Research Article

Thermo-Acoustic Parameters of Multi-Charged Electrolytes (Sodium Thiosulphate and Sodium Chromate) in Aqueous Binary Fructose Solutions and Derivation of Surface Excess Values from Ultrasonic Velocity Measurements

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ABSTRACT

The ultrasonic velocity (U) in the solutions of sodium thiosulphate and sodium chromate has been measured in the concentration range of 1×10^{-2} to 1×10^{-1} mol dm^{-3} in aqueous binary mixtures containing fructose (5, 10, 15% (w/w) at 298.15 K only. Various important parameters such as isentropic compressibility (K_s), solvation number (S_n) and other acoustic parameters have been computed using experimentally determined sound velocities. In the light of solute-solvent and solute-solute interactions, the variation of these parameters has been enlightened. The surface tension values have been computed from ultrasonic velocity and density values. The data were analyzed using the Gibbs equation to evaluate surface excess. The results reveal the nature of solute adsorption at the interface in these solutions.

Keywords: Aqueous fructose solutions, Surface excess, Ultrasonic velocity parameters.

INTRODUCTION

Fructose, or fruit sugar having molecular formula $C_6H_{12}O_6$, is a simple monosaccharide found in many plants and it is one of the three dietary monosaccharide's, along with glucose and galactose, which are absorbed directly into the bloodstream during digestion. Pure, dry fructose is a very sweet, white, odorless, crystalline solid and is the most water-soluble of all the sugars. From plant sources, fructose is found in honey, tree and vine fruits, flowers, berries, and most root vegetables. The primary reasons that fructose is used commercially in food and beverages, besides its low cost, are its high relative sweetness. It is the sweetest of all naturally occurring carbohydrates. Fructose is generally regarded as sweeter than sucrose. Commercially, fructose is frequently derived from sugar cane, sugar beets, and corn. All forms of fructose, including fruits and juices, are commonly added to foods and drinks for palatability and taste enhancement, and for browning of some foods, such as baked goods. The study of carbohydrates has become a subject of increasing interest, because of physical, biological, and industrially useful properties of these compounds. Over all, fructose is very important to human physiological systems and has many pharmaceutical applications. The study of the effect of ion-solvent interaction and interfacial tension involving multi-charged electrolytes is also of much interest to solution chemists. In continuation of our studies on acoustic measurements of solutions of various electrolytes in mixed solvent systems containing dextrose, the present study on surface excess also aims at determining the surface properties and molecular interactions of these multi-charged electrolytes and the effect of these ions in different weight percentages of fructose solutions.

MATERIALS AND METHODS

All chemicals used were of G.R. or B.D.H., AnalaR grades. Conductivity water (Sp.cond.~ 10^{-6} S cm^{-1}) was used for preparing water + fructose (5.0, 10.0 and 15.0 %,(w/w)) mixtures .The fructose content in the mixed solvents was accurate within ±0.01%. The salt solutions were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression[1] considering the density values at the respective temperatures. Solutions were kept for 2h in a water thermostat maintained at the required temperature accurate to within ±0.05K before use for density measurements. Density measurements were done using a specific gravity bottle (25 ml. capacity) as described earlier.[2] At least five observations were taken and differences in any two readings did not exceed ±0.02%. Ultrasonic velocity measurements on the solutions of the salts were made by using an Ultrasonic Interferometer (Mittal Enterprises, New Delhi, India) at a frequency of 2MHz at 298.15K only.[3-5] The accuracy of the sound velocity measurement is within ±0.5m/s. The salt content of the solutions varied over a concentration range of 1.0×10^{-2} to 1.0×10^{-1} M for all these measurements.

Theoretical aspects

The experimental ultrasonic velocities (U) of the solutions of sodium thiosulphate and sodium chromate in mixed solvents at different concentrations were measured by using ultrasonic interferometer.

From the ultrasonic velocity and density data, the values of adiabatic isentropic compressibility, K_s, have been calculated by using the relation (1).[6-9]

$$K_s = \left(\frac{1}{U^2 d} \right) \dots\dots\dots (1)$$

Where,

U = ultrasonic velocity of the solution, d = density of the solution

The values of K_s obtained for solutions of different concentrations were fitted to an equation of the form;

$$K_s = K_s^o + Ac + Bc^{3/2} + Cc^2 \dots\dots\dots (2)$$

Where A, B and C are the constants.

The apparent molar isentropic compressibility ($K_{s,\phi}$) has been computed from equation

$$K_{s,\phi} = 1000 \, K_s c^{-1} - K_s^0 d_0^{-1} (1000c^{-1}d - M) \dots (3)$$

The $K_{s,\Phi}$ data were fitted to an equation of the form;

$$K_{s,\Phi} = K_{s,\Phi}^o + F'c^{1/2} + G'c \dots\dots\dots (4)$$

To obtain $K_{s,\Phi}^o$ (the limiting apparent molar compressibility).

The salvation number, (S_n) of the solute can be calculated from the isentropic compressibility by the equation:[10-13]

$$S_n = n_1 n_2^{-1} [1 - V K_s (n_1 V_1^0 K_s^0)^{-1}] \dots\dots\dots (5)$$

Where,

$V =$ Volume of the solution containing n_2 moles of the salt of molecular mass, M

V_1^0 = molar volume of the solvent,

n_1 = number of moles of the solvent

K_s^0 = the apparent isentropic molar compressibility at infinite dilution.

The acoustic impedance (Z), molar compressibility (W) and the increase in internal pressure (π_i) due to electrostatic field of the ion have also been calculated by using the following equations, respectively,

$$Z = Ud \dots\dots\dots (6)$$

$$W = K_s^{-1/7} \overline{M} d^{-1} \dots\dots\dots (7)$$

and

$$\pi_i = (K_s^0 - K_s) \dots\dots\dots (8)$$

$$\overline{M} = \frac{\sum n_i m_i}{\sum n_i}$$

Where,

The surface tension (S) values have been computed from the ultrasonic velocity and density values by using equation (9) given below [14].

$$S = 6.3 \times 10^{-4} \times d \times U^{3/2} \dots\dots\dots (9)$$

The stoichio molalities (m) have been converted to mean ionic activities ($a_\pm$) using the mean ionic activity coefficients ($\gamma_\pm$) as follows:[15]

$$a_\pm = (Q \, \alpha \, m \, \gamma_\pm) \dots\dots\dots (10)$$

Where,

$$Q = (\nu_+^{\nu+} \, \nu_-^{\nu-})^{1/\nu}$$

$\nu = (\nu_+ + \nu_-)$ is the total number of moles of ions (ν_+ is the number of moles of positive ions and ν_- is that of negative ions) produced by one mole of solute, and α is the degree of dissociation obtained from conductance measurements.

The mean ionic activity co-efficient ($\gamma_\pm$) is determined by Debye-Huckel limiting law as;

$$\log \gamma_\pm = -A \, |z_+| \, |z_-| \, I^{1/2}$$

Where z_+ and z_- are the valencies of positive and negative ions, respectively, A is the Debye-Huckel constant (A = $1.823 \times 10^6 / (DT)^{3/2}$) and I is the ionic strength of the solution given by;

$$I = \tfrac{1}{2} \Sigma m_i z_i^2,$$ where m_i is m_+ or m_-.

Assuming that the Gibbs equation applies to the above electrolytes, the surface excess Γ_2 can be obtained from the equation;

$$\Gamma_2 = - (a_\pm/2RT) \times (dS/da_\pm) \dots\dots\dots (11)$$

Where $a_\pm$ is the bulk mean ionic activity and ($dS/da_\pm$) is the slope of the plot of S vs. $a_\pm$.

RESULTS AND DISCUSSION

The ultrasonic velocities in the solutions of sodium thiosulphate and chromate in aqueous binary mixture of fructose was found to increase as the proportion of fructose as well as the concentration of sodium salts increase in water. The values of U were fitted to an equation (1), and the constants F, G and H calculated for different weight percentages of dextrose, are given in Table 1.

The values of isentropic compressibility, K_s were calculated by Eqn (2) and were fitted to Eqn (3). The values of the constants A, B and C of Eqn (3) are shown in Table 2. As observed, the K_s^o values decrease with the increase of the weight percentage of the fructose and the concentration of the sodium salts in water.

Table 1: Values of Uo (m/s) and the constants F, G and H at 298.15K

| Electrolyte	Wt% of Fructose	Uo (m/s)	F	G	H
$Na_2S_2O_3$	5	1514	111.2	363.5	-7.68
	10	1528	652.7	-1082.7	-54.28
	15	1540	2345.3	-6647.8	2753.8
Na_2CrO_4	5	1514	314.3	-218.5	-673.5
	10	1528	922.7	-2005.4	725.6
	15	1540	2893.1	-8319.3	3047.4

Table 2: Values of K_s^o (pa^{-1}) and the constants A, B and C at 298.15K

Electrolyte	Wt % of Fructose	$K_s^0 \times 10^{10}$ (pa^{-1})	$A \times 10^{10}$	$B \times 10^8$	$C \times 10^7$	$K_{s,\phi}^{\,0} \times 10^8$ (m^3/mol/pa)	$S_n^o \times 10^{-5}$
$Na_2S_2O_3$	5	4.27	-1.29	-4.01	1.57	-9.49	38.244
	10	4.15	-2.14	-3.94	1.52	-33.1	37.192
	15	3.89	-1.35	-3.64	1.42	-10.5	35.988
Na_2CrO_4	5	4.26	-1.21	-3.99	1.56	-9.39	38.246
	10	4.14	-2.19	-3.95	1.53	-35.2	37.195
	15	3.85	-1.31	-3.59	1.40	-9.07	35.990

The limiting apparent molar compressibility $(K_{s,\Phi}^{\,o})$ was obtained from Eqn (5) and the values are given in Table 2. It was observed that apparent molar isentropic compressibility $(K_{s,\phi})$ increases with increase in concentration of the solution. The values of $K_{s,\phi}$ and $K_{s,\Phi}^{\,o}$ were found to be negative.

The negative $K_{s,\phi}^{\,0}$ values can be explained in terms of loss of compressibility of surrounding solvent molecules due to strong electrostrictive forces in the vicinity of ions causing electrostrictive salvation of the ions. As observed, the $K_{s,\phi}^{\,0}$ values increase with increased proportion of fructose in water. This indicates that electrostrictive salvation of ions decreases as the fructose content increases. As observed, both the sodium salts show an irregular trend in $K_{s,\phi}^{\,0}$ with increase of fructose content in water.

As seen in Table 2, the values of solvation number, S_n^o of the salts are very high in water + fructose mixtures. This is owing to the fact that the salvation layer formed around the ions is thick and /or hard in water +fructose mixtures. However, any discrepancy in the values of $K_{s,\phi}^{\,o}$ and S_n^o may be due to characteristic structural changes. S_n^o values for the sodium chromate are higher than that of sodium thiosulphate. However, it was observed that as the weight percentage of fructose increases in water, the salvation number decreases. The reason could be that the ion-solute interaction is much stronger and bulky fructose molecules are entering more and more in salvation cage leading to low hydration shell.
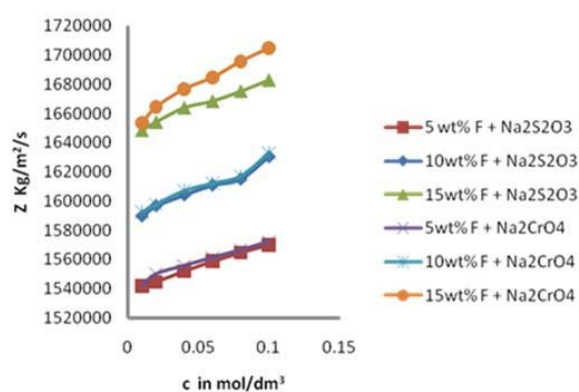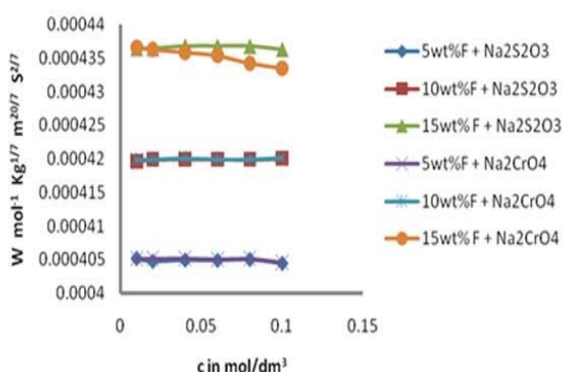

Figure 1: Plot of Z versus c *of* the solution of sodium thiosulphate and chromate at different wt% of fructose solutions.

The values of acoustic impedance, Z as derived by means of equation 6 are graphically presented in figure 1. As observed, the values of Z increase with increase in the concentration of the solution as well as with increase in the fructose content in water.

The increase in *Z* values with solute concentration can be attributed to the effective solute – solvent interactions. Since the acoustic impendence is a measure of the resistance offered by the liquid medium to the sound wave, and is a function of the elastic property of the medium, i.e. the bulk modulus of elasticity, which depend on the structural changes of the solution, the higher *Z* values of sodium chromate in the aqueous fructose solutions as compared to that of thiosulphate and increasingly higher values with increase in the solute concentration and also with increase in fructose content in water point to the fact that the solution medium in each case starts gaining its elastic property. A comparison

of the Z values of chromate solutions in aqueous fructose media with that of solutions of thiosulphate shows that the Z values are lower for the thiosulphate solutions which may be due to its lower molecular mass as a result, the solutions of sodium thiosulphate start losing the elastic property.

Figure 2 shows the variation of molar compressibility (W) for both sodium thiosulphate and chromate solutions in different wt% of fructose solutions. As observed, the values of W increase with increase in wt% of fructose for both the electrolytes. It is also found that in 5 and 10wt% of the mixed solvent, the molar compressibility is almost same which may be due to their small difference in their molecular masses.
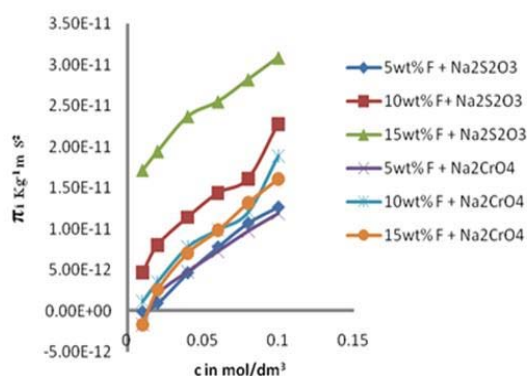

Figure 2: Plot of W versus c of the solutions of sodium thiosulphate and chromate in different wt% of fructose solutions.

The increase in internal pressure, π_i due to electrostatic field of ions is given by the following equation:

$$\pi_i = (K_s^0 - K_s)$$

Where, K_s^0 and K_s are the isentropic compressibility of the solvent and the solution, respectively.

Positive values of π_i indicate the presence of some specific interactions between unlike molecules in the components. Typical plot of π_i versus c is shown in Fig. 3 for solutions of sodium thiosulphate and chromate in different wt% of fructose solutions.

Figure 3: Plot of π_i vs c of the solutions of sodium thiosulphate and chromate in different wt% of fructose solutions.
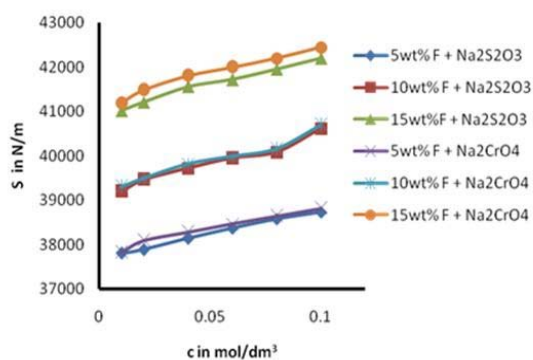
The values of surface tension, S as calculated by equation (9) are shown in Table 3 and Table 4 and their variation with concentration of the solutions is displayed in Figure 4.

Table 3: Variation of S, $a_{\pm}$ and Γ_2 with concentration for Sodium thiosulphate.

| Electrolyte	c mol/dm³	S N/m	$a_{\pm}$ (mol/kg)	Γ_2
5wt%F + Na₂S₂O₃	0.01	37807	1.53E-5	-0.0222
	0.02	37889	3.05E-5	-0.0442
	0.04	38144	6.04E-5	-0.0878
	0.06	38370	9.00E-5	-0.1308
	0.08	38577	1.19E-4	-0.1734
	0.1	38733	1.48E-4	-0.2154
10wt%F + Na₂S₂O₃	0.01	39198	1.50E-5	-0.0294
	0.02	39462	2.99E-5	-0.0586
	0.04	39720	5.93E-5	-0.116
	0.06	39947	8.83E-5	-0.173
	0.08	40087	1.17E-4	-0.2294
	0.1	40619	1.45E-4	-0.2849
15wt%F + Na₂S₂O₃	0.01	41018	1.47E-5	-0.0265
	0.02	41211	2.93E-5	-0.0527
	0.04	41563	5.81E-5	-0.1044
	0.06	41717	8.65E-5	-0.1556
	0.08	41952	1.15E-4	-0.2062
	0.1	42199	1.42E-4	-0.256

Table 4: Variation of S, $a_{\pm}$ and Γ_2 with concentration for Sodium chromate.

Electrolyte	c mol/dm³	S N/m	$a_{\pm}$ (mol/kg)	Γ_2
5wt%F + Na₂CrO₄	0.01	37830	1.53E-5	-0.0215
	0.02	38092	3.05E-5	-0.0427
	0.04	38287	6.04E-5	-0.0848
	0.06	38468	9.00E-5	-0.126
	0.08	38646	1.19E-4	-0.167
	0.1	38816	1.48E-4	-0.208
10wt%F + Na₂CrO₄	0.01	39313	1.50E-5	-0.0292
	0.02	39497	2.99E-5	-0.0581
	0.04	39820	5.93E-5	-0.115
	0.06	39986	8.83E-5	-0.1717
	0.08	40156	1.17E-4	-0.2277
	0.1	40704	1.45E-4	-0.2828
15wt%F + Na₂CrO₄	0.01	41184	1.47E-5	-0.0275
	0.02	41488	2.93E-5	-0.0546
	0.04	41809	5.84E-5	-0.1083
	0.06	42000	8.65E-5	-0.1613
	0.08	42199	1.15E-4	-0.2138
	0.1	42446	1.42E-4	-0.2655

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Figure 4: Plot of Surface Tension vs c for sodium thiosulphate and sodium chromate solution in different solutions of water+ fructose mixtures.

The values of surface excess, Γ_2 of the solutions of the electrolytes in water+ fructose solutions are shown in Table 3 and Table 4 and the plots of Γ_2 vs mean activity $a_\pm$ are shown in figure 5 and 6 for sodium thiosulphate and sodium chromate solutions, respectively. As observed, the surface tension values go on increasing with increase in concentration of electrolytes such as sodium thiosulphate and sodium chromate in aqueous fructose solutions. This qualitative picture leads to the conclusion that multi charged electrolytes under study can be said to be negatively adsorbed at the surface. Solutes such as ionic salts usually increase the surface tension of aqueous solutions above the value of pure water and in such solutions the surface layers are poorer in that solute.
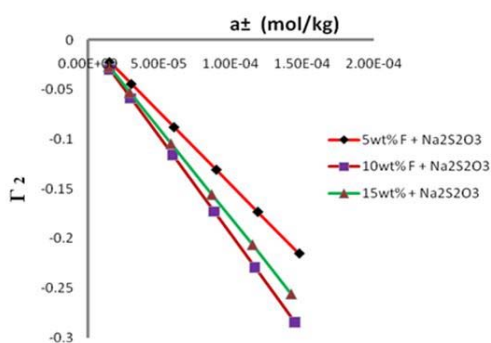
Figure 5: Plot of Γ_2 vs $a_\pm$ for sodium thiosulphate in different weight percentages of fructose.
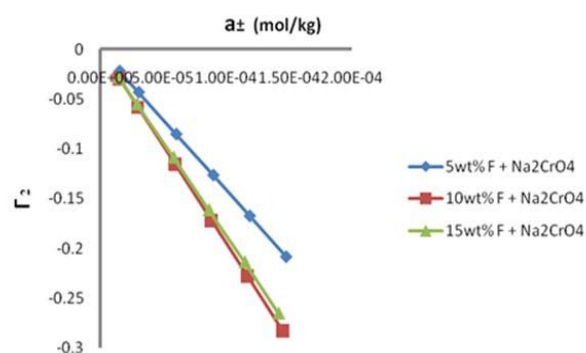
Figure 6: Plot of Γ_2 vs $a_\pm$ for sodium chromate in different weight percentages of fructose.

As observed, the values of Γ_2 are negative for both the electrolytes in all the solvents indicating that the ionic solutes are negatively adsorbed at the surface of the aqueous fructose solution.

CONCLUSION

The ultrasonic velocities were found to increase for both the electrolytes with increase in proportion of fructose as well as the concentration of electrolytes. The higher sound velocity value of sodium chromate is due to its higher mass. The isentropic compressibility, K_s^o and solvation number, S_n^o values decrease as the weight percentage of the dextrose in water increases which may be due to occupation of the interstitial spaces of water by dextrose molecules thereby making the medium less compressible. Thus, it represents the degree of electrostrictive solvation. The surface tension values go on increasing with increase in concentration of the electrolytes in aqueous fructose solutions. This leads to the conclusion that multi charged electrolytes under study can be said to be negatively adsorbed at the surface

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