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Study of excess acoustic parameters of citric acid in ionic solutions

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ABSTRACT

The density, viscosity and speed of sound have been measured for the systems (1M NaCl +citric acid) and (1M $MgCl_2$ +citric acid) at different temperatures 298.15, 303.15and 308.15K. The excess acoustic parameters such as excess ultrasonic velocity, excess adiabatic compressibility, excess acoustic impedance, excess intermolecular free length and excess relative association have been calculated for the solutions. The results are interpreted in terms of molecular interactions.

Key words: Citric acid, ultrasonic velocity, viscosity, excess acoustic parameters, molecular interactions.

INTRODUCTION

Organic compounds have carbon-hydrogen groups. They are large molecules having high molecular weight. Carbohydrates **[1]**, protein **[2]**, lipids **[3]**, nucleic acids, vitamins, enzymes, hormones etc are the organic compounds present in protoplasm of cell of living organism. Citric acid has six carbon atoms; a complete turn of the cycle results in the elimination of two carbon atoms as carbon dioxide, and oxaloacetate with four carbon atoms is again produced. This can then condense with more acetyl coenzyme a to reform citrate. Citric acid is a tribasic, 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 is an organic acid, a natural preservative and also used to add an acidic or sour taste to foods and soft drinks. In biochemistry, it is important as an intermediate in the citric acid cycle ,which is a part of a metabolic path involved in the chemical conversion of carbohydrates, fats and proteins into the metabolisms of virtually all *living things* .It can be used as cleaning agent and acts as antioxidant and lubricant. The citric acid or citric acid cycle occurs in the mitochondrion of cell. In aerobic organisms; the citric acid cycle is part of a metabolic pathway involved in the respiration. It provides precursors for many compounds including some amino acids and is therefore functional even in cell performing fermentation (an aero basic respiration). It is used as a stabilizer in various formulations, as a drug component and as a anticoagulant in blood for transfusion and also used to make water acidic for ionization. It brings about sharp change in solvation of ions **(4-5).**

Thermodynamic excess functions are found to be very sensitive towards mutual interaction between component molecules of the liquid mixture. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules**.**

MATERIALS AND METHODS

All the chemicals used were of AR grade and dried over anhydrous $CaCl_2$ in desiccators before use. All solutions were prepared in deionized and distilled water (degassed by boiling), the aqueous solutions of NaCl, $MgCl_2$ and citric acid in double distilled water, were prepared by weighing the all chemicals on a digital balance with an accuracy of ± 1 x 10^{-4} g. Solutions of required liquid mixture were prepared by changing volume fraction(X) of aqueous citric acid. The solutions were kept in the special air tight conical flasks (100 ml) and were used within 12 hrs. to minimize decomposition due to bacterial contamination **[6]**. The density of the solution for the systems of NaCl and $MgCl_2$ with changing the concentration of citric acid (by weight %) has been determined by 25 ml specific gravity bottle. The mass measurements were made by using an electronic balance (±0.0001g).Viscosity for the solutions is measured by precalibrated Ostwald's viscometer. The speed of sound has been measured by using a constant frequency (2MHz) ultrasonic interferometer with an accuracy of ±2m/s.

1. Theory

Sodium chloride (NaCl) is also known as common salt or table salt with molecular weight 58.44g/mol. It is white crystalline solid, highly ionic compound and highly soluble in water. Sodium, in plasma provides over than 90% of the total base of the body, sodium as an ion initiates and maintains contraction of heart. It is essential for normal functions of cells, essential for contraction of voluntary and involuntary muscles, and as compound it maintains blood reaction, controls the reaction of urine, maintains osmotic pressure of body fluids and maintains water balance. Magnesium chloride is ionic compound. It is white crystalline solid Magnesium ion Mg^{2+} (usually added as the chloride) is an important component in the polymerase chain reaction, a procedure used to amplify DNA fragments. It is generally used in experimental biology whenever RNA and DNA and their enzymes are to function in vitro, since Mg^{2+} is a necessary associate ion for nucleotides in biology.

Excess thermodynamic parameters have been found to be highly useful in elucidating solute-solvent interactions in aqueous solutions and binary mixtures. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of the liquid mixture. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules **[7].**

Excess parameter play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through charge transfer, dipole-induced dipole and dipole-dipole interactions **[8-9]**

The density, viscosity and sound velocity have been determined by using following formulae

$$\rho = m/v \qquad (1)$$
$$\eta_2 = (t_2/t_1)(\rho_2/\rho_1)\eta_1 \qquad (2)$$
$$u = n\lambda \qquad (3)$$

Where η_2, ρ_2, η_1 and ρ_1 are values for viscosity, density of solution and solvent respectively.

The excess parameters such as u^E, β^E, L_f^E, z^E and R_A^E have been calculated using the following equation

$$P^E = P_{mix} - [(1-X)\,P_1 + X\,P_2] \qquad (4)$$

Where P^E is u^E or β^E or L_f^E or z^E or R_A^E and X represents volume fraction of the component and subscript 1 and 2 stands for component 1 and 2. P_{mix} is for parameters of mixture or solution.

RESULTS AND DISCUSSION

Excess acoustic and thermodynamic parameters have been found to be highly useful in elucidating solute solvent interactions in aqueous solutions and binary mixtures. The experimental values of ultrasonic velocity, density, viscosity and other derived excess parameters are reported in Table 1 for the system (1M NaCl+ citric acid) and Table 2 for (1M MgCl2 +citric acid) for different temperatures. The other excess parameters have been calculated using the standard formula (4) and reported in the Tables.

i) Excess ultrasonic velocity (u^E):-

The values of ultrasonic velocity have been calculated using the standard relation as stated above . From Tables, it is clear that the values of u^E are positive at all increasing concentration of solute except at volume fraction x= 0.6 and at x = 0.8 (for 1M $MgCl_2$ + 1M citric acid), at all temperatures for (1M NaCl + 1M citric acid) and thereafter by increasing volume fraction (x) of citric acid in the liquid mixtures the values of excess ultrasonic velocity are decreasing. The excess values in (1 M NaCl + 1 M citric acid) high and positive as compared to (1 M $MgCl_2$ + 1M citric acid).More positive values of u^E in case of (1 M $MgCl_2$ + 1M citric acid) indicates that the molecular interaction between (1M $MgCl_2$ and 1 M citric acid) is more stronger than the (1 M NaCl and 1 M citric acid).

ii) Excess adiabatic compressibility (β_a^E):-

The variations in excess adiabatic compressibility β_a^E with volume fractions at different temperatures are presented in Tables1-2. It is observed that the values of β_a^E are negative at low volume fractions but positive at high volume fractions of citric acid (i.e. initially at X=0.2), at all temperature and at x=0.4at 298.15K in case of (1M $MgCl_2$+ 1M Citric acid) at lower volume fraction but negative in case of (1M NaCl +1 M Citric acid) .The negative values of more negative in case of 1M NaCl than 1M $MgCl_2$ at higher temperature and same volume fraction.

From Tables 1-2, it is clear that the negative values of β_a^E more in (1M NaCl+1M citric acid).These observation support the view point that the mixture has a tendency for a closed packing in the intermediate composition range. The rupture of H-bonded structures is the main cause of excess β_a .The values of β_a^E decreases **[9=13]** with increase in temperature indicates that as the temperature is raised the system attains ideal behavior in which β^E should be zero. This means that system is temperature sensitive and interaction between the component increases with rise in temperature.

The positive values of β_a^E for the system suggest the presence of weak interaction between unlike molecules. The size of component molecules almost not equal, it is seen that their molecules do not pack well into each other's structures .This results in expansion of volume and hence positive β_a^E.

The negative value of β_a^E suggests significant interaction between component molecules in the mixture forming donor –acceptor complex between carbonyl group and ions of electrolytes. As a result there is contraction in volume resulting negative values of β_a^E with volume fraction (X).

iii) Excess acoustic impedance (z^E):-

From tables, it is clear that the values of are positive at all concentration of volume fractions except at X= 0.8 at all temperatures. But the excess values are higher in case of (1M $MgCl_2$ + 1M citric acid) than in (1M NaCl + 1M citric acid).

iv) Excess intermolecular free length (L_f^E) :-

The changes in excess intermolecular free length have been calculated with the help of equation (4).The values of L_f are shown in Tables 1-2. It is seen that the values of L_f^E more negative in aqueous $MgCl_2$ and less negative in aqueous NaCl. This shows strong interaction with $MgCl_2$ but more specific interaction with NaCl. It is seen that L_f^E values are positive at lower concentration of 1M $MgCl_2$ and negative for NaCl at all temperature and volume fractions.

Negative (L_f^E) in the present investigation is an indication of strong interactions in the liquid mixtures at low volume fractions of citric acid As the volume fraction X increases L_f becomes more positive showing weak interaction between solute and solvent particles, as well as small interstitial accommodation of citric acid molecules in sodium chloride and magnesium chloride solution. This trend suggests that hetero association and homo association of molecular decreases. The excess value of (L_f) being negative at low temperature and at lower volume fraction (x) suggests weak interaction of citric acid with electrolytes. However the excess in free length shows positive values at higher temperature and volume fraction, but the changes are very small.

v) Excess relative association (R_A^E):-

From the Tables it is clear that the values of (R_A^E) are less positive for the system (1M NaCl+1M citric acid) but high and more positive for the system (1M $MgCl_2$+1M citric acid). The values of R_A^E are positive for liquid mixtures as the volume fraction increases. This shows the ion-ion interactions in case of citric acid and the ionic solution is weak as compared to ion-dipole interactions, as in case of Glycine in the ionic solution.

Table 1. For the system (1M NaCl +1M Citric acid)

Sr.No.	Vol. Frac. (X)	U m/s	ρ Kg/m^3	η N.s/m^2	u^E m/s	β^E m^{2}N^{-1}	z^E Nm^{-2}	L_F^E A^0	R_A^E
					298.15K				
1	0.2	1634.00	999.7	7.9582	+59.21	-0.0234	+0.0589	-0.0166	-0.0130
2	0.4	1549.41	999.9	8.3388	+117.73	-0.6228	+0.1181	-0.0316	-0.0732
3	0.6	1500.12	1001.1	8.5386	+114.26	-0.6042	+0.1144	-0.0307	-0.0241
4	0.8	1504.10	1001.8	8.6710	+96.59	-0.5192	+0.1133	-0.0262	-0.0203
					303.15K				
1	0.2	1603.22	998.35	7.9345	+35.54	-0.1339	+0.0763	-0.0231	-0.0199
2	0.4	1562.94	998.75	8.4714	+10.96	+0.0896	+0.0155	-0.0098	-0.0294
3	0.6	1532.04	999.9	7.6415	-03.79	+0.1777	-0.0342	-0.0009	-0.0400
4	0.8	1485.31	1001.3	8.4261	-34.53	+0.4170	-0.0996	+0.0167	-0.0465
					308.15K				
1	0.2	1608.00	997.2	7.1399	+40.10	-0.1468	+0.0711	-0.0209	-0.0180
2	0.4	1560.13	997.9	7.5875	+08.22	+0.0769	+0.0005	-0.0062	-0.0233
3	0.6	1536.04	998.3	7.5905	+00.13	+0.1904	-0.0380	-0.0130	-0.0338
4	0.8	1472.04	1022.3	7.5136	-47.88	+0.4441	-0.0860	+0.0187	-0.0107

Table 2. For the system (1M $MgCl_2$+1M Citric acid)

Sr.No.	Vol. Frac. (X)	U m/s	ρ Kg/m^3	η N.s/m^2	u^E m/s	β^E m^{2}N^{-1}	z^E Nm^{-2}	L_F^E A^0	R_A^E
					298.15K				
1	0.2	1631.26	1082.2	13.5430	+44.71	-0.1877	+0.0383	-0.0100	-0.0146
2	0.4	1532.24	1080.5	14.7521	-34.40	+0.1672	-0.0422	-0.0090	+0.0045
3	0.6	1520.24	1078.4	13.7800	-26.40	+0.1230	-0.0299	+0.067	+0.0053
4	0.8	1543.44	1075.4	14.9213	+16.75	-0.1001	+0.0193	-0.0050	-0.0026
					303.15K				
1	0.2	1655.36	1081.1	12.5641	+36.95	-0.2566	+0.1041	-0.0168	-0.0248
2	0.4	1592.48	1080.3	13.5524	+43.44	-0.1020	+0.0543	-0.0075	-0.0072
3	0.6	1600.16	1076.1	12.5974	+48.32	-0.2547	+0.0753	-0.0147	-0.0131
4	0.8	1560.00	1074.5	13.7120	+49.14	-0.1857	+0.0490	-0.0101	-0.0066
					308.15K				
1	0.2	1543.92	1080.5	11.6951	+34.33	+0.2603	-0.0646	+0.0084	+0.0079
2	0.4	1616.48	1080.0	12.7140	+52.41	-0.1945	+0.0436	-0.0144	-0.0062
3	0.6	1554.88	1075.7	13.1413	+51.98	-0.0086	+0.0010	-0.0030	+0.0044
4	0.8	1957.12	1073.1	13.2742	+42.92	-0.1260	+0.0299	-0.0078	-0.0100

CONCLUSION

The trend of ultrasonic velocity in the aqueous $MgCl_2$ and NaCl with the addition of citric acid is decreasing; this shows that citric acid is of structure breaking nature. In pure aqueous medium it freely dissociates by donating H^+ ions and releasing CO_2 molecules. This is nothing but oxidation process .But in aqueous ionic solutions its interaction with ions is more. Therefore cluster formation of ions takes place. Moreover in ionic solution, salt formation occurs. This may be due to solute solvent interaction or ion dipole interaction.

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