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Thermodynamic Interaction Studies Of Carbohydrates With Mixed Solvent Of Aqueous Electrolytes At 303 K *

Acoustic and volumetric Interaction studies D (+) glucose, D(+) galactose and D(+) ribose with mixed solvent of aqueous NaCl, $MgCl_2$ and $CaCl_2$ at 303 K.

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***Abstract*—The present experimental investigation was carried out in order to explore the possible molecular interaction of D (+) glucose, D(+) galactose and D(+) ribose with mixed solvent of aqueous NaCl, $MgCl_2$ and $CaCl_2$ at 303 K. The experimental values of densities and ultrasonic velocities have been used to calculate the adiabatic compressibility, acoustic impedance, apparent molal volume, apparent molal adiabatic compressibility, and limiting apparent molal volume and limiting apparent molal adiabatic compressibility, at infinite dilution. It has been observed that there exist strong solute-solvent interaction for saccharides with aqueous electrolytes were obtained and interpreted by the stereochemistry of the mono saccharide molecules and structural interaction model. There are discussed in terms of the structure making and hydrogen bonding effect.**

Keywords—D(+) glucose; D(+) galactose; D(+) ribose; Aqueous electrolytes; adiabatic compressibility; acoustic impedance; limiting apparent molal volume and limiting apparent molal adiabatic compressibility.

I. INTRODUCTION

The carbohydrates are very important for some physiological process. They are not only basic materials but also play significant role in the configuration of biological molecules. In foods and Biosystems, saccharides play very important roles in aqueous solutions with ionic dissociative components such as sodium and potassium. The thermodynamic properties of carbohydrates in aqueous and non-aqueous solvent is an important step for understanding their behavior biological fluids containing different ionic species. Monosaccharides are basic unit structure and sodium and potassium ions are involved in the membrane potential charge. 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). There has been number of physicochemical studies of amino acids in aqueous alcohol and carbohydrates solutions (3 -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 NH_3^+, Na^+, K^+, Mg^{+2} , COO^- ,OH^- 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). We have made systematic effort to investigate the volumetric properties of amino acids in concentrated electrolytic solution (8). It was found that NaCl and $MgCl_2$ increase the apparent molar volume of glycine. This increase could be attributed to the interactions of the ions of NaCl, $MgCl_2$ 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.

Recently we have made systematic effort to investigate the volumetric properties of amino acids in concentrated electrolytic solution (6). The volumetric studies have been used to the solute –solute and solute-solvent interaction in these ternary systems. This suggests D(+)Lactose in aqueous sodium butyrate solution is strong structure maker than D(+)galactose in aqueous sodium butyrate solution. These parameters reflect that the solute-co solute interactions are dominating over solute-solvent interactions for the saccharides in aqueous sodium butyrate solutions.

In the present paper, we report densities, ρ and ultrasonic velocities, u of ternary systems of D(+) glucose, *D*(+) galactose and D(+) ribose with mixed solvent of aqueous NaCl , $MgCl_2$ and $CaCl_2$ have been determined experimentally at 303K. From these experimental data a number of thermodynamic parameters namely, the adiabatic compressibility K_s, acoustic impedance, apparent molal volume ϕ_v, apparent molal adiabatic compressibility, $\phi K_{s,}$ and partial molal volume $\phi^0{}_v$ 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.

II. EXPERIMENTAL

A. Chemicals and preparation

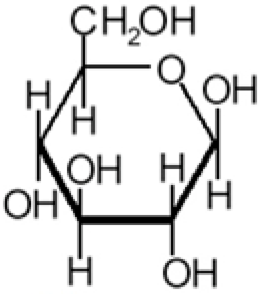
D(+) glucose, (>99% purity) *D*(+) galactose (>98% purity) and D(+) ribose (99.8% purity), NaCl , $MgCl_2$ $CaCl_2$ (>98% purity) and $CaCl_2$ (>99% purity) were procured from E Merck Germany and S d Fine Ltd. was used as such without further purifications, except drying in an oven for 24 hrs. The ultrasonic velocities and densities of the glucose, galactose and ribose 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, $MgCl_2$ and $CaCl_2$ and these were used as solvent to prepared D(+) glucose *D*(+)galactose and D(+)ribose solutions. All the solutions were prepared by mass in dry box and were stored in special air-tight bottles and kept in dark to avoid photochemical degradation. The weighing was done on an electronic balance (model: GR-202R, AND Japan) with a precision of ± 0.01 mg.

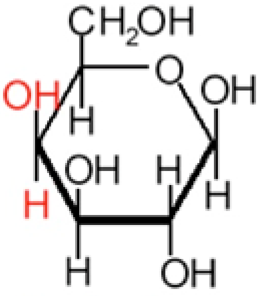
B. Measurement of density and ultrasonic velocity

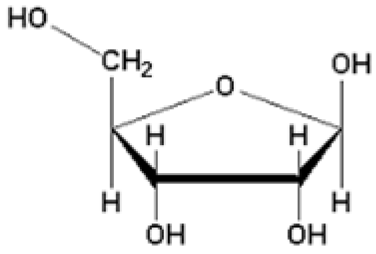
The densities were measured with a single capillary pycnometer (made of Borosil glass) of bulb capacity of $8x10^{-6}m^3$. The marks of the stems were calibrated using double distilled water at 303 K. The pycnometer was kept for about 30 minutes in a thermostatic water bath so that the thermal fluctuation 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 ± 0.02%K in an electronically controlled thermostatic water bath. The velocity and density data were found to be accurate with in ± 0.10%and ± 0.01% respectively.

III.RESULT AND DISCUSSION

The densities and ultrasonic velocities of the D(+), glucose, *D*(+)galactose and D(+)ribose in mixed solvent of aqueous NaCl , $MgCl_2$ and $CaCl_2$ (m) were determined at 303 K are recorded in Table 1 and 2. In “Fig.1 and 2” 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 (9 and 10) 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 D(+), glucose, *D*(+)galactose and D(+)ribose (du/dc) can be shown to depend upon the concentration derivations of the density and adiabatic compressibility of the system investigated.


Glucose

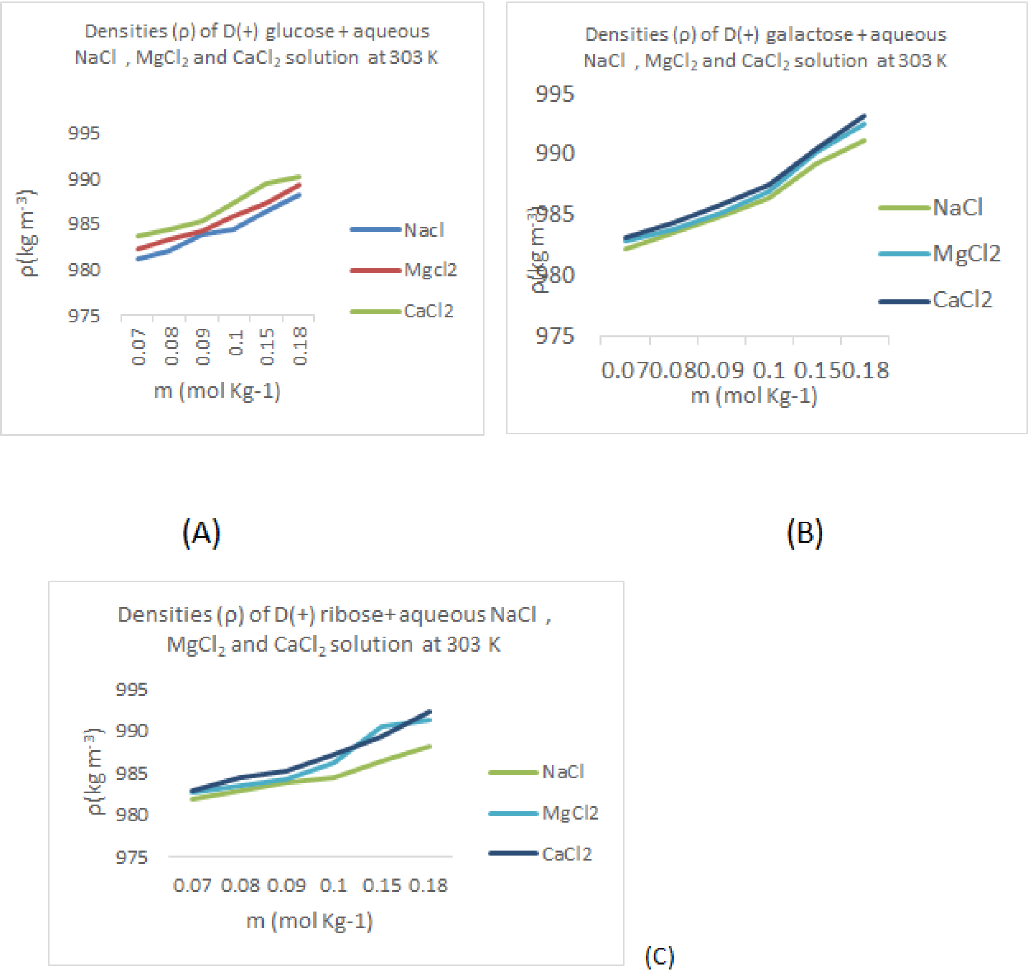

Galactose


D-Ribose

Thus in the relation:

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

The quantity $(1/\rho)(d\rho/dc)$ is negative while $(1/K_s)(\ d\ K_s\ /dc)$ is positive and the net value is negative. This makes du/dc positive, showing that u increases with the concentration of the ternary systems. This makes du/dc is positive, showing that u increases with the concentration in these ternary systems which is in good agreement with the results reported for adenosine mono, di and tri phosphates + dioxane + H_2O(11).



(A)

(B)

(C)

Fig 1. Densities (ρ) of D(+) glucose, (A), D(+) galactose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

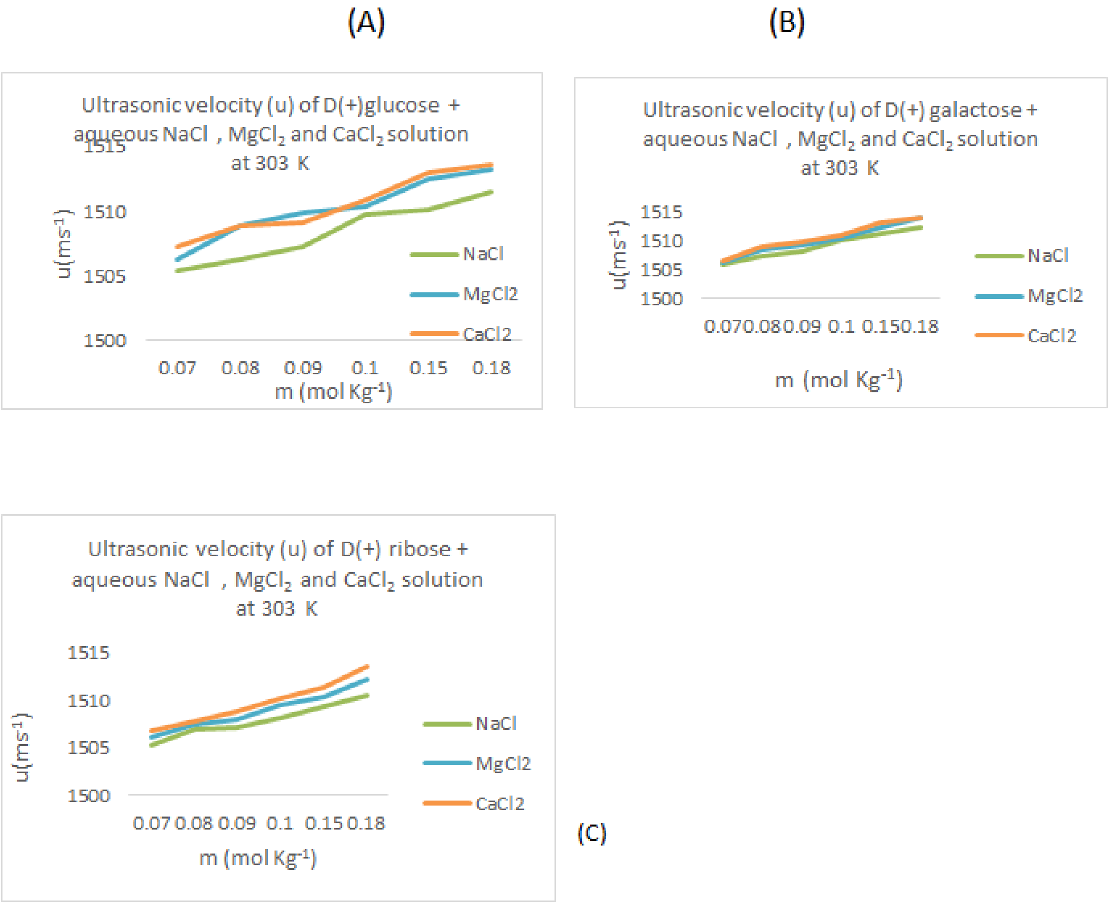


Fig 2. Ultrasonic velocities (u) of D(+) glucose, (A), D(+) galactose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

A. Adiabatic Compressibility

The adiabatic compressibility of the D(+), glucose, D(+)galactose and *D*(+) ribose with mixed solvent of aqueous NaCl, $MgCl_2$ and $CaCl_2$ were determined at 303 K from the density and velocity data. The adiabatic compressibility was calculated by this relation

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

The per usual of "Fig. 3" exhibits the values of the adiabatic compressibility ,K_s is found to be decrease with the concentration of solute (D(+) glucose, D(+)galactose and *D*(+) ribose) in all the ternary systems. Such a decrease in adiabatic compressibility observed in the ternary systems (glucose + water + electrolytes, galactose + water + electrolytes and ribose + 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^+, Mg^{+2} and Ca^{+2}) are attach to the molecules of glucose, D(+)galactose and *D*(+) ribose because of solute-solvent interactions. Since the solvent molecules are oriented in ionic field (i.e. electrostatic field of ions (-CH_2OH 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^+,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 (10 and 11).

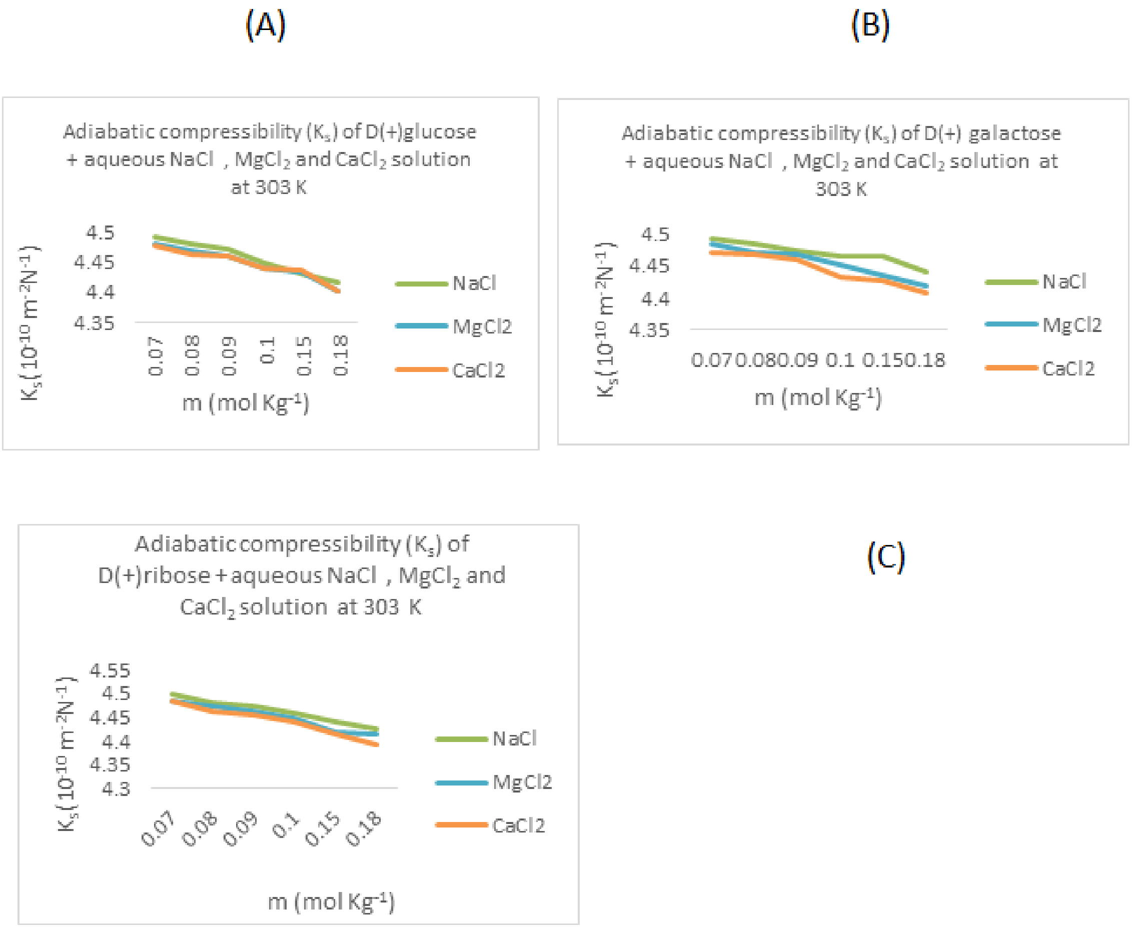


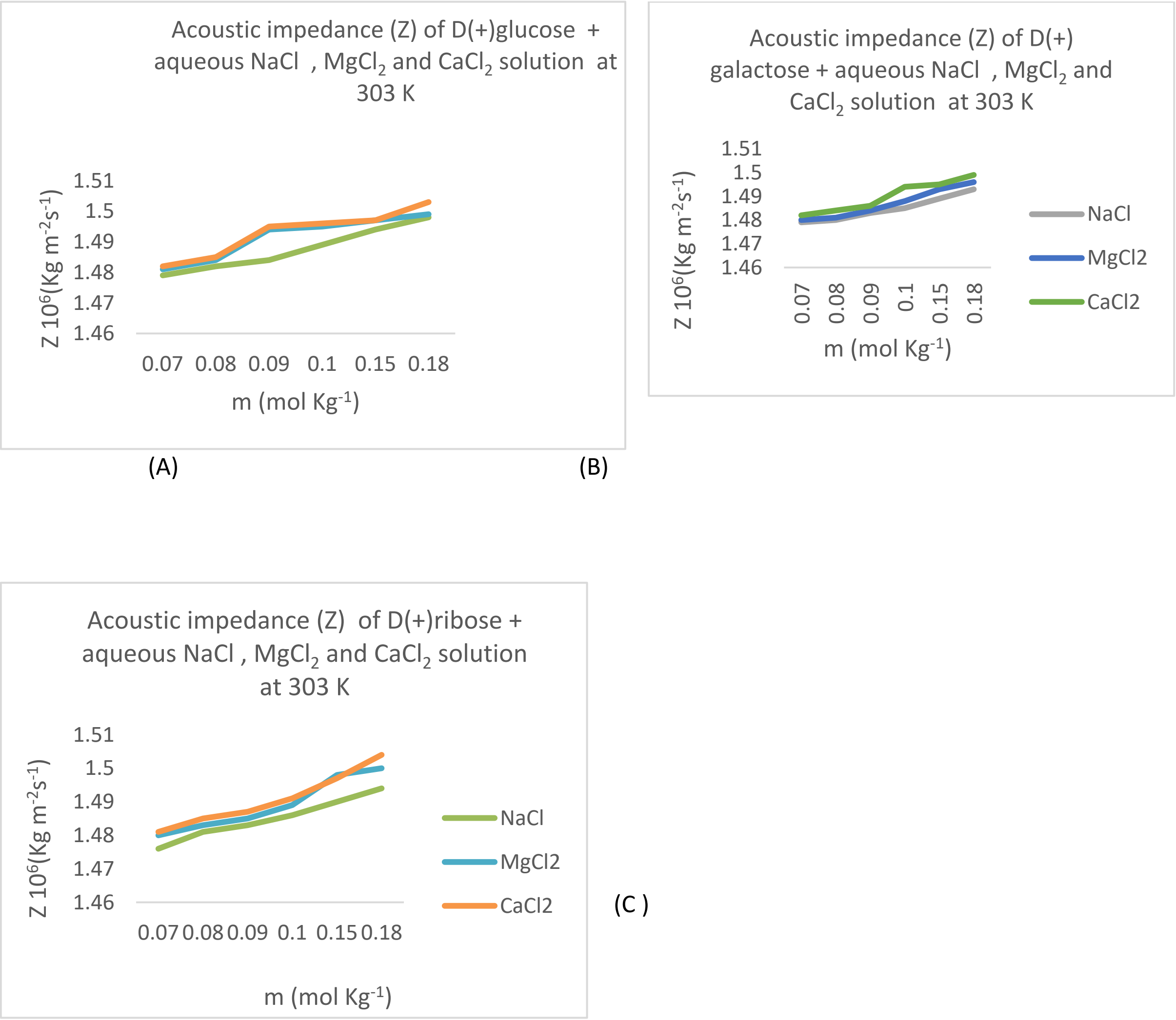
Fig. 3. Adiabatic Compressibility of D(+) glucose, (A), D(+) galactose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

B. Acoustic impedance

The values of acoustic impedance, Z of these ternary systems were calculated by the following relation and are reported in "Fig. 4".

$$Z = u \, . \, \rho \qquad (3)$$

In "Fig. 4",the values of Z increase with increase in molality of electrolytes which indicates solute-solvent interaction are strong and they behave as structure makers. 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^+, 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 (glucose, galactose and ribose) and solvent (aqueous NaCl, $MgCl_2$ and $CaCl_2$) molecules, which maximum complex ion formation and become responsible for the propagation of ultrasonic wave.


Acoustic impedance (Z) of D(+)glucose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

Acoustic impedance (Z) of D(+) galactose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

Acoustic impedance (Z) of D(+)ribose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

(A)

(B)

(C)

Fig. 4. Acoustic Impedance of D(+) glucose, (A), D(+) galactose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

C. *Apparent molal volume*

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

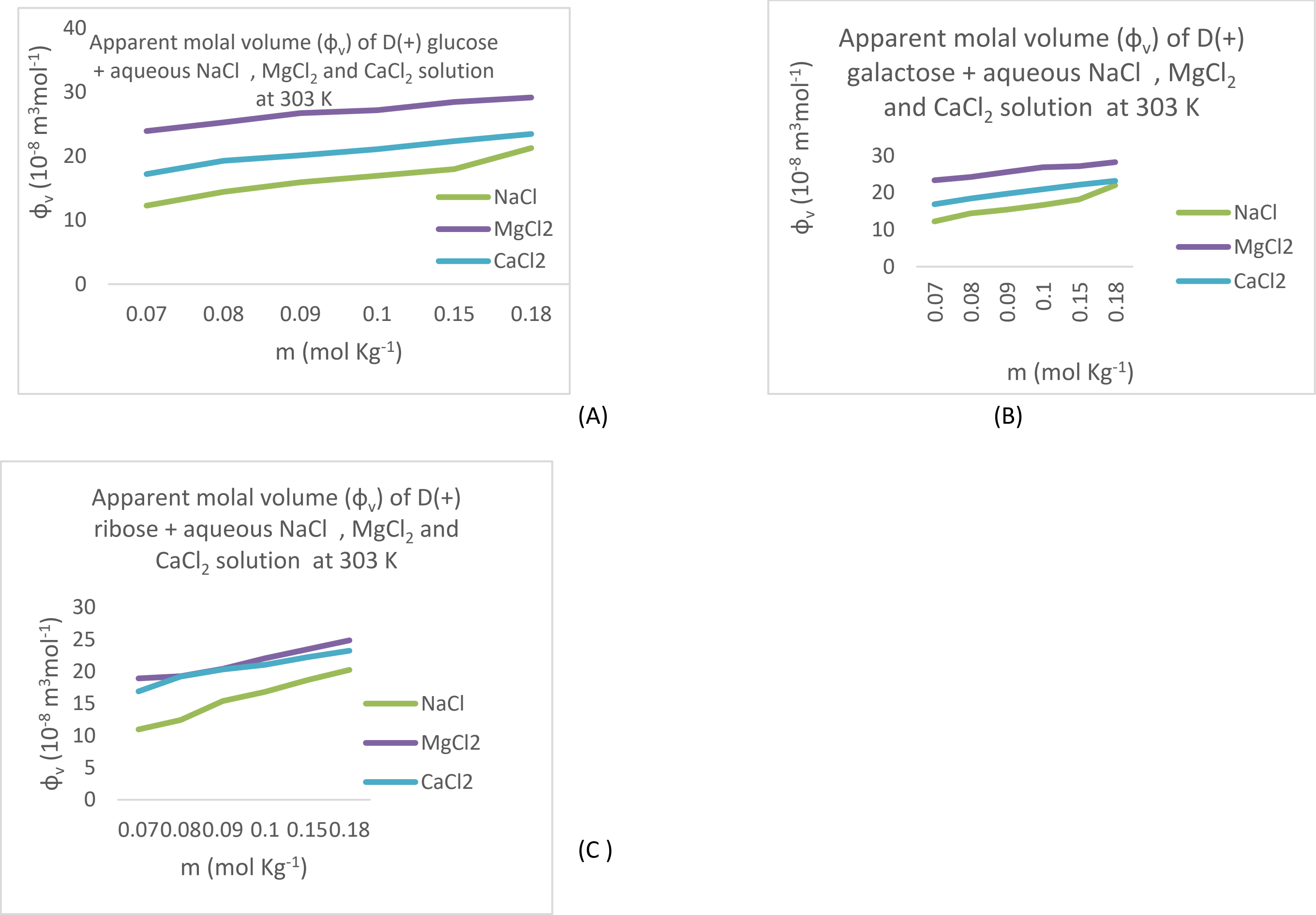
$$\phi_v = [1000\,(\rho^0 - \rho) / m\,\rho\,\rho^0] + M/\rho \qquad (4)$$

Where M is the molecular mass of the solutes, ρ^0 and ρ are densities of solvent and solution. In "Fig. 5" are given the calculated values of ϕ_v of these ternary systems. 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 Redlich–Meyer (13) type equation gives us an important quantity called limiting apparent molal volume ϕ^o_v. The quantity provides the solute-solvent interactions, because the solute-solute interactions can be ignored at infinite dilution and each solute molecule can only interact with solvent molecules which are surrounded The linear variation was obtained by least square fitting to the following Equation.

$$\Phi_v = \phi^0_v + S_v\, m \qquad (5)$$

The quantity S_v is the experimental slope and called as virial coefficient. The derived values ϕ^0_v of along with S_v are summarized in Table 3.Table 3 shows that the values of ϕ^0_v are positive of these ternary systems which indicates ion-solvent interactions are strong. The values of ϕ^0_v are less in presence of metal ions (Na^+) than those of divalent ions (Ca^{+2} and Mg^{+2}).

A mutual comparison of these electrolytes shows the values of ϕ^0_v are larger in case of Ca^{+2} and Mg^{+2} than in Na^+. 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 which is in good agreement with the results reported in glucose – alcohol – water mixture(11).



(A) (B)

(C)

Fig 5. Apparent molal volume, ϕ_v of D(+) glucose, (A), D(+) galactose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

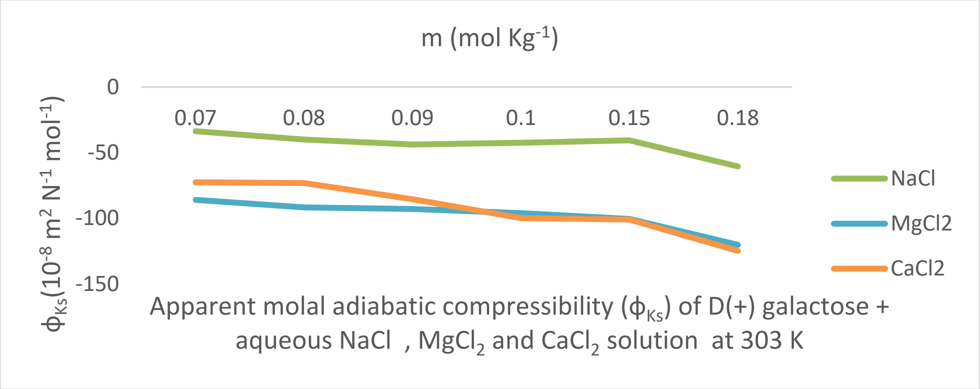
D. Apparent molal adiabatic compressibility

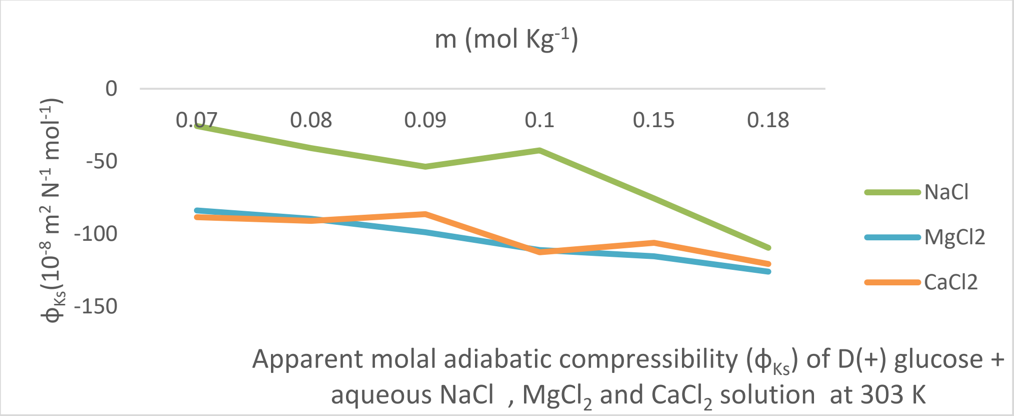
The density and adiabatic compressibility values were employed for calculated apparent molal adiabatic compressibility, ϕK_s of glucose, galactose and ribose in aqueous metal halides namely NaCl , $MgCl_2$ and $CaCl_2$ solution at different molality and at 303 K using the Equation.

$$\phi K_s = [1000\,(\rho^0 K_s - \rho K_s^0) / m\rho\,\rho^0] + M\,K_s/\rho \qquad (6)$$

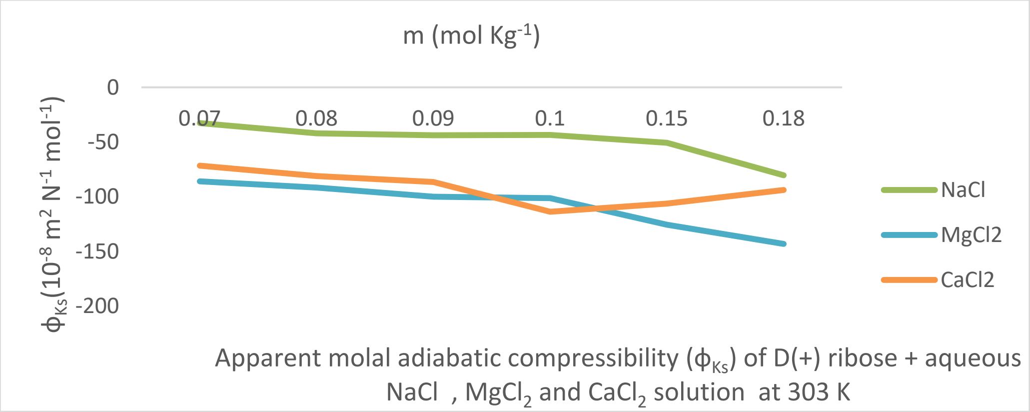
The "Fig. 6" shows that the less negative values of ϕK_s over the entire range of molality of the ternary systems which indicates strong solute-solvent interactions. The less negative values of ϕK_s are due to loss of structural compressibility of solvent on increase in the population of four bonded solvent molecule in the vicinity of the solute molecules.

(A)





(B)



(C)

Fig. 6. Apparent molal adiabatic compressibility, ϕ_{Ks} of D(+)galactose (A), D(+),glucose, (B) and D(+) ribose (C) + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K.

The limiting molal adiabatic compressibility, $\phi^{o}K_s$ are obtained from the plot of ϕK_s versus m by least square method. The molality dependence of this parameter has been expressed in terms of the following Equation.

$$\phi_{Ks} = \phi^{0}_{Ks} + S_{Ks}\, m \qquad (7)$$

Where ϕ^{0}_{Ks} is the limiting molal adiabatic compressibility. It provides information regarding solute-solvent interaction. S_{Ks} is the experimental slope. The values of ϕ^{0}_{Ks} and S_{Ks} are also included in Table 3. The less negative values of ϕK_s are due to loss of structural compressibility of solvent on increase in the population of four bonded solvent molecule in the vicinity of the solute molecules. The magnitude of negative values of ϕ^{0}_{Ks} 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 . The values of S_{Ks} are positive of these ternary systems which is indicating the presence of solute-solute interactions. From this tabulation, one can notice that the suggesting the weak solute-solute interactions in the ternary systems by others (13).

CONCLUSION

The acoustic and volumetric studies have been used to the solute –solute and solute-solvent interaction in these ternary systems. It can be concluded that the existence of molecular interaction is in the order of D(+) glucose > D(+) Galactose > D(+) ribose. This suggests D(+)glucose in aqueous electrolytes solution is strong structure maker. It has been observed that there exist strong solute-solvent interaction for saccharides with aqueous electrolytes were obtained and interpreted by the stereochemistry of the mono saccharide molecules and structural interaction model. A mutual comparison of these electrolytes shows the values of ϕ^0_v are larger in case of Ca^{+2} and Mg^{+2} than in Na^{+}. 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.

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TABLE 1

Densities (ρ) of D(+) Glucose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

m (mol Kg^{-1})	ρ(kg m^{-3})	ρ(kg m^{-3})	ρ(kg m^{-3})
0.07	982.2	982.2	983.7
0.08	982.1	983.2	984.4
0.09	983.9	984.2	985.3
0.10	984.4	985.9	987.2
0.15	986.3	987.2	989.5
0.18	988.2	989.2	990.2

Densities (ρ) of D(+)galactose aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

0.07	982.1	982.9	983.1
0.08	983.6	983.8	984.4
0.09	984.9	985.2	985.9
0.10	986.4	987.0	987.5
0.15	989.3	990.2	990.5
0.18	991.2	992.5	993.2

Densities (ρ) of D(+)ribose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

0.07	981.9	982.7	982.9
0.08	982.8	983.4	984.5
0.09	983.9	984.3	985.2
0.10	984.4	986.2	987.1
0.15	986.3	990.5	989.2
0.18	988.2	991.2	992.2

TABLE 2

Ultrasonic velocity (u) of D(+)glucose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

m (mol Kg^{-1})	u(ms^{-1})	u(ms^{-1})	u(ms^{-1})
0.07	1505.4	1506.3	1507.2
0.08	1506.3	1508.9	1508.9
0.09	1507.2	1509.8	1509.1
0.10	1509.7	1510.3	1510.8
0.15	1510.1	1512.5	1513.0
0.18	1511.5	1513.2	1513.6

Ultrasonic velocity (u) of D(+) galactose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

0.07	1505.2	1506.2	1506.8
0.08	1506.9	1507.5	1507.8
0.09	1507.2	1508.0	1508.9
0.10	1508.1	1509.5	1510.1
0.15	1509.4	1510.3	1511.4
0.18	1510.5	1512.2	1513.5

Ultrasonic velocity (u) of D(+)ribose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

0.07	1505.8	1506.2	1506.5
0.08	1507.2	1508.3	1508.9
0.09	1508.1	1509.1	1509.8
0.10	1509.9	1510.2	1510.8
0.15	1511.1	1512.1	1512.9
0.18	1512.2	1513.8	1513.9

TABLE 3

Limiting apparent molal volume ($\phi^o{}_v$) Limiting apparent molal adiabatic compressibility ($\phi^0{}_{Ks}$) and its experimental slope, (S_v) and (S_{Ks}), of D(+) glucose, D(+) galactose and D(+) ribose + aqueous NaCl , $MgCl_2$ and $CaCl_2$ solution at 303 K

m(mol.Kg^{-1})	$\phi^0{}_v$ (10^{-8} m^3 mol^{-1})	S_v (10^{-8} $m^3 mol^{-3/2}$ $l^{-1/2}$)	-$\phi^0{}_{Ks}$ ($10^{-8} m^5 N^{-1} mol^{-1}$)	-S_{Ks} (10^{-8} $m^5 N^{-1} mol^{-3/2}$ $l^{-1/2}$)
		glucose + water + NaCl		
0.5	28.52	65.00	7.15	4.38
		glucose + water + $CaCl_2$		
0.5	29.40	82.02	8.29	11.10
		glucose + water + $MgCl_2$		
0.5	33.20	75.01	9.24	16.00
		galactose + water + NaCl		
0.5	27.42	61.00	13.15	7.18
		galactose + water + $CaCl_2$		
0.5	29.32	78.02	9.29	6.67
		galactose + water + $MgCl_2$		
0.5	32.20	69.08	15.2	12.98
		ribose + water + NaCl		
0.5	25.32	63.60	6.91	4.21
		ribose + water + $CaCl_2$		
0.5	28.38	79.12	8.17	10.50
		ribose + water + $MgCl_2$		
0.5	28.90	73.08	9.14	14.80