



ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(3):165-168

Studies of acoustic and thermodynamic properties of Citric acid in double distilled water at different temperatures

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ABSTRACT

Ultrasonic velocity, density and viscosity have been measured for citric acid in double distilled water at 298.15K, 303.15K, 308.15K, 313.15K and 318.15K. Thermodynamic parameters such as adiabatic compressibility (β), acoustic impedance (z), intermolecular free length (L_f) and Relative association number (R_A) have been obtained from the experimental data for all the solutions of citric acid with various concentrations and temperatures, with a view to investigate the exact nature of the molecular interaction. Adiabatic compressibility and intermolecular free length decreases with increase in concentration and temperature and gradually increases with concentration of solutes. These parameters have further used to interpret the hydrophilic part of the solute and molecular interactions in the solutions.

Key words: Acoustic, thermodynamic parameters, citric acid, molecular interaction, hydrophilic.

INTRODUCTION

The ultrasonic velocity (u), density (ρ) and viscosity (η) can be used to study the physico-chemical behavior and molecular interactions such as ion-solvent interaction and solvent-solvent in pure liquids, liquid mixtures and solutions^[1-3]. The nature and degree of molecular interactions in different solutions changes depending upon the nature of solvent, the structure of solute molecule and extent of solution taking place in the solution^[4-5].

Acoustical impedance (z), adiabatic compressibility (β), intermolecular free length (L_f), relative association (R_A) are function of ultrasonic velocity. As these parameters throw more light on ion-ion and ion-solvent interactions, an ultrasonic and thermodynamic study of Citric Acid^[6-8]. Citric acid is a triadic, environmentally acceptable, and versatile chemical. As it occurs in metabolism of almost all living things, its interactions in an aqueous solution is of great value to

the biological scientists. Citric acid can be used as cleaning agent and acts as antioxidant . It has wide applications in medicine and industry.

EXPERIMENTAL SECTION

Citric acid (99.8%), of AR grade, obtained from Fine Chem. Industries, Mumbai was kept in a desecrator containing CaCl_2 for 24 hrs After desiccation it is mixed in double distilled water with changing concentration by weight 1- 5% .The prepared solutions was used within 12 hrs.

Table-1: Ultrasonic velocities, densities, adiabatic compressibility's, acoustic impedances, free lengths, relative association numbers of Citric acid in double distilled water at 2MHz at 303.15K
Double distilled Water +Citric acid

m	u	ρ	η	$\beta \times 10^{-10}$	$z \times 10^6$	L_f	R_A
mol kg ⁻¹	ms ⁻¹	kgm ⁻³	Nm ⁻² s	m ² N ⁻¹	Nm ⁻²	A ⁰	
0.0000	1502.28	1000.0	8.91	4.4310	1.5020	0.4329	1.0000
0.0521	1470.77	1011.6	10.28	4.5698	1.5085	0.4396	1.0188
0.1040	1481.53	1020.7	10.98	4.4635	1.5188	0.4345	1.0255
0.1580	1508.06	1021.0	10.11	4.3064	1.5403	0.4268	1.0201
0.2080	1528.10	1025.0	10.40	4.1780	1.5660	0.4203	1.0190
0.2600	1533.09	1033.4	10.30	4.1168	1.5698	0.4173	1.0264

Table-2: Ultrasonic velocities, densities, adiabatic compressibility's, acoustic impedances, free lengths, relative association numbers of Citric acid in double distilled water at 2MHz at 308.15K
Double distilled Water +Citric acid

m	u	ρ	η	$\beta \times 10^{-10}$	$z \times 10^6$	L_f	R_A
mol kg ⁻¹	ms ⁻¹	kgm ⁻³	Nm ⁻² s	m ² N ⁻¹	Nm ⁻²	A ⁰	
0.0000	1511.76	1000.0	8.91	4.3756	1.4787	0.4302	1.0000
0.0521	1509.00	1010.4	11.0194	4.3275	1.4983	0.4287	1.0111
0.1040	1527.62	1020.5	10.3247	4.2243	1.5267	0.4214	1.0170
0.1580	1548.02	1021.2	10.8441	4.1186	1.5433	0.4157	1.0131
0.2080	1556.00	1022.4	10.7983	4.0797	1.5585	0.4133	1.0126
0.2600	1558.96	1032.6	10.2934	4.0649	1.6022	0.4027	1.0221

Table-3: Ultrasonic velocities, densities, adiabatic compressibility's, acoustic impedances, free lengths, relative association numbers of Citric acid in double distilled water at 2MHz at 313.15K
Double distilled Water +Citric acid

m	u	ρ	η	$\beta \times 10^{-10}$	$z \times 10^6$	L_f	R_A
mol kg ⁻¹	ms ⁻¹	kgm ⁻³	Nm ⁻² s	m ² N ⁻¹	Nm ⁻²	A ⁰	
0.0000	1516.72	1000.0	8.91	4.3470	1.5167	0.4288	1.0000
0.0521	1563.28	1008.0	11.0194	4.0594	1.5757	0.4309	0.9980
0.1040	1548.00	1020.0	10.3247	4.0912	1.5789	0.4160	1.0131
0.1580	1552.62	1020.8	10.8441	4.0638	1.5849	0.4146	1.0129
0.2080	1556.35	1021.8	10.7983	4.0403	1.5996	0.4134	1.0131
0.2600	1564.00	1032.5	10.2934	3.9559	1.6148	0.4092	1.0220

The ultrasonic velocities in pure solvent as well as in mixed solutions were measured using multi frequency ultrasonic interferometer (Model-F-81, supplied by M/s Mittal Enterprises, New Delhi) at a constant frequency 2 MHz .The temperature of the solutions placed in the interferometer cell was changed through 5⁰C (from 298.15K to 318.15K)by circulating water around the cell from a thermostat. The viscosity of the solutions at different temperatures and concentrations were measured with Ostwald's viscometer apparatus.

The density measurements were made by a 25 ml specific gravity bottle, the accuracy in density measurements was found to be $\pm 0.001\text{g/cc}$. All the weighing were made on digital balance with an accuracy of $\pm 1 \times 10^{-5}\text{kg}$.

Table-4: Ultrasonic velocities, densities, adiabatic compressibility's, acoustic impedances, free lengths, relative association numbers of Citric acid in double distilled water at 2MHz at 318.15K
Double distilled Water +Citric acid

m	u	ρ	η	$\beta \times 10^{-10}$	$z \times 10^6$	L_f	R_A
mol kg ⁻¹	ms ⁻¹	kgm ⁻³	Nm ⁻² s	m ² N ⁻¹	Nm ⁻²	A ⁰	
0.0000	1524.05	1000.0	8.91	4.3053	1.5240	0.4268	1.0000
0.0521	1599.92	1006.0	10.61	3.8833	1.6095	0.4052	0.9898
0.1040	1554.32	1019.0	10.54	4.0589	1.5838	0.4052	1.0124
0.1580	1553.20	1020.6	12.02	4.0615	1.5851	0.4144	1.0141
0.2080	1568.29	1021.0	0.966	3.9821	1.6012	0.4103	1.0113
0.2600	1573.30	1032.1	0.9558	3.9143	1.6238	0.4068	1.0212

RESULTS AND DISCUSSION

Various acoustic and thermodynamic parameters used in the present study are computed^[13] using following relations

Adiabatic compressibility (β) is calculated by the relation

$$\beta = 1/u^2 \rho \quad \text{m}^2\text{N}^{-1} \quad \dots\dots (1)$$

where u and ρ are ultrasonic velocity and density of aqueous solution of citric acid

Acoustic Impedance (z) is calculated by using formula

$$z = \rho u \quad \text{kg m}^{-1}\text{s}^{-1} \quad \dots\dots (2)$$

Intermolecular free length (L_f) is obtained using formula

$$L_f = k\beta^{1/2} \quad \text{A}^0 \quad \dots\dots (3)$$

where k is Jacobson's temperature dependent constant

temp 303 308 313 318K

$k \times 10^4$ 6.31 6.36 6.42 6.47

Relative association (R_A) is obtained using the relation

$$R_A = (\rho_0/\rho) \times (u_0/u)^{1/2} \quad \dots\dots(4)$$

From the tables 1-4 we observe the trends of all acoustical parameters with variation in concentration and temperature..The ultrasonic velocity increases with molal concentration of solute as well as rise in temperature. This increase in ultrasonic velocity in the aqueous solution of citric acid may be attributed to the cohesion brought by the ionic hydration .The increase in density with molal concentration suggest a solute-solvent interaction exist between the citric acid and water .In other words the increase in density may be interpreted to the structure maker of the solvent due to H-bonding^[9-10].The viscosity is an important parameter in understanding the

structure as well as molecular interaction occurring in the solutions. From above tables, values of viscosities increase with concentration but decreases with temperature. These variations attributed to structural changes^[11]. The values of adiabatic compressibility (β) show decreasing trend with concentration as well as temperature which suggest the making and breaking of H-bonding. The intermolecular free length depends upon the intermolecular attractive and repulsive forces. Eyring and Kincaid^[12] have proposed that L_f is a predominating factor in determining the variation of ultrasonic velocity of solution. The values of intermolecular free length listed in the tables shows decreasing trend with concentration and temperature Hence it can be concluded that there is significant interaction between solute and solvent molecules due to which the structural arrangement is also affected. Thus it is clear from the above parameters that there is a strong association between water and citric acid molecules showing hydrophilic nature.

CONCLUSION

a strong intermolecular H-bonding interaction exist between citric acid and water. From the acoustical parameters it is concluded that H-bonding interaction is very strong at higher temperature and concentration.

Acknowledgement

One of the authors is thankful to the Head of the Dep't of Physics, Dr. BAMU, Aurangabad for providing necessary facilities, prof Dr .K.M .Jadhav and shri .S.R. Kanhekar for helpful discussion. One of the authors (A.P.T.) is thankful to Principal, YMA, Ambajogai for encouraging the work.

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