¹³ Secs.		
	1%	3%	5%	1%	3%	5%
0.1	1.48	1.47	1.46	5.87	6.53	7.21
0.2	1.50	1.47	1.47	7.42	7.7	10.2
0.3	1.51	1.48	1.47	7.56	10.6	14.9
0.4	1.51	1.48	1.47	7.90	11.2	19
0.5	1.51	1.48	1.48	7.88	14.1	25.4
0.6	1.52	1.48	1.49	10.08	23	40.4
0.7	1.52	1.48	1.49	10.64	23.7	64.2
0.8	1.52	1.48	1.49	11.75	25.8	69.8
0.9	1.53	1.49	1.49	10.99	27.5	69.8
1	1.53	1.49	1.50	14.24	34.5	75

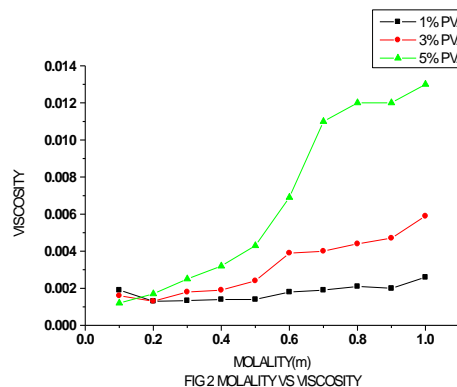
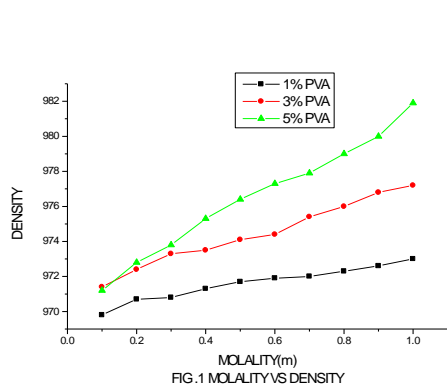
TABLE:4PVA-WATER SYSTE
INTERNAL PRESSURE AND FREE VOLUME FOR 1%, 3% AND 5% PVA-WATER SYSTEM

MOLALITY(M)	INTERNAL PRESSURE (π_i) x 10 ⁸ atmos			FREE VOLUME (V_F) x 10 ⁻⁷ m ³		
	1%	3%	5%	1%	3%	5%
0.1	4.509	1.58	1.15	1.741	6.16	8.52
0.2	7.086	1.51	1.18	0.7874	5.65	6.14
0.3	4.065	1.55	1.21	1.57	4.15	4.28
0.4	3.596	1.34	1.12	1.77	4.77	3.82
0.5	3.000	1.18	1.79	2.24	4.61	1.64
0.6	2.703	1.21	0.95	2.073	2.93	2.44
0.7	2.050	0.902	0.846	2.824	4.18	1.93
0.8	1.388	0.598	0.511	4.279	6.57	3.42
0.9	0.676	0.281	0.194	11.328	16.4	11.9
1	0.205	0.913	0.514	42.039	57.4	61.5

TABLE: 5
STABILITY CONSTANT VALUES FOR 1% , 3% and 5% of PVA +WATER

MOLALITY(m)	STABILITY CONSTANT (K)		
	1%	3%	5%
0.1	0.5588	0.0240	0.02804
0.2	0.3194	0.06002	0.10071
0.3	0.0199	0.16188	0.12125
0.4	0.00805	0.0200	0.2034
0.5	0.3206	0.01900 x 10 ⁻⁴	0.5139
0.7	0.03208	0.8147	0.1623
0.8	0.8953	0.1274	0.01802
0.9	1.1481	0.06033	0.5459

IV. GRAPHS:



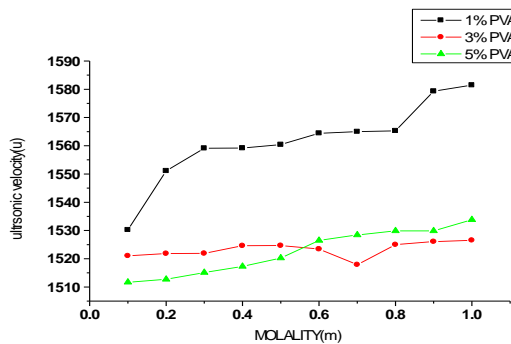


FIG.3 MOLALITY VS ULTRASONIC VELOCITY

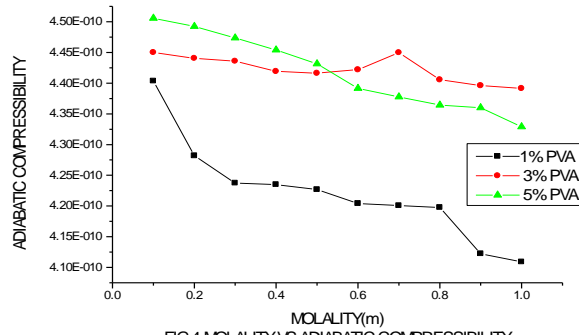


FIG.4 MOLALITY VS ADIABATIC COMPRESSIBILITY

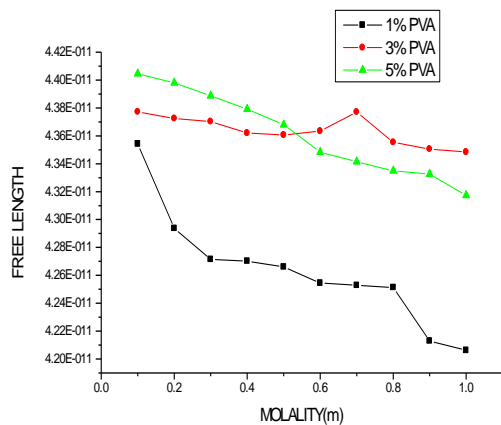


FIG.5 MOLALITY VS FREE LENGTH

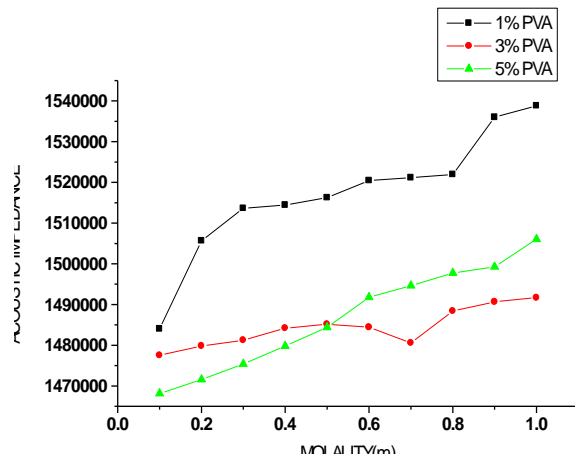


FIG.6 MOLALITY VS ACOUSTIC IMPEDANCE

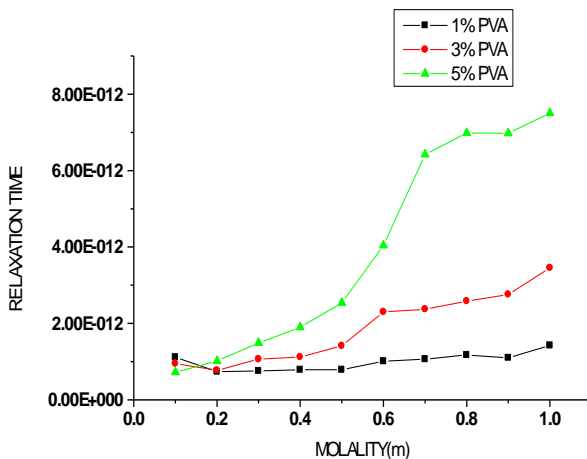


FIG.7 MOLALITY VS RELAXATION TIME

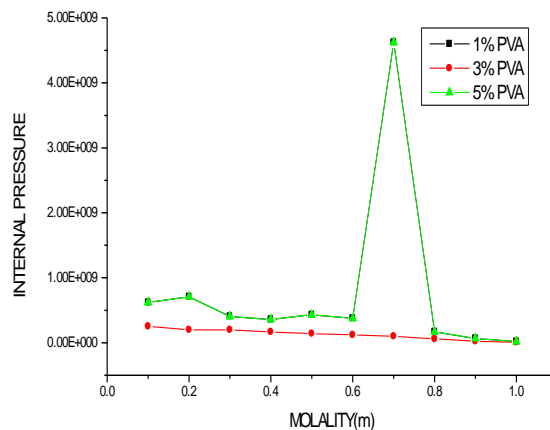
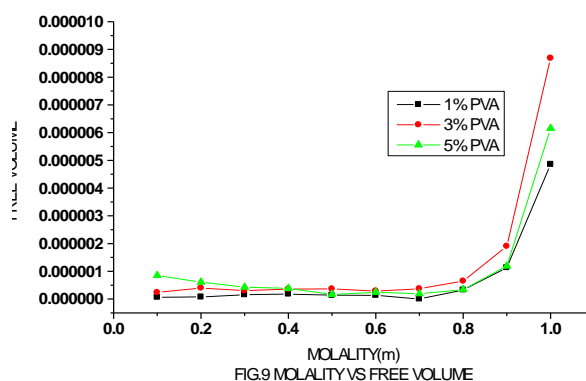


FIG.8 MOLALITY VS INTERNAL PRESSURE



V. CONCLUSION

Ultrasonic studies reveals hydrogen bonding between Polyvinyl alcohol and water and addition of polymer reduces the effective molecular area. The strength of the bond in 5% PVA - H₂O < 3% PVA - H₂O < 1% PVA - H₂O < system, signifying strong molecular interaction in 1% PVA - H₂O system.

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