Ultrasonic studies of dicarboxylic acids in diferent compositions of Dioxane-Water

M.P. RAUT*, S.T. MHASKE, N.Y, BHAMBHURKAR and A.R. RAUT*

Department of Chemistry, Government Vidarbha Institute of Science and Humanities Amravati (India)

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ABSTRACT

Acoustic properties like partial molal volume (ϕ) apparent molal Compressibility($\phi_{k(s)}$), adiabatic compressibility(β_s), intermolecular freee path length (L_1), specific acoustic impendence (Z) and relative association(R_A) have been evaluated by studying ultrasonic velocities and densities of dicarboxylic acid ltaconic acid. Malonic acid, Maleic acid and Succinic acid in different percentage of dioxane-water mixture of 0.001 molal concentration of dicarboxylic acids at 303K. Results obtained suggests that solute-solute interacations increases in percentage of dioxane. The results have been interpreted in terms of lon-lon and lon-solvent interactions in solutions.

Key words: Ultrasonic studies, dicarboxylic acids, dioxane-water.

INTRODUCTION

In order to gain insight to the behaviour of solute molecule in solvent, it is very necessary to study the properties of liquids and solution¹⁻² which depends upon the volume of electrolyte. Dependence of viscosity on concentration of solute and varying percentage of solvent mixtures is used as function of studying ion-ion or ion-solvent interactions³⁻⁴.

Some dicarboxyilc are used in present investigation in the view of studying their behaviour and interactions involved with solvent. The investigations are carried out to infers the solution behaviour of these dicarboxyilc.

EXPERIMENTAL

All compounds were of high purity (Merck), dioxane is purified by standard method⁵ and different percentage compositions are prepared by adding double distilled water. Pure Itaconic acid (ITC), Malonic acid (MAL), Maleic acid (MIA), Succinic acid (SUC) (BDH) were used and solutions are prepared in double distilled water and different dioxance compositions. Oswald-Sprengel type pycknometer is used. It is calibrated at this temperature 25°C by using double distilled water. The pycknometer with the test solutions was immersed in water bath maintained at desired tempereature with ± 0.01 accuracy. The readings are taken in triplicate and the average of three is used in calculations. The sound velocity were measured differentially by using single crystal variable path ultrasonic interferometer (Mittal Enterprises, India) working at 4 MHz. The temperature stability was maintained by circulating thermostated water around the cell by using constant temperature bath with constancy of temperature ± 0.1 K.

RESULTS AND DISCUSSIONS

The apparent molal volume has been calculated by using equations

$$\phi_{s} = [1000(d_{0}-d_{s})]/m.d_{0}.d_{s}+M/d_{s}$$

Percentage Dioxance-water	d(gcm ⁻¹)	U ₀ ×10³ ms ⁻¹	β _s ×10⁵ (bar⁻¹)	L _r ×10²	φ _γ cm³ mol⁻¹	φ _{k(s)} cm⁻³ mol⁻¹bar⁻¹	R _A	Z×10 ⁻⁴ g ⁻³ ms ⁻¹
			Itaconic	acid (ITC)				
100	0.8960	1.221	5.8484	4.2105	328.6702	0.0598	1.023	0.1588
90	0.8923	1.242	5.6222	4.0010	330.50	0.0311	1.028	0.1549
80	0.8726	1.289	5.4120	3.9820	332.7999	0.0328	1.079	0.1563
70	0.8703	1.321	4.8200	3.8120	336.8240	-0.0286	0.991	0.1981
60	0.8683	1.418	4.6100	3.7220	340.2550	-0.3110	0.9620	0.1601
			Malonic	acid (MAL)				
100	0.8920	1.320	5.8210	4.3800	412.8702	0.0520	1.0338	0.1630
90	0.8876	1.354	5.7990	4.3759	418.7102	0.0498	1.0128	0.1648
80	0.8822	1.398	5.7550	4.2990	415.6610	0.0320	0.9571	0.1698
70	0.8753	1.400	5.2030	3.8790	423.7220	-0.0210	0.8851	0.1672
60	0.8684	1.452	4.8760	3.8710	428.1920	-0.0189	0.8610	0.1701
			Maleic a	acid (MIA)				
100	0.9972	1.349	5.8770	4.8116	432.8545	0.0889	1.0084	0.1711
90	0.9910	1.368	5.8621	4.7220	432.7136	0.1215	1.0088	0.1792
80	0.9786	1.388	5.8251	4.7115	431.9049	0.2884	-1.0038	0.1762
70	0.9775	1.398	5.7968	4.6228	430.9656	0.1804	-10027	0.1810
60	0.9749	1.416	5.7941	4.5910	438.3823	0.0910	09761	0.1922
			Succinic	acid (SUC)				
100	0.9985	1.372	5.8810	4.8500	436.2100	1.0091	1.0082	0.1869
90	0.9967	1.389	5.8788	4.8512	436.5192	1.0089	1.0096	0.1842
80	0.9891	1.393	5.8751	4.8488	435.5870	-1.0079	0.0052	0.1839
70	0.9872	1.431	5.8712	4.8469	434.7171	-1.0059	1.0034	0.1827
60	0.9853	1.462	5.8687	4.8452	433.4142	-1.0037	0.7221	0.1811

Table 1: Acoustic properties of dicarboxylic acids in different percentage of dioxane-water at 303K.

Where

M= molecular weight of solute $d_0, d_s =$ densities of solvent and solutions

The apparent molal compressibility was deduced by using equations.

$$\phi_{ks} = 1000(\beta_s - d_0)/m.\beta_0.d_s + \beta_s M / d_s$$

Relative associations (R_A) , specific acoustic impendence (Z) and intermolecular free length (L_f) are calcualted by using following equations.

$$Z = U_s d_s$$
$$R_A = (d_s / d_0) (U_0 / U_s)^{1/3}$$
$$L_f = K. \beta_s$$

The experimental value of density and ultrasonic velocity have been used to compute different parameter and are presented in table 1.

Experimental results reveal that ultrasonic velocity decreases with increase in concentration of dioxane. The may be attributed to the solute-solvent interactions⁶⁻⁷. But ultrasonic velocities

increase with increase in the percentage of organic solvent⁸⁻⁹.

The value of ϕ_s are found to decrease with increase in concentration of solute. The positive vlaue of ϕ_{μ} shows that the electrostatic force in the vicinity of ion causes solvation of solute, but the value of ϕ_{μ} are found to be decreasing with increase in percentage of organic solvent which may be due to weak electrostatic force in the vicinity causes ionic association¹⁰⁻¹¹. Intermolecular free path length (L, decrease with increasing percentage of ionic solvent indicates solute-solvent interactions¹²⁻¹³. This may be due to decrases number of free ion showing the occurrence of ionic association due to solute-solvent interacations. Decrease in β_s value with increasing percentage of dioxane shows that there is a strong ordered arrangement which is water centered and gets disturbed when percentage of dioxance increases. Value of R₄ indicates the breaking up of the solvent structure on addition of solute to it and the solvation of solute simultaneously¹⁴. Decrease in value of R₄ indicates that there is a breaking up of solvent molecules structure on addition of solute to it. Linear variation of values R_A and non-linear variation of Z with increasing percentage of organic solvent indicates the percentage of different interacation taking place in solution¹⁵⁻¹⁶.

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