Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 2(3), 2012, 532-539
ISSN 2277-2669

ULTRASONIC STUDIES ON INTERACTION OF BENZOIC ACID, SALICYLIC ACID AND 4-HYDROXY BENZOIC ACID IN WATER-DIOXANE AND WATER-DMF MIXTURES AT 303.15 K

S. S. DHOK[a], V. B. KHOBRAGADE[b], P. D. SAWALAKHE[*] and M. L. NARWADE

Prof. Ram Meghe Institute of Technology & Research, BADNERA (M.S.) INDIA
Department of Chemistry, Vidyabharati Mahavidyalaya, AMRAVATI (M.S.) INDIA

(*Received : 17.02.2012; Revised : 14.03.2012; Accepted : 23.03.2012*)

ABSTRACT

The ultrasonic velocity and density of aromatic acids-Benzoic acid, salicylic acid and 4-hydroxy benzoic acid in different compositions of dioxane-water and DMF-water have been studied at 303.15K. The data obtained were used to evaluate adiabatic compressibility, apparent molar compressibility (ϕ_k), apparent molar volume, (ϕ_v), intermolecular free length, specific acoustic impendence and relative association. These data were utilized in the establishment of solute-solvent interactions under prevailing conditions. The data supports strong solute solvent interaction in the order of Salicylic acid >4-hydroxy benzoic acid >Benzoic acid in both Dioxane-water and DMF-water systems.

Key words: Salicylic acid, 4-Hydroxy benzoic acid, Benzoic acid, Dioxane-Water mixture, DMF-Water mixture, Ultrasonic study.

INTRODUCTION

Knowledge of thermo acoustic properties is of great significance in understanding the physicochemical behavior and molecular arrangement in various liquid mixtures and solution. A large number of studies were carried out in the past few decades on ultrasonic velocity in the binary and ternary liquid mixtures. Still it exits as a potential tool in investigating the physical and chemical behavior and in evaluating the intermolecular interactions in liquid mixtures namely dipole-dipole, polar-nonpolar and hydrogen bonding.

Thermoadynamics and transport properties of liquid systems have been extensively used to study the departure of the real liquid system from ideality. A departure from the linear behavior of velocity as a function of concentration in the liquid system is an indication of the existence of the interaction between different species.

In recent years, several researchers[1,2] have studied the complex formation in protic and aprotic solvents using ultrasonic velocity measurements. However the investigations regarding the interaction of

Available online at www.sadgurupublications.com
[*]Author for correspondence; E-mail: pdsawal@gmail.com, vandana2079@gmail.com, sarikadhok07@gmail.com

some aromatic acids in the different compositions of solvent is of particular interest. In this view, aromatic acids such as Benzoic acid, Salicylic acid and 4-hydroxy benzoic acid have been selected. These acids are slightly soluble in water. The solubility of benzoic acid, salicylic acid & 4-hydroxy benzoic acid is 0.29 g, 0.2 g, 0.5 g per 100 mL of water at 20^0C respectively. On contrary they are highly soluble in alcohols, Dioxane, Dimethyl-formamide etc. Narwade et al. have studied ultrasonic velocity of peptide[3], substituted acetophenones[4], substituted thiadiazoles & carboxylate[5], isoxazole and pyrazole[6] in binary liquid mixtures. Rohankar[7] has investigated the ultrasonic velocity of monochloroacetic acid and trichloroacetic acid in THF and Dioxane-water mixture. Aromatic acids also plays an important role in animal and plant physiology. Benzoic acid is the simplest aromatic carboxylate acid, widely occurring in many plants and resins.

Salicylic acid is widely used in organic synthesis and medicinal antiacne treatment, and functions as a plant hormone. 4-hydroxy benzoic acid is one of the main catechins metabolite found in human after consumption of green tea in fusion. It is also naturally present in the fruit of acai palm. Taking into consideration, the medicinal, physiological importance and their solubility in solvents, it is interesting thought to study their interactions in solvent mixtures.

In this view, the density and ultrasonic velocity of these aromatic acids have been measured in Dioxane-water and DMF-water mixtures at 303.15K. Various ultrasonic parameters are obtained from the data and used to explore the molecular interactions.

EXPERIMENTAL

Materials and methods

The solvent was purified by standard procedure[8]. Solution of different concentration were prepared by dissolving known weight of substances. The different compositions of water with Dioxane and DMF by masses were obtained. The chemicals Salicylic acid, 4-hydroxy benzoic acid, Benzoic acid with a reported purity of 99.8% (AR Grade) on mole basis was used without further purification. The other chemical solvents were distilled just before use. The purity of these chemicals have been verified by measuring their densities and speed of sound and comparing these values with the literature at 303.15 K. Good agreement between measured and literature[8] values is observed. Mixtures were prepared by mixing the appropriate volumes in specially designed glass stoppered bottles. The masses were recorded on a digital electronics balance (Contech make Electronic Balance) with accuracy ± 0.0001 g. Care was taken to avoid the evaporation of the solvent from the mixtures.

The density of various systems at 303.15 K has been measured using density bottle (10 mL capacity, borosil make). The ultrasonic velocity of mixtures was measured using a ultrasonic interferrometer supplied by mittal enterprises New Delhi (Research model F-81) with an accuracy of ± 0.01% and frequency 4 MH_Z. The instrument was calibrated by measuring the velocity of double distilled water. The temperature of all the systems was controlled by circulating water around the liquid cell from thermostatically controlled water bath. The densities of distiled water, Dioxane and DMF are in good agreement with the literature[8].

RESULTS AND DISCUSSION

The values of different thermodynamic parameters such as adiabatic compressibility (Φ_k), apparent molar volume (Φ_v), intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A) have been calculated at 303.15 K using ultrasonic velocity (U) and density (ρ) of different compositions with the help of equations[9,10].

The apparent molar compressibility (Φ_k) and apparent molal volume have been calculated by using Eqns. (1) and (2)[11].

$$\Phi_k = \frac{1000\,(\beta_s\rho_o - \beta_o\rho_s)}{m\rho_s\rho_o} + \frac{\beta_s M}{d_s} \qquad \ldots(1)$$

$$\Phi_v = \frac{1000\,(\rho_o - \rho_s)}{m\rho_s\rho_o} + \frac{M}{\rho_s} \qquad \ldots(2)$$

where, ρ_o and ρ_s represent densities of solvent and solution respectively, m is the molarity, M is the molecular weight of solute, β_s and β_0 are the adiabatic compressibilities of solution and solvent respectively. Specific acoustic impedance (Z), relative association (R_A) and free length (L_f) are the function of ultrasonic velocity and are computed by Eqns. (3)-(5)[12].

$$Z = U_s\,\rho_s \qquad \ldots(3)$$

$$R_A = \rho_s/\rho_o\,[(U_o/U_s)]^{(1/3)} \qquad \ldots(4)$$

$$L_f = K\sqrt{\beta_s} \qquad \ldots(5)$$

where, U_0 and U_s are velocity of ultrasonic wave in solvent and solution and K is Jacobson's constant.

Table 1, Table 2 & Table 3 shows the values of ρ_s, β_s, Φ_k, Φ_v, Z, L_f and R_A obtained in present investigation at different concentration for Salicylic acid, 4-hydraoxy benzoic acid, Benzoic acid respectively.

Table 1: Ultrasonic velocity and related parameters of salicylic acid in dioxane-water and DMF-water mixture at 303.15 K

X wt. fract.	ρ g/cm^3	U_S x 10^3 cm/sec	β_s x 10^{-12} cm^2/dyne	Φ_k x 10^{-9}cm^2/ dyne. mol	Φ_v cm^3 mol^{-1}	Z x 10^3 g/s.cm^2	L_f x 10^{-6} ^{0}A	R_A
Dioxane- water system								
Dioxane	ρ_0 = 1.032	U_0 = 1376	β_0 = 0.51178					
0.01	1.02573	1523.2	0.4201	-8.5783	726.8561	1562.39	4.0898	0.9607
0.02	1.02709	1561.6	0.3992	-5.3083	365.9733	1603.90	3.9868	0.9541
0.03	1.02775	1578.4	0.3905	-3.8127	267.8413	1622.20	3.9431	0.9513
0.04	1.02864	1594.4	0.3824	-3.0526	266.0395	1640.06	3.9031	0.9489
0.05	1.02994	1540.8	0.4089	-1.9231	172.7503	1586.93	4.0349	0.9610
0.06	1.03060	1561.6	0.3978	-1.7787	155.761	1609.39	3.9798	0.9574
0.07	1.03224	1504	0.4282	-1.1011	130.4713	1552.48	4.1290	0.9710
0.08	1.03313	1414.4	0.4838	-0.2806	120.3265	1461.25	4.3889	0.9919
0.09	1.03443	1356.8	0.5251	0.06007	108.1148	1403.51	4.5724	1.0070
0.10	1.0352	1379.2	0.5078	0.0139	103.3541	1427.74	4.4965	1.0023

Cont…

X wt. fract.	ρ g/cm^3	U_S x 10^3 cm/sec	β_s x 10^{-12} cm^2/dyne	Φ_k x 10^{-9}cm^2/ dyne. mol	Φ_v cm^3 mol^{-1}	Z x 10^3 g/s.cm^2	L_f x 10^{-6} ^{0}A	R_A

			DMF-water system					
DMF	ρ_0 = 0.9322	U_0 = 1496	β_0 0.4793					
0.01	0.9906	1576	0.4814	-2.7524	-2933.26	1513.90	4.3780	1.0443
0.02	0.9996	1592	0.3947	-5.9106	-3479.76	1591.90	3.9642	1.0502
0.03	0.9985	1640	0.3723	-4.6437	-2236.43	1637.54	3.8501	1.0388
0.04	0.9948	1660	0.3595	-3.7678	-1549.06	1663.30	3.7837	1.0307
0.05	0.9949	1660	0.3595	-3.0056	-1213.45	1663.47	3.7835	1.0308
0.06	0.9830	1672	0.3638	-2.3500	-783.568	1643.57	3.8059	1.0161
0.07	0.9911	1664	0.3643	-2.0433	-771.49	1649.19	3.8085	1.0261
0.08	0.9769	1608	0.3958	-1.21495	-472.30	1570.85	3.9697	1.0230
0.09	0.9608	1544	0.4365	-0.46031	-211.16	1483.47	4.1689	1.0198
0.10	0.9465	1488	0.4771	-0.03136	-16.2710	1408.39	4.3584	1.0171

Table 2: Ultrasonic velocity and related parameters of 4 -hydroxy benzoic Acid in Dioxane-water and DMF- water mixture at 303.15 K

X wt. fract.	ρ g/cm^3	U_S x 10^3 cm/sec	β_sx10^{-12} cm^2/dyne	Φ_k x10^{-9} cm^2/dyne.mol	Φ_v cm^3 mol^{-1}	Z x 10^3 g/s.cm^2	L_f x 10^{-6} ^{0}A	R_A
			Dioxane- water system					
0.01	1.0369	1558.4	0.3937	-11.5696	-324.704	1615.60	3.9592	0.9639
0.02	1.0470	1558.6	0.3931	-5.9710	-562.200	1631.89	3.9556	0.9732
0.03	1.0576	1581.28	0.3781	-4..5640	-651.241	1672.36	3.8800	0.9784
0.04	1.0681	1584	0.3731	-3.6167	-689.444	1691.87	3.8554	0.9875
0.05	1.0786	1562.6	0.3796	-2.83085	-709.234	1685.46	3.8876	1.0017
0.06	1.0892	1532.8	0.3907	-2.2372	-721.311	1669.52	3.9441	1.0181
0.07	1.0976	1488	0.4114	-1.6781	-701.497	1633.22	4.0472	1.0227
0.08	1.1018	1444.8	0.4347	-1.2126	-642.389	1591.93	4.1602	1.0504
0.09	1.1102	1424	0.4441	-1.01022	-634.710	1581.02	4.2050	1.0635
0.10	1.1202	1348.8	0.4906	-0.51904	-639.645	1510.92	4.4191	1.0927
			DMF-water system					
0.01	0.9494	1444	0.4418	-4.81707	-1797.94	1465.87	4.1941	1.0305
0.02	0.9937	1592	0.3970	-5.6769	-3181.74	1581.97	3.9758	1.0441
0.03	0.9969	1616	0.3841	-4.2423	-2182.95	1610.99	3.9106	1.0422
0.04	0.9939	1652	0.3668	-3.5769	-1525.90	1645.89	3.8215	1.0315
0.05	0.9910	1664	0.3644	-2.8782	-1133.62	1649.98	3.8090	1.0260

Cont…

X wt. fract.	ρ g/cm^3	U_S x 10^3 cm/sec	β_sx10^{-12} cm^2/dyne	Φ_k x10^{-9} cm^2/dyne.mol	Φ_v cm^3 mol^{-1}	Z x 10^3 g/s.cm^2	L_f x 10^{-6} ^{0}A	R_A
0.06	0.9974	1664	0.3620	-2.4701	-1030.39	1659.67	3.7965	1.0326
0.07	0.9865	1640	0.3768	-1.8358	-625.88	1617.86	3.8733	1.0263
0.08	0.9779	1600	0.3994	-1.26526	-485.57	1564.64	3.9878	1.0257

0.09	0.9672	1496	0.4205	-0.8221	-215.93	1516.56	4.0917	1.0375
0.10	0.9412	1464	0.4957	0.1978	44.153	1377.90	4.4426	1.0169

Table 3: Ultrasonic velocity and related parameters of benzoic acid in dioxane-water and DMF- water mixture at 303.15 K

X wt. fract.	ρ g/cm^3	U_S x 10^3 cm/sec	β_sx10^{-12} cm^2/dyne	Φ_k x10^{-9} cm^2/ dyne.mol	Φ_v cm^3 mol^{-1}	Z x 10^3 g/s.cm^2	L_fx 10^{-6} ^{0}A	R_A
				Dioxane- water system				
0.01	1.00723	1543.04	0.4169	-7.89925	2504.20	1554.19	4.0742	0.9214
0.02	1.01647	1573.28	0.3974	-5.1958	860.372	1599.19	3.9778	0.9419
0.03	1.02637	1573.28	0.3936	-3.6979	296.1578	1614.77	3.9587	0.9511
0.04	1.03051	1578.66	0.3893	-2.9053	165.6015	1626.84	3.9370	0.9538
0.05	1.03162	1548.92	0.4038	-2.0342	125.5155	1598.26	4.0097	0.9609
0.06	1.04006	1552.4	0.3989	-1.8401	-7.7379	1614.58	3.9853	0.9680
0.07	1.0372	1514.64	0.4202	-1.2463	48.3394	1570.98	4.0903	0.9733
0.08	1.0350	1474.64	0.4443	-0.8843	82.8819	1526.25	4.2059	0.9800
0.09	1.03322	1424	0.4772	-0.3211	130.9065	1471.30	4.3589	0.9898
0.10	1.02765	1354.4	0.5304	0.2596	118.8803	1391.48	4.5954	1.0052
				DMF-water system				
0.01	1.0053	1552	0.4127	-10.3134	-7675.03	1560.22	4.0536	1.0652
0.02	0.9983	1600	0.3906	-6.09704	-3429.14	1597.28	3.9436	1.0471
0.03	0.9974	1632	0.3764	-4.5132	-2215.32	1627.75	3.8712	1.0393
0.04	0.9964	1640	0.3731	-3.4470	-1605.42	1634.09	3.8542	1.0366
0.05	0.9944	1664	0.3631	-2.9357	-1219.44	1654.68	3.8022	1.0295
0.06	0.9890	1656	0.3687	-2.2976	-903.072	1637.78	3.8314	1.0239
0.07	0.9859	1656	0.3698	-1.9405	-710.892	1632.65	3.8371	1.0223
0.08	0.9753	1624	0.3887	-1.3965	-467.390	1583.88	3.9340	1.0179
0.09	0.9610	1576	0.4189	-0.8163	-230.134	1518.53	4.0839	1.0131
0.10	0.9431	1520	0.4589	0.2851	5.504	1433.51	4.2745	1.0063

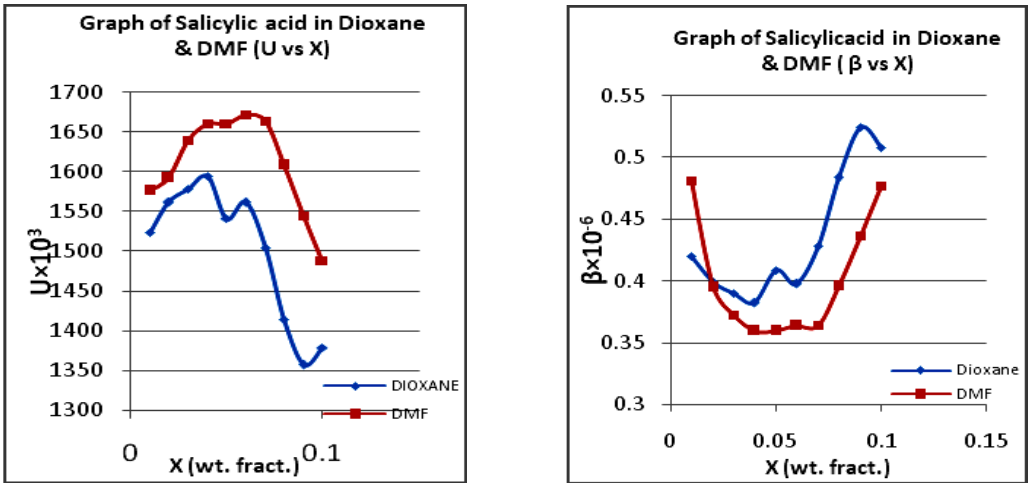
A perusal of Table 3 shows that ultrasonic velocity increases in case of Benzoic acid with the increasing content of Dioxane and then falls. However the adiabatic compressibility (β) and free length (L_f) values show an opposite trend to that of ultrasonic velocities. The variation of ultrasonic velocity in a solution depends on the intermolecular free length (L_f) on mixing. On the basis of model for a sound prorogation proposed by Eyring and Kincaid[13]. Ultrasonic velocity increases on decreasing of free length (L_f) and vice-versa. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in fluids and their solution.

In a present investigation it has been observed that intermolecular free length decreases initially and thereafter increases. The values of acoustic impedance (Z) also show the same trend of increasing or decreasing with composition. The variation of R_A values have also been supported with the increasing trend of R_A values with decreasing values of L_f. This indicates significant interaction between solute and the solvent molecule of Dioxane as well All these parameters show upper range in DMF-water system, indicating the greater extent of molecular interaction. This may be attributed to the initial breaks of the solute-solvent structure after the addition of DMF. This effect is less pronounced in the case of Dioxane which may be attributed to the presence of donor nitrogen in DMF and hence more affinity of solute with solvent.

Furthermore, these parameters show the maxima or minima at 0.04 M concentration in Dioxane-water composition. In the case of DMF-water composition the maxima or minima observed at slightly higher concentration range that is around 0.06 M. This indicates the formation of complex at maxima or minima due to maximum molecular interaction and the structure making by hydrogen bonding[15].

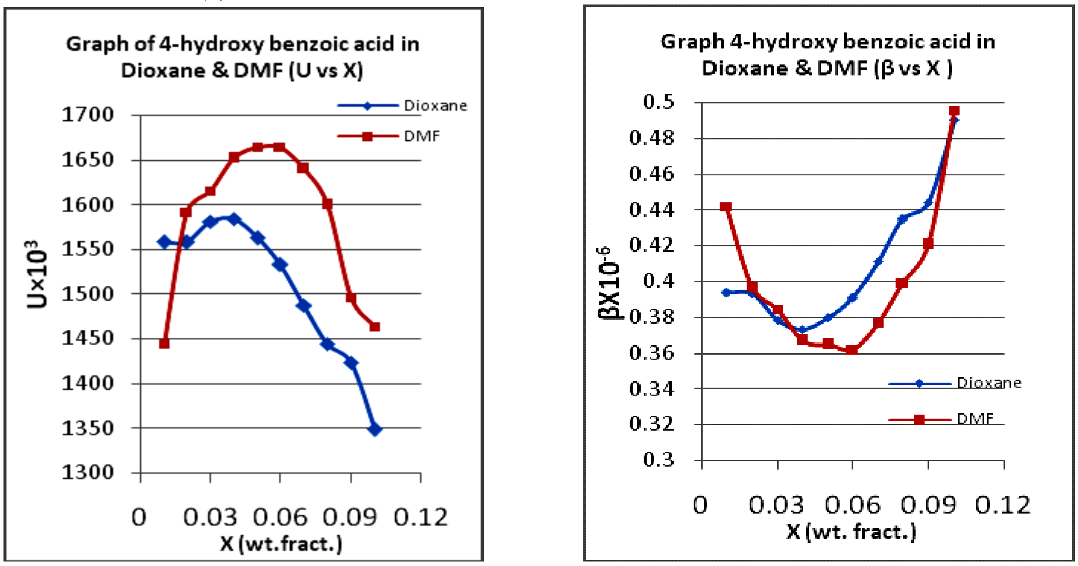
In the comparison with present aromatic acids it has been observed from Table 1-3 that the values of ultrasonic velocities and other parameters increased or decreased respectively in the order of Salicylic acid, 4-hydroxy benzoic acids and Benzoic acid at maxima or minima. Among these aromatic acids the higher values of ultrasonic velocity in the case of Salicylic acid indicates strong molecular interaction between solute and Dioxane or DMF .It may be attributed to the self association of Salicylic acid molecules due to intramolecular hydrogen bonding .It has also been supported by the fact that the interactions are weak in the case of 4-hydroxy benzoic acid and Benzoic acid , whose structure shows intermolecular association and hence lower complexation with the added solvent.

The values of Φ_k becomes more and more negative while apparent molar volume(Φ_v) decreases with the molar concentration of the solvent which indicates the strong solute-solvent interactions.



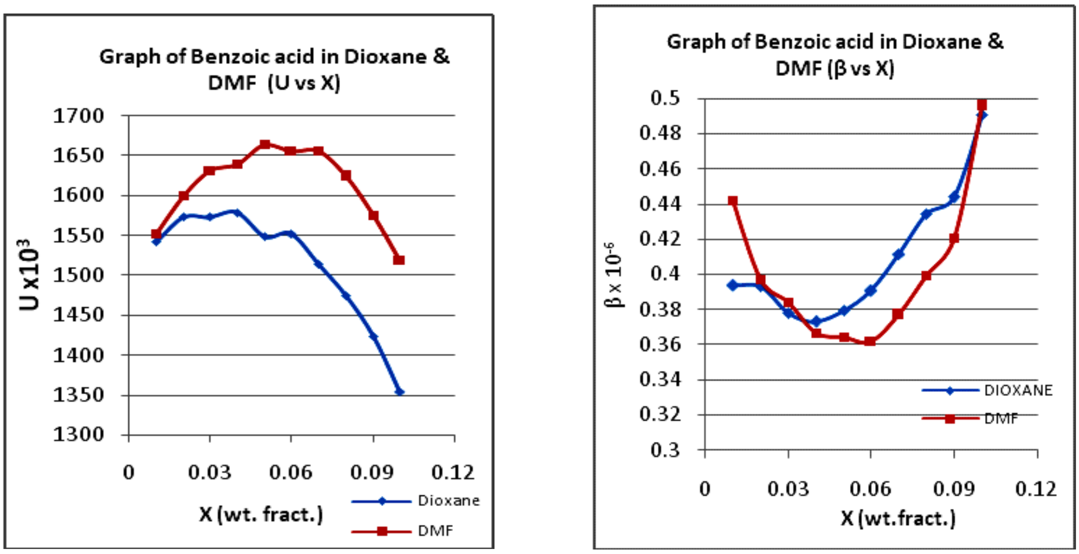
(a) (b)

Fig. 1(a) & 1(b): Graph of salicylic acid in dioxane and DMF showing variation of ultrasonic velocity U_s and adiabatic compressibilities β_s of solution with concentration



(a) (b)

Fig 2(a) & 2(b): Graph of 4-hydroxy benzoic acid in Dioxane and DMF showing variation of ultrasonic velocity U_s and adiabatic compressibilities β_s of solution with concentration



(a) (b)

Fig. 3(a) & 3(b): Graph of Benzoic acid in Dioxane and DMF showing variation of ultrasonic velocity U_s and adiabatic compressibilities β_s of solution with concentration

CONCLUSION

The variation in the derived ultrasonic parameters supports the strong solute- solvent interaction on addition of the solvent DMF or Dioxane in the aqueous solution of benzoic acid, salicylic acid and 4-hydroxy benzoic acid. The maximum intraction have been observed at the molar concentration 0.04 which suggests the complexation at velocity maxima or adiabatic compressibility minima by the formation of hydrogen bonds between the solute and the added solvent. In case of salicylic acid maximum interaction have been observed. It may be attributed to its self association due to intramolecular hydrogen bonding in aqueous solution and structure breaking on addition of the solvent.

ACKNOWLEDGEMENT

The authors are very thankful to the Dr. V.T. Ingole, Principal, Prof. Ram Meghe Institute of Technology & Research, Badnera and Dr. S. S. Sonare, Head of First Year Engineering Sciences, PRMIT & R, Badnera, for providing necessary facilities.

REFERENCES

1. S. S. Kor and S. S. Batti, J. Pure Appl. Phys., **7**, 784 (1968).
2. S. V. Soitkar and S. N. Jajoo, Acoustic Lett., **7**, 191 (1984).
3. P. J. Sondawale and M. L. Narwade, Ultra Science, **11(2)**, 162 (1999).
4. P. B. Agrawal, Acta Ciencia India, XXIXC1, 5 (2003).
5. P. B. Agrawal, Mohd. Idress Mohd Siddique and M. L. Narwade, Indian J. Chem., **42A**, 1050 (2003).
6. Ikhe, Rajput and M. L. Narwade, Indian J. Chem., **44A**, 2495 (2005).
7. P. G. Rohankar, Indian J. Chem., **40A**, 860 (2001).
8. A. I. Vogel, Quantitative Organic Chemistry, ELBS, London (1959).
9. R. Bhat, J. C. Ahluwalia, J. Phy. Che., **89**, 1099 (1985).
10. G. R. Hedwig, H. Hociland, Biophysics.chem., **49**, 175 (1994).
11. J. O. M Bockris and A. K. N. Reddy, Modern Electrochemistry, Vol. I, Plenum, Roselta, New York (1970).
12. V. J. Rajendran, Pure Appl. Ultrason., **17**, 65 (1995).
13. B. Eyring, J. F. Kincaid, J. Chem. Phys., **6**, 620 (1938).
14. A. Ali and Anilkumar Nain, Ind. J. Pure Applied Phys., **421** (2001).