
Thermodynamic and Interactions studies of D(+) Fructose with aqueous alkali metals halides at different molalities and constant temperature

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Abstract: The present experimental investigation was carried out in order to explore the possible thermodynamic and interactions studies of D(+) fructose with mixed solvent of aqueous alkali metal halides at different molalities and constant temperature. Experimental values of densities and ultrasonic velocities were carried out of the ternary mixture solution D(+)fructose with aqueous NaCl, KCl, MgCl₂ and CaCl₂ under different molalities and at 303K. The related and relevant parameters correlated to the present study such as adiabatic compressibility K_s , acoustic impedance Z , apparent molal volume ϕ_v , apparent molal adiabatic compressibility, ϕK_s , and partial molal volume ϕ_v^0 and partial molal adiabatic compressibility, $\phi^0 K_s$ at infinite dilution. The present investigation has exploited the possible molecular associations such as ion-ion, ion-solvent, interactions in these systems. It has been observed that there exist strong solute-solvent interaction and complex formation between in these ternary systems.

Keywords: D(+)fructose, Aqueous Electrolytes, Apparent Molal Volume and Apparent Molal Adiabatic Compressibility, Adiabatic Compressibility, Acoustic Impedance

1. Introduction

Carbohydrates are very important for some physiological process. They are not only basic material but also play significant role in the configuration of biological molecules. The study of thermodynamic properties of carbohydrates in aqueous and non-aqueous solvent is an important step for understanding their behavior biological fluids containing different ionic species. Also, it can provide useful information regarding conformational stability and interaction in the ternary system (1). Ultrasonic technique has been found to be more accurate and comprehensive in understanding solute-solvent interactions. To understand the role played by the biological molecules in living organism (2 & 3). There has been number of physicochemical studies of amino acids in aqueous carbohydrates solutions (4-6). Amino acids have zwitter-ion and are the constituents of the most important class of biopolymers, i.e. Proteins. Disarrangement water and electrolyte balance in living systems cause a wide variety of health problems. In physiological media such as blood,

membranes, cellulose fluids etc., the dipolar character of amino acids (in presence of ions such as Na⁺, K⁺, Mg⁺² and Cl⁻ etc., dissolved in body water) has an important bearing on their biological functions. Carbohydrates located at cell surfaces are important receptors for the bioactive structures of enzymes, hormones, viruses, antibodies etc. The electrolyte – carbohydrates and protein - carbohydrates interactions are important for immunology, biosynthesis pharmacology, medicine and cosmetic industry. The complex conformational and configurationally factors determining the structure of carbohydrates in aqueous electrolytes solutions (7-9).

Recently, we have made systematic effort to investigate the ultrasonic properties of carbohydrates and amino acids in concentrated electrolytic solution (10 & 11). It was found that glucose interacts with aqueous electrolytes which indicate solute-solvent interactions are strong and complex formation in these ternary systems. The L-Proline and L-Glutamine with aqueous NaCl and MgCl₂ increase the apparent molar volume of these systems. This increase could be attributed to the interactions of the ions of the NaCl, MgCl₂ L-Proline and L- Glutamine electrolytes and zwitter-

ion head group of amino acids, causing the transfer of hydrated water molecule to the bulk state.

In the present paper, we report densities, ρ and ultrasonic velocities, u of ternary systems of D(+)fructose with mixed solvent of aqueous NaCl, KCl, MgCl₂ and CaCl₂ have been determined experimentally at 303K. From these experimental data a number of thermodynamic parameters namely, the adiabatic compressibility K_s , acoustic impedance Z , apparent molal volume ϕ_v , apparent molal adiabatic compressibility, ϕK_s , and partial molal volume ϕ_v^0 and partial molal adiabatic compressibility, at infinite dilution respectively have been calculated. These parameters were utilized to study various interactions taking place in the solutions of these ternary systems were measured at 303K.

2. Experimental

2.1. Chemicals and Preparation

D(+)fructose (99.5% purity), NaCl, KCl, MgCl₂ and CaCl₂ (99.8% purity) were procured from E Merck Germany and S d Fine Ltd. was used as such without further purifications, except drying in an oven for 24 hrs. The ultrasonic velocities and densities of the fructose in aqueous electrolytes solutions at various concentrations as well as in triple distilled de-ionized water were measured experimentally. The triple distilled water was used to make aqueous solvent of NaCl, KCl, MgCl₂ and CaCl₂ and these were used as solvent to prepared D(+)fructose solutions. All the solutions were stored in special air-tight bottles and kept in dark to avoid photo chemical degradation. The weighing was done on an electronic balance (model: GR-202R, and Japan) with a precision of ± 0.01 mg.

2.2. Measurement of Density and Ultrasonic Velocity

The densities were measured with a single capillary pycnometer (made of Borosil glass) of bulb capacity of $8 \times 10^{-6} \text{m}^3$. The marks of the stems were calibrated using double distilled water at 303 K. The pycnometer was kept for about 30 minutes in a thermostatic water bath so that the thermal fluctuation in density was minimized. The ultrasonic velocities in solutions were measured using a single crystal variable path interferometer at 3MHz. The temperature of the test solutions was maintained at $303 \pm 0.02\% \text{K}$ in an electronically controlled thermostatic water bath. The velocity and density data were found to be accurate with in $\pm 0.10\%$ and $\pm 0.01\%$ respectively.

3. Results and Discussion

The densities and ultrasonic velocities of the D(+)fructose with mixed solvent of aqueous NaCl, KCl, MgCl₂ and CaCl₂ (0.068, 0.075, 0.084, 0.096, 0.112, 0.137, 0.179, m) were determined at 303K are recorded in Table 1. The values of ρ and u increase and non-linearly with increase in concentration of all the ternary systems under investigation, which appear to be due to hydrophobic properties of solutes

i.e. H-bond forming. Solutes may occupy the interstitial spaces in solvent or get solvated forming new weaker bonds. It was suggested (12) that what is experimentally observed for any systems reflect the compromise between the tendency for the ions and sugar to interact with each other and inclination of the solutes to associate with the solvent. The change in structure of solvent or solution as a result of H-bond formation leads to decrease in intermolecular free length. The variation of ultrasonic velocity with the concentration of fructose, (du/dc) can be shown to depend upon the concentration derivations of the density and adiabatic compressibility of the system investigated.

Thus in the relation:

$$du/dc = -u/2 [1/\rho (d\rho/dc) + (1/K_s)(dK_s/dc)] \quad (1)$$

The quantity $(1/\rho)(d\rho/dc)$ is positive while $(1/K_s)(dK_s/dc)$ is positive and the net value is negative. This makes du/dc positive, showing that u increases with the concentration of the ternary systems which is in good agreement with the results reported for glycine and D-L alanine from water to aqueous sodium sulphate [13]

3.1. Adiabatic Compressibility

The adiabatic compressibility of the fructose + water + NaCl, KCl, MgCl₂ and CaCl₂ were determined at 303 K from the density and velocity data. The adiabatic compressibility was calculated by this relation

$$K_s = 1/u^2 \rho \quad (2)$$

The per usual of Table 2 exhibits the values of the adiabatic compressibility, K_s is found to be decrease with the concentration of solute (D(+)fructose) in all the ternary systems. Such a decrease in adiabatic compressibility observed in the ternary systems (fructose + water + electrolytes) clearly confirms the conclusion drawn from the ultrasonic velocity data. It is well known fact that when a solute dissolves in a solvent. Some of the solvent ions (Na^+ , K^+ , Mg^{+2} and Ca^{+2}) are attach to the molecules of fructose because of solute-solvent interactions. Since the solvent molecules are oriented in ionic field (i.e. electrostatic field of ions ($-\text{CH}_2\text{OH}$ and CHO)). The solvent molecules are more compactly packed in the primary salvation shells. This is the reason, why solvent is compressed by the introduction of the ions. Thus the electrostatic field of the ions causes the compression of the medium giving rise to phenomenon called 'Electrostriction'. Since the water molecules are compressed, they do not respond to a further application of pressure. So the solutions become harder to compress. This will lead to the decrease in compressibility values. This may further ascribed that such a decrease in adiabatic compressibility, K_s is attributed to the influence of the electrostatic field of the ions (Na^+ , K^+ , Mg^{+2} and Ca^{+2}) on the accompanying molecules. It may be inferred that the weakening of hydrogen bond strength formed by the solute and solvent molecules and maximum complex formation may also be the reason for decrease in compressibility. Thus is in accordance with the

view proposed by others [15 &16].

3.2. Acoustic Impedance

The values of acoustic impedance, Z of these ternary systems (fructose + water + electrolytes) were calculated by the following relation and are reported in Table 1.

$$Z = u \cdot \rho \quad (3)$$

The values of Z increase with increases in molality of electrolytes which indicates solute-solvent interaction are strong and they behave as structure makers are shown in Table 1. The specific acoustic impedance of the medium for the particular type of wave being propagated and through it. The transmission of acoustic wave from one medium to another is important for transmission phenomenon in fluids. It may also correlated with ionic size Na^+ , K^+ , Mg^{+2} and Ca^{+2} of ions. A definite correlation the specific acoustic impedance and dielectric constant of the solvent medium. The behavior of acoustic impedance can be explained on the basis of lyophobic interaction between solute (fructose) and solvent (aqueous NaCl , KCl , MgCl_2 and CaCl_2) molecules, which maximum complex ion formation and become responsible for the propagation of ultrasonic wave.

Table 1. Densities (ρ) and ultrasonic velocity (u) of $D(+)$ fructose + aqueous NaCl , KCl , MgCl_2 and CaCl_2 solution at 303 K

m (mol Kg^{-1})	ρ (kg m^{-3})	u (ms^{-1})	K_s ($10^{-10} \text{ m}^2 \text{N}^{-1}$)	Z ($10^6 \text{ Kg m}^{-2} \text{s}^{-1}$)
0.5 m fructose + water + NaCl				
0.068	981.5	1505.2	4.497	1.477
0.075	982.4	1506.4	4.496	1.480
0.084	983.4	1508.2	4.471	1.483
0.096	984.0	1508.9	4.463	1.485
0.112	984.6	1510.4	4.461	1.487
0.137	985.5	1511.6	4.441	1.489
0.179	988.0	1513.4	4.420	1.495
0.5 m fructose + water + KCl				
0.068	981.5	1505.4	4.495	1.478
0.075	982.2	1506.5	4.486	1.480
0.084	983.4	1507.2	4.478	1.482
0.096	983.7	1508.0	4.472	1.483
0.112	985.9	1509.1	4.444	1.488
0.137	985.7	1512.0	4.438	1.490
0.179	989.9	1513.0	4.413	1.498
0.5 m fructose + water + CaCl_2				
0.068	987.3	1506.2	4.464	1.487
0.075	988.7	1508.2	4.446	1.491
0.084	989.4	1509.1	4.438	1.493
0.096	992.4	1510.9	4.415	1.499
0.112	992.9	1513.1	4.399	1.502
0.137	993.0	1515.1	4.387	1.504
0.179	993.4	1516.2	4.378	1.506
0.5 m fructose + water + MgCl_2				
0.068	986.6	1506.2	4.468	1.486
0.075	987.5	1507.3	4.456	1.488
0.084	988.3	1508.3	4.448	1.491
0.096	996.7	1509.4	4.403	1.504
0.112	997.2	1511.5	4.389	1.498
0.137	998.5	1514.7	4.365	1.507
0.179	998.9	1516.4	4.355	1.515

3.3. Apparent Molal Volume

Table 2. Apparent molal volume (ϕ_v) apparent molal adiabatic compressibility (ϕ_{Ks}) of $D(+)$ fructose + aqueous NaCl , KCl , MgCl_2 and CaCl_2 solution at 303 K.

m (mol Kg^{-1})	ϕ_v ($10^{-8} \text{ m}^3 \text{mol}^{-1}$)	$-\phi_{Ks}$ ($10^{-8} \text{ m}^2 \text{N}^{-1} \text{mol}^{-1}$)
0.5 m fructose + water + NaCl		
0.068	12.23	33.90
0.075	14.38	39.90
0.084	15.31	43.79
0.096	16.75	42.44
0.112	18.78	40.31
0.137	20.35	50.47
0.179	22.24	80.29
0.5 m fructose + water + KCl		
0.068	11.21	38.45
0.075	13.57	42.90
0.084	16.91	43.09
0.096	18.50	46.38
0.112	20.01	38.40
0.137	21.92	58.39
0.179	22.05	78.38
0.5 m fructose + water + CaCl_2		
0.068	16.75	70.54
0.075	17.48	72.91
0.084	18.75	74.40
0.096	19.76	111.33
0.112	21.01	113.00
0.137	22.10	104.62
0.179	23.01	93.12
0.5 m fructose + water + MgCl_2		
0.068	23.30	85.80
0.075	24.25	91.50
0.084	25.5	90.91
0.096	26.91	88.71
0.112	27.85	96.00
0.137	28.01	145.07
0.179	28.20	143.01

The apparent molal volume, ϕ_v were calculated from measured density data of fructose in aqueous metal halides namely NaCl , KCl , MgCl_2 and CaCl_2 solution at different molality and at 303 K using the following equation:

$$\phi_v = [1000 (\rho^0 - \rho) / m \rho^0] + M/\rho \quad (4)$$

Where M is the molecular mass of the solute, ρ^0 and ρ are densities of solvent and solution. The calculated values of ϕ_v of these ternary systems are given in Table 2. In these cases where molality dependence of ϕ_v , having definite trend points. The ϕ_v values increase due to reduction in the electrostriction effect at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end.

The partial molal volume at infinite dilution ϕ_v^0 was calculated by taking an average data points. The linear variation is obtained by least square fitting to the following equation.

$$\Phi_v = \phi_v^0 + S_v m^{1/2} \quad (5)$$

The intercept which is the limiting apparent molal volume at infinite dilution ϕ_v^0 is the experimental slope, S_v which is considered to be volumetric pair wise coefficient. The

derived values ϕ_v^0 of along with S_v are summarized in Table 3. The values of ϕ_v^0 are positive of these ternary systems which indicate ion-solvent interactions are strong. The values of ϕ_v^0 are less in presence of metal ions (Na^+ and K^+) than those of divalent ions (Ca^{+2} and Mg^{+2}). A mutual comparison of these electrolytes shows the values of ϕ_v^0 are larger in case of Ca^{+2} and Mg^{+2} than in Na^+ and K^+ . The Ca^{+2} and Mg^{+2} ions are being smaller in size, has an intense force field and hence strong hydration co-sphere around them therefore, hydration of MgCl_2 and CaCl_2 (Solute - solvent interaction) will be much more than that of NaCl and KCl .

3.4. Apparent Molal Adiabatic Compressibility

The density and adiabatic compressibility values were employed for calculated apparent molal adiabatic compressibility, ϕ_{K_s} of fructose in aqueous metal halides namely NaCl , KCl , MgCl_2 and CaCl_2 solution at different molality and at 303 K using the equation

$$\phi_{K_s} = [1000 (\rho_{K_s}^0 - \rho_{K_s}) / C \rho \rho^0] + M_{K_s} / \rho \quad (6)$$

Table 3 shows that the less negative values of ϕ_{K_s} over the entire range of molality of the ternary systems which indicates strong solute-solvent interactions. The less negative values of ϕ_{K_s} are due to loss of structural compressibility of

Table 3. Partial molal volume (ϕ_v^0) Partial molal adiabatic compressibility ($\phi_{K_s}^0$) and its experimental slope, (S_v) and (S_{K_s}), of D(+)/fructose + aqueous NaCl , KCl , MgCl_2 and CaCl_2 solution at 303 K

m(mol.Kg ⁻¹)	ϕ_v^0 (10 ⁻⁸ m ³ mol ⁻¹)	S_v (10 ⁻⁸ m ³ mol ^{-3/2} l ^{-1/2})	$-\phi_{K_s}^0$ (10 ⁻⁸ m ⁵ N ⁻¹ mol ⁻¹)	$-S_{K_s}$ (10 ⁻⁸ m ⁵ N ⁻¹ mol ^{-3/2} l ^{-1/2})
fructose + water + NaCl				
0.5	25.38	63.70	7.02	4.280
fructose + water + KCl				
0.5	27.38	60.01	6.73	6.919
fructose + water + CaCl ₂				
0.5	28.40	79.02	8.02	10.86
fructose + water + MgCl ₂				
0.5	28.80	73.01	9.01	14.98

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solvent on increase in the population of four bonded solvent molecule in the vicinity of the solute molecules.

The partial molal adiabatic compressibility, $\phi_{K_s}^0$ at infinite dilution are obtained from the plot of ϕ_{K_s} versus $m^{1/2}$ by least square method. The molality dependence of this parameter has been expressed in terms of the following equation

$$\Phi_{K_s} = \phi_{K_s}^0 + S_{K_s} m^{1/2} \quad (7)$$

Where $\phi_{K_s}^0$ is the partial molal adiabatic compressibility at infinite dilution. It provides information regarding solute-solvent interaction. S_{K_s} is the experimental slope. The values of $\phi_{K_s}^0$ and S_{K_s} are also included in Table 3. The magnitude of negative values of $\phi_{K_s}^0$ are higher in MgCl_2 and CaCl_2 systems suggesting that the presence of strong solute-solvent. The Ca^{+2} and Mg^{+2} ions are being smaller in size, has an intense force field and hence strong hydration co sphere around them and maximum complex ion formation. The hydration of MgCl_2 and CaCl_2 (Solute - solvent interaction) will be much more than that of NaCl and KCl . The values of S_{K_s} fructose + water+ electrolytes are positive which is indicating the presence of strong ion-pair interactions. From this tabulation, one can notice that the values of in mixed ternary system less than the pure system suggesting the weak interactions in the ternary system by others[16].

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