ULTRASONIC STUDIES OF INTERMOLECULAR INTERACTIONS IN SOME CARBOHYDRATES

(DEXTROSE, FRUCTOSE AND INOSITOL) AT 398.15 K.

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Abstract:

Ultrasonic velocity, density and viscosity have been measured experimentally of aqueous solution of dextrose, fructose and inositol at 398.15 K over the entire composition range. The thermodynamic and other parameters like adiabatic compressibility, free length, free volume, internal pressure, Gibb's free energy and enthalpy etc. have been worked out. These parameters are analyzed in the light of bonding and non-bonding inter molecular interactions as well as discrimination in functional group isomerism.

Keywords: Ultrasonic velocity, Aqueous solution, Internal pressure, Gibb's free energy, Isomerism.

Introduction:

The study of bonding and non-bonding inter molecular interactions play an important role in the development of molecular sciences. Large studies have been made on the molecular interaction in liquid systems by various spectroscopic methods (Shanmuga P.C, 2019). Ultrasonic investigation provides wide applications in characterizing thermodynamic and physiochemical behavior of liquid mixture (Palani R, 2011). These acoustical parameters provide qualitative information about physical nature and strength of molecular interaction in liquid mixtures (Palani R, 2011). During the last two decades the ultrasonic study of the carbohydrates in aqueous electrolytic medium, has gained much importance in assessing the nature of molecular interaction present in

the mixture (Sanjibita D, 2012). The study of the carbohydrates or saccharides has become a subjects of growing interest because of multi dimensional, physical, biochemical and scientifically useful molecules (Anjana,2011). Due to complex molecular structure of polysaccharides, straight study is complicated. Therefore, the useful approach is to study simpler form of compounds, such as dextrose, fructose and inositol which are building blocks of polysaccharides (Mujahid K ,2011). Most of the studies on carbohydrates have been carried out in pure and mix solvent. Most of the studies have been done concerning to the intermolecular interaction of carbohydrates in electrolytes and non electrolytes medium (Rajesh M.,2006). Present work is emphasis on the molecular interaction and isomeric relationships.

MATERIALS AND METHODS

The solutions of dextrose, fructose and inositol were prepared by dilution method. All the chemicals are of AR grades of 99.99 % purity. The solution of these compound is prepared in the range 0.1 M to 0.9M.

The ultrasonic velocity in the liquid mixtures have been measured by means of ultrasonic interferometer (Mittal type : Model: M-83) functioning at frequency 2MHz with an overall accuracy of ±0.1 m/s, an electronically digital operated constant temperature water bath has been used to flow water through the double walled measuring cell, made up of a steel containing the experimental solution at the preferred temperature. An Ostwald's viscometer was used for the measurement of viscosity of liquid mixtures with an accuracy of 0.0001 N s/m^2. The viscometer was calibrated before used. Time flow of water and liquid solutions were measured. Densities were determined using specific gravity bottle by relative measurement method with accuracy of ±0.1 kg.m$^{-3.}$

Results and Discussions: Using experimatentally measured values of ultrasonic velocity and density are evaluated (Saravanakumar K.2010) . The parameters are considered on the basis of theory as given below:

Adiabatic compressibility can be intended from speed of sound (U) and density (ρ) of the measurement.

$$\beta = 1/U^2\rho$$

Intermolecular free length can be determined as:

$$L_f = K\,\beta^{1/2}$$

where K values from different temperatures were taken from the work of Jacobson**.**

Free volume (V$_f$) in terms of ultrasonic velocity (U) and the viscosity of liquid (η)as:

$$V_f \;=\; [M_{eff}\,U\,/\,K\,\eta]$$

M$_{eff}$-effective molar mass, K= 4.28×10^9 , η -viscosity of solution.

 Relaxation time is obtained using equation;

$$\tau = \left(\frac{4}{3}\right)\eta\,\beta_a \quad \text{sec} \qquad (6)$$

Internal pressure (π$_i$) can be calculated by expression.

$$\pi_i = bRT\,(K\eta/u)^{1/2}(\rho^{2/3}/M)^{7/6}\ Nm^{-2} \qquad\qquad (7)$$

where R is the gas constant, M is the effective molecular weight, ρ is the density, u is the velocity of sound, T is the temperature, η is the viscosity and K is the temperature independent constant.

Gibb's free energycan be calculated from the following relation (Mujahid K.,2011) .

$$\Delta G = KT\log(KT\tau/\,h) \qquad\qquad (8)$$

where, τ is relaxation time, K is Boltzmann constant, T is absolute temperature and h is Plank's constant.

Table-1. Values of density(ρ), Viscosity(η),Ultrasonic velocity(u), compressibility, free volume, free length, internal pressure, relaxation time and Gibb's Free energy at 298.15 K of aqueous solution of Dextrose.

Conc. m, mola l	Density (ρ), Kgm^{-3}	Viscosity (η) X 10^{-3} Nsm^{-2}	Ultrasonic Velocity (u) ms^{-1}	Comprss-bility (β) x10^{-10} m^2/N	Free Volume (V$_f$) x10^{-8} m^3	Free Length (L$_f$) x10^{-11} m	Internal pressure π_i x10^{9}Nm^{-2}	Relaxation time (r) x10^{-13}s	Gibb's free energy (ΔG) x10^{-21} KJ/mol.
0.9	1058.1	1.003	1560	3.8835	2.6760	3.8625	1.9966	5.3385	4.9394
0.8	1049.9	0.995	1556	3.9339	2.6783	3.8875	2.0291	5.2190	4.8462
0.7	1041.8	0.945	1557	3.9594	2.7522	3.9001	2.0463	4.9889	4.6605
0.6	1034.4	0.883	1551	4.0187	2.8754	3.9291	2.0542	4.7313	4.4423
0.5	1025	0.850	1542.4	4.1009	2.8602	3.9691	2.0951	4.6477	4.3688
0.4	1019.5	0.818	1538.8	4.1423	2.8544	3.9891	2.1418	4.5179	4.2522
0.3	1012.9	0.789	1532	4.2064	2.8237	4.0198	2.1964	4.4251	4.1668
0.2	1007.3	0.768	1529.6	4.2431	2.7608	4.0373	2.2651	4.3449	4.0915
0.1	1001.9	0.743	1524	4.2974	2.7086	4.0631	2.3361	4.2572	4.0075
0.0	997.4	0.713	1512.8	4.3809	2.6677	4.1024	2.4106	4.1648	3.9171

Table-2. Values of density(ρ), Viscosity(η),Ultrasonic velocity(u), compressibility, free volume, free length, internal pressure, relaxation time and Gibb's Free energy at 298.15 K of aqueous solution of Fructose.

Conc. m, mola l	Density (ρ), Kgm^{-3}	Viscosity (η) X 10^{-3} Nsm^{-2}	Ultrasonic Velocity (u) ms^{-1}	Comprss-bility (β) x10^{-10} m^2/N	Free Volume (V$_f$) x10^{-8} m^3	Free Length (L$_f$) x10^{-11} m	Internal pressure π_i x10^{9}Nm^{-2}	Relaxation time (r) x10^{-13}s	Gibb's free energy(ΔG) x10^{-21} KJ/mol.
0.9	1058.3	1.04	1575	3.8091	2.6951	3.8253	1.9921	5.261	4.879
0.8	1050.0	0.997	1566.4	3.8815	2.6970	3.8615	2.0245	5.159	4.799
0.7	1042.1	0.921	1561.6	3.9350	2.8732	3.8880	2.0176	4.832	4.529

0.6	1034.5	0.871	1563.6	3.9538	2.9709	3.8973	2.0321	4.591	4.318
0.5	1026.4	0.830	1547.2	4.0699	2.9781	3.9541	2.0690	4.504	4.239
0.4	1020.1	0.801	1534.4	4.1641	2.9331	3.9996	2.1232	4.447	4.187
0.3	1013.3	0.765	1533.6	4.1960	2.9623	4.0149	2.1622	4.279	4.029
0.2	1008.2	0.750	1528.2	4.2479	2.8568	4.0396	2.2404	4.247	3.998
0.1	1002.1	0.728	1522.4	4.3055	2.78843	4.0669	2.3139	4.179	3.931
0.0	997.4	0.713	1512.8	4.3809	2.66774	4.1024	2.4106	4.164	3.917

Table-3. Values of density(ρ), Viscosity(η),Ultrasonic velocity(u), compressibility, free volume, free length, internal pressure, relaxation time and Gibb's Free energy at 298.15 K of aqueous solution of inositol.

Conc. m, molal	Density (ρ), Kgm^{-3}	Viscosity (η) X 10^{-3} Nsm^{-2}	Ultrasonic Velocity (u) ms^{-1}	Comprss-bility (β) x10^{-10} m^2/N	Free Volume (V$_f$) x10^{-8} m^3	Free Length (L$_f$) x10^{-11} m	Internal pressure π_i x10^{9}Nm^{-2}	Relaxation time (r) x10^{-13}s	Gibb's free energy(ΔG) x10^{-21} KJ/mol.
0.9	1065.6	1.04	1589.6	3.7139	2.7208	3.7772	1.9951	5.1449	4.7874
0.8	1056.4	0.977	1584.8	3.7689	2.8294	3.8051	2.0003	4.9097	4.5946
0.7	1046.8	0.915	1568	3.8854	2.9194	3.8634	2.0124	4.7402	4.4500
0.6	1038.9	0.876	1565.4	3.9280	2.9506	3.8845	2.0425	4.5879	4.3155
0.5	1032.0	0.834	1562.4	3.9695	3.0004	3.9050	2.0716	4.4140	4.1565
0.4	1016.3	0.811	1558.4	4.0515	2.9468	3.9451	2.1143	4.3810	4.1256
0.3	1008.7	0.773	1537.6	4.1932	2.9278	4.0135	2.1644	4.3218	4.0695
0.2	1003.1	0.738	1533.6	4.2386	2.9423	4.0352	2.2111	4.1708	3.9231
0.1	1001.9	0.716	1518.4	4.3291	2.8475	4.0781	2.2972	4.1329	3.8855
0.0	997.4	0.713	1512.8	4.3809	2.6677	4.1024	2.4102	4.1648	3.9171

Table 1-3 shows the values of density, viscosity and ultrasonic velocity of solution of dextrose, fructose and inositol. With increase in concentration all these four parameters (compressibility, free volume, free length, internal pressure) are decreased indicate strong molecular interaction(Kumar R.,2013). These parameters are nearly same for

dextrose and fructose but slightly differ for inositol. All these three molecules are functional group isomers. Dextrose contains five –OH (hydroxyl) and one –CHO (aldehyde) groups, fructose contains five –OH and one –CO- (ketone) and inositol contains six –OH groups. Number of –OH groups in inositol are greater as compared to dextrose and fructose. It means that inositol molecules possessed stronger hydrogen bonding and association due to six –OH group as compared to dextrose and fructose. From the above result, it is found that functional group isomers play very important role in intermolecular association and dissociation.

Derived parameters like adiabatic compressibility, free length, free volume, internal pressure, relaxation time and Gibb's free energy are very important are shown in Table.1-3. A measure of how strongly molecules are held in liquid mixtures is their adiabatic compressibility, free length, free volume, internal pressure, relaxation time and Gibb's free energy. These are considered to be very important thermodynamic parameters. These parameters give information about how closed the liquid molecules are held, freedom of motion, the amount of empty space in liquid mixture, bulk properties of mixture (melting point, boiling point, solubility and fractional distillation) and different types of forces (dipole-dipole, ion-dipole, ion-induced dipole and dipole-induced dipole) in liquid molecules exit. Of these some parameters are directly and some are inversely related to the strength of intermolecular forces that exit in liquid mixtures. Intermolecular forces may be long range or short range forces. Long range forces are dispersion forces and electrostatic induction. They occur when molecules come close together causing a significant overlap of electron density having a specific geometry (Shanmuga P.C, 2019).

Adiabatic compressibility is the fractional decrease of volume per unit increase of pressure in isolated system. If the molecules are strongly associated, lesser will be its compressibility values and vice versa (Atkins

P.W.,1998). From Table 1-3, compressibility, free length and free volume are inversely related to concentration of solutions of dextrose, fructose and inositol.

From Table.1-3, internal pressure values inversely related to the concentration of solution. Internal pressure is cohesive forces, resultant of force of attraction and force of repulsion among the molecules. The solute molecules present in solvent is under the attractive and repulsive forces. The reduction in internal pressure is owing to the loosening of cohesive forces leading to the breaking up of the structure of solvent (Glasstone S.,1964). It also gives information about the stiffness and compactness of medium. In case of pure solvent, compactness and stiffness is less. But, when solute is added in solvent, medium becomes more stiffed and compact. Hence internal pressure decreased with increased in concentration. If the medium is more condensed, internal pressure would be less and vice-versa. The lower values of internal pressure show molecules in liquid medium are held by strong attractive forces and vice-versa.

Relaxation time is very important parameter to measure intermolecular force of attraction. It relates directly to the strength of attractive forces. When energy, in the form of ultrasonic waves pass through liquid medium, the normal state of molecules get disturbed. The excited molecules comeback their normal state. The time required for this phenomenon is called relaxation time. If the molecules of the medium are strongly held, to overcome these forces more time is needed. Hence relaxation time is more for such system and vice versa. In our present system, at higher concentration, the value of relaxation time is also higher (Praharaj M. K.,2012).

The Gibb's free energy directly related to the relaxation time. It means that higher the strength of attractive forces, higher will be the value of Gibb's free energy and vice-versa.

References:

Anjana, Rajindra K. B., (2011). "Ultasonic and Volumetric investigations of L-Threonine in aqueous and in mixed aqueous solution." Schol.Res.Lib.,Vol. 3,pp 370-379.

Atkins P.W. 'Physical Chemistry' (1998). Oxf. Univ. Press, Melbourne Tokyo, Sixth Edition.pp87.

Kumar R., Mohamad K.M.G., Prasad S.,Gayatri G.S.and Shabeer T.K., (2013). "Ultrasonic and Viscometric study of molecular interaction of antibiotic doxycycline hycalte" Ind.j. Pure & App.Phys. Vol.5,pp701-707.

Mujahid K.and Ansari H. R., (2011). "Acoustical Behaviour of Glucose, Sucrose and Maltose in Aqueous Ammonium Chloride Solution(0.5M) at different temperatures" Gold. Res.Tho., Vol.1,pp1-4.

Palani R., Geetha A., and Poornima S.V.S.L., (2011). "Ultrasonic Studies of some Biomolecules in Aqueous Gaunidine Hydrochloride Solutions at 298.15K" E-J.of Chem. Vol.8,pp1146-1151.

Palani R., Srinivasan G, Geeta L. (2011). "Ultrasoni Studies on Molecular Interaction of Arginine in Aqueous Disaccharides at 298.15K" Int. J. 0f Chem Tech Res., Vol. 3. pp284-289.

Praharaj M. K., Abhiram S., Mishra P. R. and Mishra S. (2012). "Study of Acoustical andThermodynamic Properties of Aqueous Solution of NaCl at different Concentrations and Temperatures through Ultrasonic Technique" Schol. Res. Lib.,Vol.4, pp 837-845

Rajesh M.,Joshi B.K, Joshi S and Kandpal N.D., (2006). "Intermolecular Forces of Sugar in Water" Mon. Fur Chemie Vol.137, pp375-379.

Samuel Glasstone, 'Thermodynamics For Chemists' (1965) D. Van Nost.Comp,Inc., Affl. East-West Press Pvt.Ltd. New Delhi.,Eleventh Prin. pp62.

Sanjibita D.and Upendra N. D., (2012). "Studies on Solute-Solvent Interactions of Amino acids in Water+D-glucose mixtures at Different Temperatures." J. of Chem. And Phar.Res., Vol.4,pp754-762.

Saravanakumar K., Baskaran R. and Kubendra T.R., (2010). "Acoustic and Thermodynamic Properties of Binary Liquid Mixture Benzene." Sci.Alert, pp1616-1621.

Shanmuga P. C., Nithya S, Velraj G, Kanappa A.N, (2010). 'Molecular interactions studies in liquid mixture using Ultrasonic technique' Int. J. of Adv. Sci. and Tech., Vol. 18. pp 59-73.