Academic Sciences International Journal of Pharmacy and Pharmaceutical Sciences

ISSN- 0975-1491 Vol 4, Issue 4, 2012

Research Article

ULTRASONIC STUDIES OF ASPIRIN BY RELATIVE ASSOCIATION, RELAXATION TIME AND FREE VOLUME

SUNANDA S. ASWALE[1], SHASHIKANT R. ASWALE[1], APARNA B. DHOTE[2]

[1] Lokmanya Tilak Mahavidyalaya, Wani, Dist. Yavatmal, Maharashtra. 445304, [2] Nilkanthrao Shinde Science &Arts College, Bhadrawati, Dist.Chandrapur, Maharashtra Email: sraswale@gmail.com; ssasale@rediffmail.com, dhotea@rocketmail.com,

Received: 16 July 2012, Revised and Accepted: 28 Aug 2012

ABSTRACT

The ultrasonic Studies in liquids are useful in understanding the nature and strength of molecular interactions. Ultrasonic velocity, density and viscosity have been measured for aspirin in aqueous solution at 303.15K, 308.15K and 313.15K. Experimental data have been used to estimate the relative association, relaxation time and free volume. It is observed that dipole-dipole interaction exists between aspirin and water. These above parameters are used to discuss the structural and molecular interactions.

Keywords: Relative association, Dipole-dipole, Free volume, aspirin

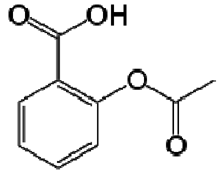
INTRODUCTION

The study of the propagation behavior of ultrasonic waves in solids, liquids, liquid mixtures, electrolyte solutions, suspensions, polymers etc. is now rather well established as an effective means for examining certain physical properties of these materials or media. The relations between the values of sound velocity and chemical or structural characteristics of the molecules of the liquid or liquid mixtures have been found. The nature and type of intermolecular interactions in liquid mixtures can be studied from the measurement of ultrasonic velocity in conjunction with thermo-acoustical parameters and excess thermodynamic function[1-5].

The properties of liquid mixtures basically depend on its local structure, expressed in terms of packing density, free volume or radial distribution function. However, this local structure depends on forces between molecules and their forms and volume of molecules[6]. It changes with compositions. This change in composition changes thermodynamic properties of mixtures. The variation of ultrasonic velocity and related parameters throw light on the structural changes associated with the liquid mixture having weakly interacting components[7-8] as well as strongly interaction components. When electrolyte is dissolved in solvent it causes volume contraction due to interactions between ions and solvent molecules and therefore other acoustical parameters may be affected.

Such studies as a function of concentration are useful in gaining an insight into the structure and bonding of associated molecular complexes and other molecular processes. Further they play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures[9-10].

In continuation of our earlier work [11-13], in the present investigation we tried to study molecular interaction of aqueous Aspirin solution by measuring ultrasonic velocity, density and viscosity at different frequencies, different concentrations and different temperatures. The structure of aspirin is as



Acetyl salicylic acid

From the data obtained acoustic parameters such as relative association, relaxation time and free volume were calculated. Effect of concentration, temperature and frequency on molecular interactions is studied from acoustic and thermodynamic parameters.

Experimental: The chemicals used were of analytical grade. Double distilled water was used for preparation of solutions. A special thermostatic water bath arrangement was made for density, ultrasonic velocity and viscosity measurements, in which continuous stirring of water was carried out and temperature variation was maintained within ±0.01^{0}C. Multi frequency interferometer (Mittal Enterprises, Model F-83) with accuracy of ±0.03% and frequency 2 MHz, 4MHz, 6MHz were used in the present work for measurement of ultrasonic velocities of solutions. Densities of solutions were measured using specific gravity bottle. These values were accurate up to ± 0.1 kg/m^3. All the weighing was made on CA-124 (CB/CA/CT series, Contech) digital electronic balance having an accuracy of ± 0.0001g. Viscosities of the solution were measured by Ostwald's viscometer.

RESULT AND DISCUSSION

From the observed values relative association, free volume, acoustic relaxation time was calculated.

Relative association is a function of ultrasonic velocity and is calculated by the equation,

$$R_A = \frac{d_s}{d_0}\left(\frac{v_0}{v_s}\right)^{1/3} \qquad \text{........(1)}$$

Where, v_0 and v_s are ultrasonic velocities in solvent and solution respectively

$$\tau = 4/3\ \beta\eta \qquad \text{.......(2)}$$

Free volume is calculated by following equation

$$V_f = [M_{eff}v/K\ \eta]^{3/2} \qquad \text{....... (3)}$$

Where, M_{eff} is effective molecular weight, K is a temperature independent constant which is equal to 4.28 x 10^9 for all liquids.

With increasing frequency ultrasonic velocity increases. But with increasing concentration and temperature it shows non linearity. At 2MHz and at 303.15K ultrasonic velocity increases while at 4MHz for 0.1M it decreases and at 6MHz ultrasonic velocity decreases with increasing concentration and temperature. The increase in concentration weakens the molecular forces and hence change in velocity is observed.

From table1 it is observed that the values of viscosity increase with increasing concentration of aspirin in aqueous solution. This increasing trend indicates the existence of molecular interaction occurring in these systems. As the temperature of the liquid fluid increases its viscosity decreases. In the liquids the cohesive forces between the molecules predominates the molecular momentum transfer between the molecules, mainly because the molecules are closely packed[14].

Table 1: Acoustic and thermodynamic parameters of aspirin at 2MHZ

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity ηx10^{-3} (NSm^{-2})	Relative association R_A	Relaxation time x10^{-10} (S)	Free volume $V_{f x10^{-8}}$ (m^3/mole)
303.15	0.001	1475.75	1020.74	0.8652	1.032	5.189	1.244
	0.01	1529.17	1022.17	0.8967	1.0195	5.00	1.39
	0.1	1564.86	1024.98	0.9209	1.0145	4.892	1.528
308.15	0.001	1493.38	1019.73	0.7499	1.0326	4.39	1.021
	0.01	1530.66	1020.07	0.7746	1.0255	4.32	1.12
	0.1	1527.23	1022.67	0.8134	1.0289	4.54	1.22
313.15	0.001	1526.21	1017.02	0.6970	1.0258	3.923	0.9462
	0.01	1563.78	1019.67	0.7310	1.020	3.91	1.06
	0.1	1528.47	1021.87	0.7647	1.0305	4.27	1.11

Table 2: Acoustic and thermodynamic parameters of aspirin at 4MHZ

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity ηx10^{-3} (NSm^{-2})	Relative association R_A	Relaxation time x10^{-10} (S)	Free volume $V_{f x10^{-8}}$ (m^3/mole)
303.15	0.001	1669.58	1020.74	0.8652	1.025	4.054	1.49
	0.01	1678.29	1022.17	0.8967	1.0121	4.15	1.60
	0.1	1673.00	1024.98	0.9209	1.0160	4.28	1.68
308.15	0.001	1679.29	1019.73	0.7499	1.0252	3.477	1.217
	0.01	1670.45	1020.07	0.7746	1.0274	3.63	1.27
	0.1	1676.98	1022.67	0.8134	1.0287	3.77	1.407
313.15	0.001	1677.38	1017.02	0.6970	1.026	3.24	1.09
	0.01	1666.93	1019.67	0.7310	1.0312	3.44	1.16
	0.1	1673.92	1021.87	0.7647	1.0320	3.561	1.27

Table 3: Acoustic and thermodynamic parameters of aspirin at 6MHZ

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity ηx10^{-3} (NSm^{-2})	Relative association R_A	Relaxation time x10^{-10} (S)	Free volume $V_{f x10^{-8}}$ (m^3/mole)
303.15	0.001	1753.2	1020.74	0.8652	1.0034	3.677	1.611
	0.01	1749.31	1022.17	0.8967	1.0056	3.82	1.70
	0.1	1744.80	1024.98	0.9209	1.0092	3.935	1.79
308.15	0.001	1744.71	1019.73	0.7499	1.0263	3.221	1.289
	0.01	1742.22	1020.07	0.7746	1.02741	3.34	1.36
	0.1	1740.24	1022.67	0.8134	1.0302	3.50	1.48
313.15	0.001	1746.63	1017.02	0.6970	1.0257	2.995	1.15
	0.01	1740.82	1019.67	0.7310	1.0295	3.15	1.24
	0.1	1738.01	1021.87	0.7647	1.0323	3.30	1.35

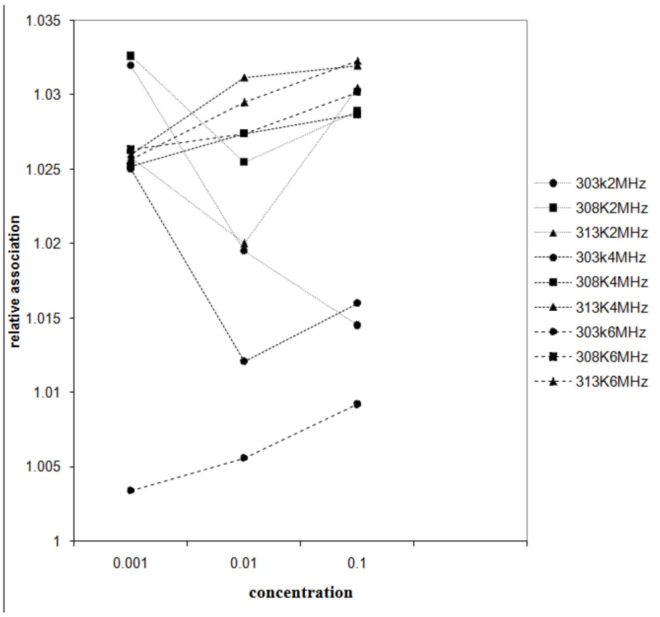


Fig. 1: variation of relative association with concentration, temperature and frequencies.

Relative association is a parameter used to assess the association in any solution relative to the association existing in water at 0°C. The addition of small quantities of strong structure breakers of water generally seems to increase the cohesion among the molecules by breaking the open structure. Fig.1 shows variation of relative association with concentration, temperature and frequency. In the present study, R_A increases with concentration and temperature at 6MHz. At 4MHz relative association decreases at 303.15 for 0.01M solution and at 308.15K, 313.15K it increases. The increase of R_A with Concentration suggests that salvation of solute predominates over the breaking up of the solvent aggregates, resulting in increased salvation of solute by free solvent molecule and thereby increase in R_A with increase in temperature. The value of R_A increases with increase in solute concentration showing significant ion-solvent interactions. At 2MHz it shows non linearity.

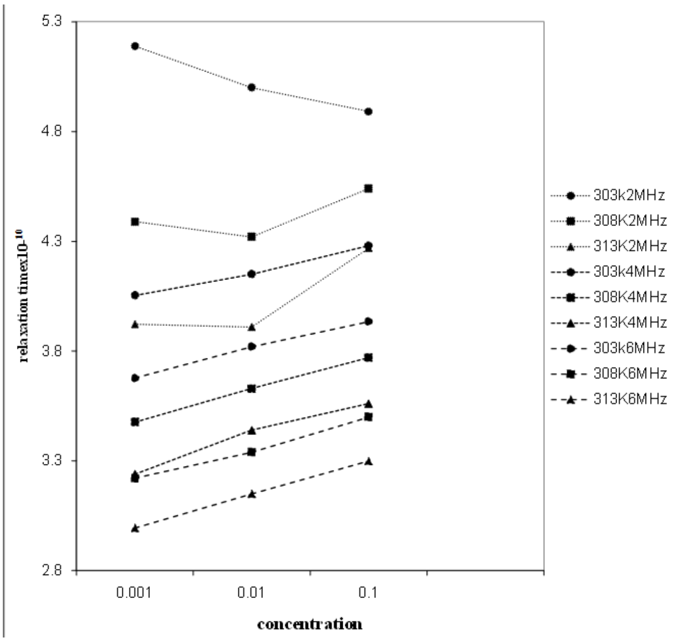


Fig. 2: variation of relaxation time with concentration, temperature and frequencies.

Fig.2 shows variation of relaxation time with concentration, temperature and frequency. Acoustic relaxation time decreases with increasing frequency. At 2MHz, 303.15K with increasing concentration relaxation time decreases. But at 308.15K, 313.15K relaxation time decreases for 0.01M and then increases. At 4MHz, 6MHz with increasing temperature relaxation time decreases and increases with increasing concentration. The dispersion of ultrasonic waves in system contains information about the characteristic time of relaxation process that causes the dispersion[15]. Increase in relaxation time indicates that degree of cooperation for relaxation of the molecules increases which increases the bulk of cluster when solute is added to solvent.

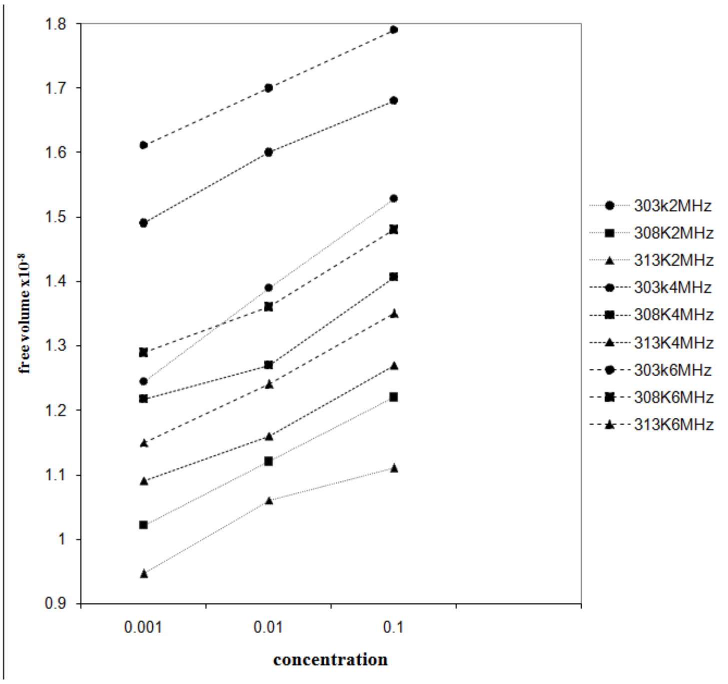


Fig. 3: variation of free volume with concentration, temperature and frequencies

Fig.3 shows variation of free volume with concentration, temperature and frequency. Free volume increases with increasing concentration and decreases with rise in temperature. Same trend was observed by M.Thirunavukkarasu [16]. When aspirin is added in water it breaks up cluster of water molecule releasing several dipoles which in turn gives less voids available in the solution resulting dipole-dipole interaction and hence free volume increases. The loan pair of electrons in carboxylic group in aspirin interacts with hydrogen of water which increases the free volume. Thus aspirin acts as structure breaker for water molecules. It enhances structure breaking property of the solvent. Increase in free volume shows enhancement in disorder in the liquid because of increase mobility of the molecules[17].

REFERENCES

1. Kagathara V.M., Sanariya M.R., Parsania P.H., Sound velocity and molecular interaction Studies on chloro epoxy resins solutions at 30°C European Polymer Journal, 2000; 36, 2371-2374.
2. Ramteke A. and Narwade M. L., Studies in acoustical properties of chloro substituted Pyrazoles in different concentration and different percentages in dioxane–water mixture, Scholars Research Library Archives of Applied Science Research, 2012; 4(1), 254-261.
3. Nand Daya, Singh DR. Vijay, studies of the thermodynamic properties of the mixture of Isomeric butyl alcohol & water**,** International Journal of Chemistry Research, 2011; 2(4), 4-7
4. Askar Ali S. J., J. Chem. Pharm. Res., Effect of temperature on the molecular dynamics ofSome binary mixtures by ultrasonic method, 2012; 4(1), 617-632.
5. Kannappan A. N. Thirumaran S. And Palani R., Volumetric and thermodynamic studies of Molecular interactions in ternary liquid mixtures at 303, 308 and 313K, Journal of Physical Science, 2009; 20(2), 97–108.
6. Patil1 P. P., Patil S. R, Borse A. U. and Hundiwale D. G., Density, excess molar volume and Apparent molar volume of binary liquid mixtures, Rasayan J. Chem., 2011; 4(3), 599-604.
7. Thirumaran S., Earnest J., Jayakumar, and Hubert Dhana Sundaram B., Molecular interaction Studies on *N*-Alkanols with DMA in Toluene at 303K, E-Journal of Chemistry, 2010; 7(2),465-472,
8. Arul G. &. Palaniappan L., Estimation of sound velocity in ternary liquid mixture of 2-Propanal in cyclohexane with toluene, J. Acoust. Soc. India*,* 2000; 28, 393–395.
9. Nikam P. S., Hasan M. & Pathak R. B., J. Pure Appl. Ultrason., Densities and speeds of sound For aniline+aliphatic alcohols (C_1–C_4) at different temperatures, 1996; 18, 19–25.
10. Thiyagarajan R., Jaafar Mohamad Suhaimi and Palaniappan L, Ultrasonic study of the self Association of aniline in ethanol-cyclohexane mixtures, Journal of Physical Science, 2007; 18(2), 81–88.
11. Aswale S.S., Aswale S. R., Tayade D. T and Raghuwanshi P. B., Intermolecular free length And apparent molar volume of bioactive α-bromo acetophenones and coumaran-3-ones in Ethanol and dioxane solvent, (2008) Proceeding of 1st International Society Bio-Technology Conference-2008, Gangtok**,** 2008, 325-330
12. Aswale S.S., Raghuwanshi P. B., Tayade D. T. And Aswale S. R., Comparative study of Intermolecular interaction by acoustic properties of α-bromo acetophenones and coumaran-3- Ones, J.Indian Chem. Soc., 2007; 84, 159-164
13. Aswale S.S., Dhote A. B., Hajare R. S., Raghuwanshi P. B. And Aswale S. R., Use of Ultrasonic to study solute-solvent interaction of Coumaran-3-ones in polar and non polar Solvents, Proceeding of Eighteen National Symposiums on Ultrasonic NSU-XVIII, Vellore, 2009, 132-138
14. http://wiki.answers.com
15. Kant Shashi, Kapil Anuradha and Sharma Kamini, Ultrasonic velocity and density Measurements of lithium Chloride in different compositions of lactose at different Temperatures, Pelagia Research Library Der Chemica Sinica, 2012; 3(3), 667-676.
16. Thirunavukkrasu M., Kanagathara N., Ultrasonic studies on non-aqueous solutions of Toluene in Carbon Tetra Chloride, International Journal of ChemTech. Research, 2012; 4(1), 459-463.
17. Chimankar Omprakash P., Shriwas Ranjeeta and Tabhane Vilas A, Intermolecular interaction Studies in some amino acids with aqueous NaOH, J. Chem. Pharm. Res., 2011; 3(3), 587-596.