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ULTRASONIC STUDIES ON SOME AQUEOUS SOLUTIONS OF CARBOHYDRATES AT THREE DIFFERENT TEMPERATURES

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Density, viscosity and ultrasonic velocity measurements have been performed by ultrasonic interferometer technique in some aqueous solutions of three carbohydrates (sucrose, D-glucose and β-D lactose) as a function of molality with different concentration of the order 0.1 to 0.5 mole/kg. At three different temperatures, via 303.15K, 313.15K and 323.15K and at atmospheric pressure, ultrasonic velocity, partial molar volumes, partial molar isentropic compressibility have been calculated and plotted against concentration. The velocity results confirm the conclusions that were originally derived from viscosity data by Einstein that the sugar molecules have a 'salvation envelope' attached with a layer of water molecules which decreases with thickness as the temperature of the solution rises. It has been observed that in such solutions it is quite legimate to look for the dispersion caused by viscosity of the solutions. The apparent molar volume occupied by solute molecules remains constant at one particular temperature, irrespective of the change in concentration of sucrose in water. The compressibility increases slowly as a function of concentration at constant temperature. The data revealed that the compressibility of these different solutions is related with three diamensional hydrogen bond water structure. It is governed by the stereochemistry of carbohydrate. By these studies an overview of the hydration characteristics and the effect of relative position of hydroxyl group within a carbohydrate molecule is given. By increasing the carbohydrate concentration in water the ultrasonic velocity increases, while there is no effect on compressibility of moles. For monomer the apparent molal compressibility depends on the hydration of the mole. The results agree with the previously obtained kinematics data of literature values.

Key words**:** Carbohydrates, Concentration, Density, Viscosity, Isentropic compressibility, Ultrasonic velocity, Apparent molar volume.

Introduction

The velocity of elastic waves in solution is defined by solute-solvent and solute-solute interactions which are determined by the chemical structure of the solute and solvent molecules. (Nobuo and Kyoshi 1974). However, a clear cut picture of results have been obtained by uncertainities about intrinsic volumes of solute molecules. Still acoustical methods have been developed, with only a minor contribution to the detailed description of the solute-solvent interactions of molecules in aqueous solutions. The successful applications of acoustical methods to the physicochemical investigation of solution became possible after the development of adequate theoretical approach and methods for the precise ultrasonic velocity measurements in small volume of liquid mixture.

Enormous literature is available on the physical and chemical nature of carbohydrates molecules and their structure, most of them are monomers and some are dimmer. Glucose is a dimmer, which is able to rotate about its linkage such that the hydrophobic surfaces were bound through intermolecular forces. These have much interaction for water molecules and it seems reasonable to expect the voids in volume associated with each solute molecule (Paul *et al* 1999). A group of physicts in USSR (Shel'nikov and Privie 1991) have worked on the bulk elastic properties of glucose, galacotose, lactose, sucrose and starch. From their data on ultrasonic velocity and the density of the solutions, the hydration number of carbohydrates in relation to the stereo chemistry have been a subject of study since a long time and due to their importance in our life (Blanshard and Mitchell 1979).

The compressibility of solution can be determined by the effect of solvent, solute and solution. (Roscoe 1952; Mark 1960). The effect of solute molecules can be separated into three parts, the compressibility of solute molecules, solute-solute interactions and the size of the molecule. If the concentration of the solution becomes very low, the second effect becomes negligible (Pryor and Roscoe 1954) measured the ultrasonic velocity of the solution of sucrose and sacchride from the temperatures of 20°C to 80°C and they showed qualitatively that the salvation envelop decreases in size with increasing temperatures, provided the sugar molecules could

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be regarded as incompressible but they did not approach to zero concentration.

It is a well-known fact that in solution of electrolytes, the water molecules are bound to the electrolytic ions that are compressed owing to the strong electric field within the ions to form a hard structure. From the literature (Arakawa and Sasaki 1972), it is seen from the adiabatic compressibility measurements, the degree of hydration can be evaluated. They assumed that the compressibility of bound water and of the ions itself is negligibly small. Shio (1958) has deduced a more general formula for the amount of bound water by taking into the account, the compressibility of bound water and of solute particles. This was applied to solutions of three carbohydrates (sucrose, β-D-lactose and glucose). Details of few parameters related with this structure study at three temperatures can be found here.

The partial molar volume V_ϕ. It is informative for a solution of the character of solute-solvent interactions. It is the sum of the intrinsic volumes of the solute and the volume contribution due to a solute-solvent interactions (Miller *et al* 1997)

V_ϕ = Vintrinsic + Vsolute + solvent

Isentropic partial molar compressibility β_o. This is a pressure derivative of partial molar volume V^o. It will directly reflect the carbohydrate+water interactions. If it is assumed that molecules of all carbohydrates are incompressible. The compressibility can be measured at constant temperature or at constant entropy. In order to determine the isothermal apparent molar compressibility, we have to know about its expansibility and heat capacity of the solution to calculate from the isentropic compressibility. The isentropic and isothermal compressibilities are different numerically, however when one is interested to use either of them. (Arakawa and Sasaki 1972).

The purpose of this study is to discuss the results of a physico-chemical study on three carbohydrates water mixtures with varying viscosity and density measured at three different temperatures. Ultrasonic velocity that potentially seems viable deals with our investigation of the thermodynamic and transport properties of these mixtures. This work is in continuation of our previous investigation by ultrasonic properties of liquids glycol and their mixtures.

Materials and Methods

All the carbohydrates (sucrose, D-glucose, β-D lactose) taken were made anhydrous. Carbohydrates were supplied by Koch Light Laboratories, France, (Analar grade) and dried in a vacuum oven at 333K before use. The low conductivity water was used for preparing the solution, which were made by passing distilled water through a cation anion resins. The specific conductance of water was 5×10^{-8} ohm/cm. All the solutions were prepared by weight percentage and the necessary corrections were applied for the water content in carbohydrates. The doubly distilled water was used for making the solution. All the samples were kept in glass stopper flasks. All the measurements were carried out at each temperature for five different concentrations of every carbohydrate. The same solutions were used for density, viscosity and isentropic compressibility measurements.

Sample preparation. The mixtures were prepared by mixing known mass of carbohydrates in pure water in an air tight ground stopper bottle taking due precautions for exposing them from the humid atmosphere. All the weights were taken on an Ohaus electronic balance accurate down to ±0.01 mg, the possible error in the mole fraction is estimated to be less than $\pm 2.5 \times 10^{-4}$ mg.

Density measurements. Density of each solution was measured at 303.15K, 313.15K and 323.15K by using Pycnometer, (Limpkins double stem with volume 18 ml). The Pycnometer was calibrated with conductance water immediately after density measurement, the error in the density measurement was estimated to be $\pm 3 \times 10^{-3}$ kg/m^3.

Viscosity measurements. The viscosity of each solute and solvent (sugar solution) was conducted independently by 'Happler's falling ball viscometer at various temperatures within an accuracy of ±1%. The apparatus is calibrated each time against the standard solutions before measurements of the viscosity. It is determined from the rate of fall of steel ball using the formula (1) (Weissberger A 1959).

Viscosity can be evaluated by Equation (1):

η = KT (ds-dl)/dt .... (1)

Where, K is the Boltzman's constant and T is the absolute temperature, ds and dl are the density of solid ball and density of liquid.

Compressibility and velocity measurements. By the interferometer technique of ultrasonic wavelength measurements, see for pictorial representation of diagram (Ahmad *et al* 2000) in which a conventional 300W of power output from Scholler (USLG-300) is an ultrasonic wave generator was employed for producing longitudinal stress waves. They excite the x cut crystal (Piezoelctric transducer) through a 50 ohm line in the presence of an air pressure of 50 Lbs/inch^2. On the top of the transducer is a water seal proof glass cell, is the liquid sample holder is placed for measuring the wavelength of the waves.

The interferometer can have a great advantage for good parallelism by micrometer position. The surface of the transducer and the parallelism is established by the application of pulse echo method. The piezoelectric transducer is driven through loosely coupled coils by a source of constant frequency (2.0 MHz) and the current across the crystal which is indicated in milliampere meter. By moving the variable ganged capacitor in the master oscillator, the sharp resonant frequency is selected from the upper face of the transducer and are sent through liquid to the reflector, By means of the micrometer the separation between the reflector and transmitter can be varied while in turn it produces the phase change of the waves incident on the receiving plate of the micrometer. It produces a variation in the output current of the generator which repeates as the phase of the wave by odd multiple of λ in the liquid mixture. The principle is known as single round (Gamsey *et al* 1969), which involves the passage of repeated pulses of ultrasonic waves through the solution and measurement of wavelength of these radiations.

Frequency measurements. The frequency of the ultrasonic waves were measured by frequency counter TRIO- FC 754-A (Keenwood) Japan, with display time 1 sec averaging over a period of 10 sec with full scale deflection of 10Hz to 500MHz.

Temperature measurements. A glass thermometer with a least count of 0.01°C/div was used for liquid temperature measurements.

Calculation of ultrasonic parameters. *Ultrasonic velocity, V*: By varying the Screw Gauge head position up or down which is connected with reflector and immersed in liquid, the reflector is moved through each λ multiplying with the frequency of the waves, the ultrasonic velocity is calculated as:

$V = (\lambda \text{ meter x frequency MHz}) \text{ m/sec}$ .... (2)

Partial molar volume V_ϕ: After measuring the density of the liquid carbohydrates solutions at different molalities, the apparent partial molar volume can be obtained by using equation 3:

$V_\phi = 1000(d-d_0)/mdd_0 + M_2/d^* \text{ cm}^3\text{/mole}$ .... (3)

Where, m is the molalities of carbohydrates, M_2 is the molar mass of the carbohydrate, the partial molar volume is obtained by plotting the apparent partial molar volume against molality (Rod *et al* 2000). d*, density of solution and d_0 is density of water.

Isentropic compressibility coefficient β_s: They were measured by monitoring the speed of sound through a solution in an adiabatic and reversible way, which ensures that the compressibility is isentropic from this data, the compressibility coefficient β_s can be obtained, by equation 4:

$\beta s = 1/u^2 \underline{\sim -} 1/V\,(dV/dP)_s$ .... (4)

Where, 'u' is the speed of sound in liquid and 'd' is the density of liquid, 'V' is the volume and 'P' is the atmospheric pressure. The 'β_s' can be used to calculate the apparent partial molar compressibility, K_ϕ via the different method.

$K_\phi = 1000(\beta_s-\beta_{so})/md + \beta_s V_\phi \text{ cm}^3\text{/mole/bar}$ .... (5)

Where, (β_s and β_{so}) are the isentropic coefficient of compressibility of the solution and water respectively, 'm' is molality of the carbohydrate, 'd' is the density of solution and 'V_ϕ' is the apparent molar volume at that concentration. By definition the limiting value of the isentropic apparent molar compressibility $K_s(\phi)$ is equal to the isentropic partial molar compressibility:

$K_2(\phi) = K_\phi(s) + mdK_\phi/dm$ .... (6)

Results and Discussion

Analysis. When anhydrous sucrose or glucose is dissolved in water, the volume of the resulting solution is almost equal to the sum of the volumes of water plus solid sugar particles. The ratio of the volume of sugar particles to the volume of solution thus gives the fractional volume of the solution occupied by the sugar molecule. Since a water molecule is much smaller in size than a sugar molecule, it is reasonable to suppose the solution to behave as suspension of solid particles occupying fractional volume c in homogeneous liquid. The solid particles are regarded as compressible, since the compressibility of individual sugar molecules must be very much less than the pure water, so that the adiabatic compressibility of the solution should be:

$\beta = \beta_o (1-c)$ .... (7)

Where, β_o is the adiabatic compressibility of water. The viscosity of sugar solution can also be treated by regarding a solution as suspension of solid particles occupying a fractional volume c in a homogeneous liquid. Here again when ultrasonic waves are passed through this suspension, the dispersion of the waves takes place due to particles and the temperature of the solution rises and the viscosity decreases. The collision force of ultrasonic waves, is of the right order, but the decrease in viscosity with rise in temperature, is observed at high concentration. The observed values of heat of solution are always higher than calculated values. Assuming that the volume of sugar molecules is effectively increased by a layer of attached water molecules (Panday *et al* 1987).

We have chosen to measure isentropic compressibility through these molar measurements. The following points are worth mentioning in regard to its molecular structure.

- By increasing the carbohydrate concentrations in water

Table 1

Measured and calculated values of results of thermodynamic measurements at three temperatures (303.15K, 308.15K and 313.15K) for sucrose + water solutions

S. no.	Temp. in K	Conc. mole/kg	Density kg/m^3	Viscosity c poise	Velocity m/sec	Partial molar volume V^E cm^3/mole	Isentropic compressibility cm^3/mole/bar x10^4
1.	303.15	0.1	1028.1	1.0021	1483.50	126.33	-17.66
		0.2	1036.0	1.0191	1488.80	128.14	-17.33
		0.3	1040.0	1.0212	1493.20	123.33	-17.06
		0.4	1041.0	1.0342	1496.10	126.25	-16.92
		0.5	1043.1	1.0591	1499.00	125.75	-16.75
2.	313.15	0.1	1046.7	1.1179	1501.50	133.33	-16.66
		0.2	1045.5	1.1190	1507.33	139.12	-16.11
		0.3	1048.3	1.1221	1519.19	140.55	-15.33
		0.4	1057.0	1.1371	1522.44	141.25	-15.25
		0.5	1059.1	1.1443	1528.22	141.33	-15.07
3.	323.15	0.1	1055.4	1.0021	1495.55	142.11	-12.55
		0.2	1063.3	1.1221	1499.33	143.14	-11.03
		0.3	1109.3	1.0212	1517.11	144.52	-10.55
		0.4	1114.7	1.0342	1529.33	145.34	-10.15
		0.5	1119.5	1.2171	1533.40	146.77	-09.87

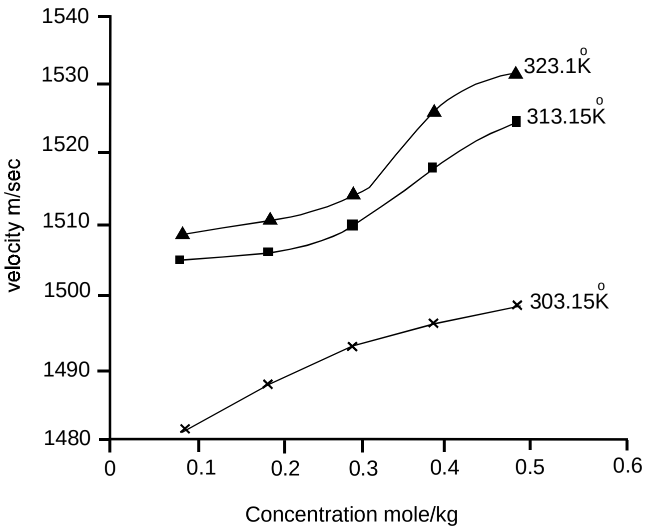

Fig 1. Variation of ultrasonic velocity with concentration at three different temperatures for sucrose + water.

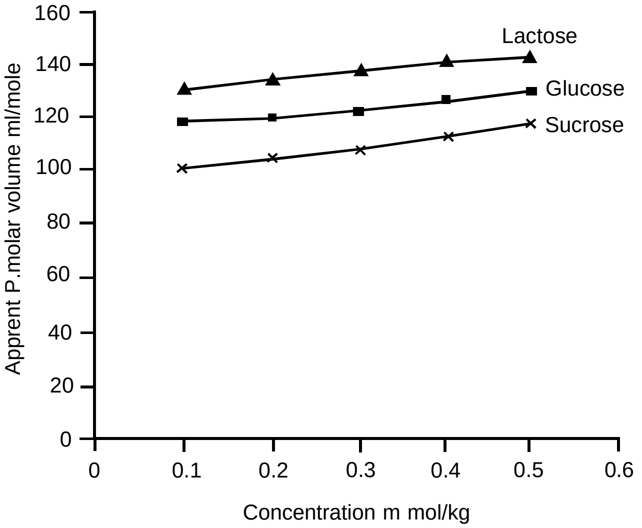

Fig 2. Apparent partial volumes as a function of concentrations of three different carbohydrates molecule at 303.15K.

the ultrasonic velocity increases, while there is slow rise in compressibility of moles at each temperature. See Fig 1, 2 and 3.

- Density is an important quantity in a sense it dictates how much free volume is available to each carbohydrate molecule in the system.

- The limiting values of isentropic compressibility directly gives insight into the compressibility of the hydration layer compared to that of pure water. The relative position of OH determines the hydration characteristics of such molecules.

- The molecular picture is that the distance between the oxygen and next nearest neighbor OH group within the carbohy-

Table 2
Measured and calculated values of results on thermodynamic measurements at three temperatures via 303.15K, 308.15K and 313.15K for glucose + water solutions

S. no.	Temp. in K	Conc. mole/kg	Density kg/m^3	Viscosity cp	Ultrasonic velocity m/sec	Partial molar volume V^E cm^3/mole	Isentropic compressibility cm^3/mole/bar x 10^4
1.	303.15	0.1	951.44	0.981	1505.00	126.33	-21.10
		0.2	953.20	0.987	1507.33	128.14	-21.30
		0.3	957.11	0.991	1512.20	123.33	-21.10
		0.4	959.55	0.998	1522.40	126.25	-20.44
		0.5	962.25	1.013	1528.20	125.75	-19.22
2.	313.15	0.1	988.30	1.022	1522.50	126.33	-19.00
		0.2	965.00	1.013	1497.00	128.14	-18.75
		0.3	967.30	1.008	1499.20	123.33	-18.55
		0.4	1008.00	1.005	1506.10	126.25	-18.44
		0.5	1015.10	1.091	1509.22	156.05	-18.33
3.	323.15	0.1	1015.10	1.087	1533.50	126.33	-18.22
		0.2	1019.50	1.097	1523.90	128.14	-18.13
		0.3	1025.30	1.118	1527.00	123.33	-18.10
		0.4	1033.00	1.125	1536.20	126.25	-18.02
		0.5	1037.30	1.132	1539.20	162.05	-18.00

The velocity of sound in distilled water = 1479 m/sec at 30°C; Formula wt of glucose (anhydrous)=342.32

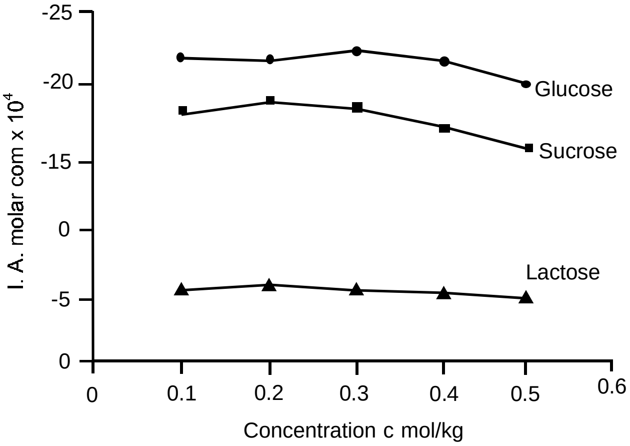

Fig 3. Isentropic apparent molar compressibility (negative values) as a function of concentrations of three different carbohydrates at 303.15K.

drate molecule is comparable with the oxygen distance between the water molecule.

- In this experimental study a molecular model resembles with that of Enistein model (Blanshard and Mitchell 1979), that a sugar molecule has a solvation envelope attached with a layer of water.

- Since glucose is a dimmer, which is able to rotate about its linkage such that hydrophilic surfaces were bound by intermolecular force and which increases the net hydrophilic character (Mark 1959).

- It is found through literature that hydration of carbohydrate is mostly dependent on the relative position of OH within the nearest neighbor in the bond structure. As we have evaluated in the above three carbohydrates, which have small partial molar volume due to extensive solute solvent interactions.

Conclusion

The following conclusions have been drawn from the above results on carbohydrates+water solutions within the limits of certain experimental errors:

- The sound velocity in such solutions depends upon concentration or viscosity. It increases with concentration of carbohydrates in water showing no complex formation which can occur in the above concentration region at one particular temperature. Density is particularly an important quantity to evaluate how much free volume is available to each molecule in the solution and there is a correspondence between free volume and density.

- At each temperature in the above three sugar solutions there is an increase in the partial molar volume which shows a formation of intermolecular hydrogen bonds (Miller *et al* 1997).

- The viscosity of sugar solutions can also be treated by regar-

Table 3

Measured and calculated values of results of thermodynamic measurements at three temperatures via 303.15K, 313.15K and 323.15K for β-D lactose + water solutions depending upon the constant values*

S. no.	Temp. in K	Conc. mole/kg	Density Kg/m^3	Viscosity cp	Ultrasonic velocity m/sec	Partial molar volume V^E $cm^3/mole$	Isentropic compressibility $cm^3/mole/bar \times 10^4$
1.	303.15	0.1	1021.33	1.1121	1509.55	103.22	-6.00
		0.2	1015.22	1.1990	1512.11	104.14	-6.00
		0.3	1019.14	1.1198	1517.32	107.33	-5.70
		0.4	1022.50	1.2390	1529.11	106.22	-5.50
		0.5	1032.25	1.2419	1533.44	109.75	-5.22
2.	313.15	0.1	1061.25	1.2401	1523.00	110.00	-5.03
		0.2	1075.33	1.2231	1527.33	111.15	-4.97
		0.3	1077.00	1.3081	1521.11	114.55	-4.80
		0.4	1083.00	1.3750	1536.11	115.15	-4.72
		0.5	1085.00	1.3910	1549.22	116.05	-4.22
3.	323.15	0.1	1088.22	1.4050	1483.55	122.22	-4.06
		0.2	1092.05	1.4130	1553.99	126.14	-4.05
		0.3	1082.07	1.4280	1.564.12	128.55	-4.00
		0.4	1177.00	1.4340	14.96.10	130.15	-4.00
		0.5	1167.33	1.4310	1582.22	131.05	-3.90

*Molar compressibility of pure water $\beta_o = 8.17 \times 10^{-4}$ cm^3/mole/bar; Formula weight of β-D lactose (anhydrous) = 342.32

ding a solution at suspension of solid particles occupying a fractional volume c in a homogenous liquid. (Roscoe 1952), when elastic waves were passed through the solution the heat energy is produced.

- The negative values of partial molar compressibilities of the three samples shows a type of linkage between their subunits at constant temperature or entropy, obvious from Fig 3. The negative values of compressibility suggests that when ions are introduced in to water they break the water structure by electro restriction force, the water around the ion is dense and less compressible.

- The amount of bound water in cc/g can be determined in by evaluation of compressibility.

- The limiting values of compressibility of the three solutions directly gives insight in the compressibilities of hydration layer compared to that of pure water i.e. 8.17×10^{-4} cm^3/mol/bar.

- The hydration number of such carbohydrate mixture depends on their composition (weight %) with water and temperature and detailed microscopic model (Uedair and Ikura 1989).

- Through this kinetic experiment we have tried to substantiate our results by measuring ultrasonic velocity at 303.15K 323.15K and 313.15K.

- These results show that OH radical plays an important role in the equilibrium and biochemical properties of solutions. The ultrasonic study seems to provide an adequate technique for the study of complex formation ion within these solutions.

- At infinite dilution the partial molar volume equal to the apparent partial volume (Gelma *et al* 1990).

- The above results are in good agreement with literature values (Paul *et al* 1999).

- Within the range of cm^3 mole/bar/concentration for each sample, the partial molar volume rises slowly for one temperature and at constant pressure as shown in Fig 2.

- Pressure derivative of partial molar volume will directly reflect carbohydrate + water interactions, if it is assumed that their molecules are incompressible.

- The viscosity of sugar solutions increases very slowly at low temperature. The solid particles occupying a fractional volume c in a homogenous liquid.

- The equilibrium composition of a carbohydrate in water is strongly affected by pressure which was reported by (O'Connor *et al* 1983).

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