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Studies in Partial Molar Volumes, Partial Molar Compressibilities and Viscosity B- Coefficient of Galactose in an Aqueous Medium at Four Temperatures

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ABSTRACT

Density, ultrasonic velocity and viscosity of galactose in an aqueous medium at four temperatures were measured. The partial molar volume($Ø_v^0$), partial molar compressibility ($Ø_k^0$) and the viscosity B- Coefficient were calculated from experimental data. Values of $Ø_v^0$ and $Ø_k^0$ are to understand solute –solvent interaction. Magnitudes of $B/Ø_v^0$ were calculated at four temperatures. There were 4.750, 4.343, 4.029 and 3.842 at 25, 30, 35 and 40^{0}c respectively. $Ø_v^0$ increases while $Ø_k^0$ and viscosity coefficient decreases with temperature. The other parameter liked $Ø_v^0/\delta t$, $\delta Ø^2{}_v/\delta t^2$, dB/dT, inter molecular free length (L_f), specific acoustic impendence (Z) and relative association were calculated. The influence of galactose on water structure is revealed through these parameters.

Key words: Density, Ultrasonic velocity, various temperatures.

INTRODUCTION

Monosaccharide and polyfunctional solutes that, besides hydrophilic group (-OH and –O-) also posses hydrophobic groups (-CH and-CH_2) in the solute molecule. It is known that in aqueous mixtures at equilibrium, several distinct species of solute exist, i.e. the molecule have either pyranose or furanose like structure with different orientation of the –OH groups (axial or equatorial) and there is a negligible fraction of species in liner form and that the hydration is dependent on the conformational structures of the solute molecules [1].

We found it instructive to investigate the volumetric behavior of monosacharides (Galactose) of D-enantiomeres in aqueous solutions over a wide range of concentration and temperature, with the aim of elucidating the effect of the structure of the solute on the volumetric properties of

system in which hydration of solute is important. Partial molar volumes, adiabatic compressibility and viscosity studies have been done to understand the salvation behavior of the monosaccharide i. e. galactose.

MATERIALS AND METHODS

Galactose (AR-Grade) was in pure form and used without any further purification. Water used was doubled distilled and had a conductance less than 1×10^{-6} mhos, a matter balance, which can read up to the fifth place of decimal, was for weighing. All weighing were done with in ±0.01 mg. The necessary buoyancy correction was applied. Densities of different solutions were determined in a 15 cm^3 bicapillary pycnometers. Typically, three pycnometers was calibrated by using double distilled water with 0.99705 gm cm^3 taken as its density at 25 ^{0}C. The pycnometer filled with liquids were kept in a transparent walled water bath with a stability of ±0.02^{0}c for 15-20 minutes to attain formal equilibrium.

The speed of sound wave was obtained by using a variable path, singal crystal interferometer (Mittle Enterprises, New Delhi, model M-4). In the present work a steel cell fitted with a quartz crystal of 2 MHz frequency was employed. The instrument was calibrated by measuring the ultrasonic velocity U of water at 25 ^{0}C (our value was 1497.05 $m.s^{-1}$ while the literature value is 1497.07 ms^{-1}). The values of speed of sound were reproducible to within $\pm$ 1.0 $m.s^{-1}$. The maximum error in the measurement of U was estimated to be around 0.15%.

Viscosity measurement were performed by using a Schott Geract (AVS350) viscosity–measuring system equipped with a series of ubbelohde viscometers. In all the determinations the kinetic energy correction has been taken into account. According to the method suggested by hagenbach (AVS 350, viscosity measuring system, instruction manual Schott Geract Hofheim, Is (Germany 1986) experiments were generally performed at least five times for each solutions and at each temperature and the result were averaged. The experimental reproducibility of the viscosity measurement, at each temperature and solution was ±0.2%. The temperature was maintained by circulating water through an ultra thermostat (JULABO F-25), which has an accuracy of ±0.02^{0}c.

Treatment of Data

The apparent molar volume $Ø_v$ of the galactose was calculated from equation (1).

$$Ø_v = \frac{1000(d0-d)}{Cd0} + \frac{M}{d0} \qquad (1)$$

Where d_0 is the density of the solvent and d that of solution at concentration C of the galactose of molecular weight M. The partial molar volume $Ø_v^0$ was derived from $Ø_v$ values by the method of least squares solving the equation (2).

$$Ø_v = Ø_v^0 + S_v . C \qquad (2)$$

Table (1) contain the values of $Ø_v$, S_v and $Ø_v^0$.

The adiabatic compressibility coefficient β was derived from the relation.

$$\beta = 100/U^2\ d \qquad (3)$$

Where U is the ultrasonic velocity and density of the solution. The apparent molar adiabatic compressibility $Ø_{k,}$ of the liquid solution was calculated from equation (4).

$$Ø_k{}^0 = \frac{1000(\beta.do - \beta ods)}{Cd0\ ds} + \frac{\beta M}{ds} \qquad (4)$$

B and β_o are the adiabatic compressibility of the solute and solvent respectively.

$$Ø_{k,} = Ø_k{}^0 + S_k\ C \qquad (5)$$

Relative viscosity (η_r) is obtained by the expression,

$$\eta_r = t_1.d_1/t_0.d_0 \qquad (6)$$

Where t_1 and d_1 are the flow and density of the solution, while $t_0$and d_0 their corresponding value for water. The viscosity of B- coefficient (3) was derived by solving equation (7) by the method of least squares.

$$\eta_r = 1 + BC \qquad (7)$$

RESULTS AND DISCUSSION

One can note from Table (1) that the apparent molar volumes $Ø_v$ for galactose are large positive number and increase with the concentration at all temperatures. The solute solvent intraction is guessed from the magnitude of partial molar volume $Ø_v{}^0$, obtained by the use of equation (2) are significantly larger in magnitude relative to $Ø_v{}^0$ of simple inorganic anions [2-4] and exhibit increase with temperatures attributed to increase in salvation. The apperent molar expansibilities are given by following equation

$$Ø_E{}^0 = \left[\frac{\partial Øv0}{\partial T}\right]$$

$Ø_E{}^0$ increase with increase of temperature. The increase in magnitude per degree temperature is positive, indicating therefore that the behavior of galactose is like the behavior of symmetrical tetralkyl ammonium salts [5] but unlike the common electrolytes, because common behaviors of electrolyte, the molar expansibilities should decrease with the increasing temperature [6,7]. The positive increase of $Ø_E{}^0$ with increase of temperature can be ascribed to “caging effect” [5].

In recent years it has been reported that Sv is not the sole criteria for determing the structure making or breaking phenomenon of electrolytes. Therefore, Hepler [8] has developed a technique of examination the sign of $(\partial^2 øv/\partial T^2)$p for various solutes in terms of long range structure making and breaking capacity of the solute in aqueous solutions using the general thermodynamic equations.

$$\left[\frac{\partial Cp}{\partial p}\right]_p = -\left[\frac{\partial Øv0}{\partial T}\right]$$

On the basis of this equation, It has been deducted that structure- making solutes should have and structure breaking solutes should have negative values of galactose are in good agreement with literature values [9-13]. The ultrasonic velocity increase with the concentration of galactose at all four temperatures. It is known that for electrolyte solutions, the compressibility β of the solurion decreases with increasing concentration [14]. This is because, as the concentration of electrolyte increases, a large portion of the water molecules is eletrostricted and the amount of bulk water decrease casuing the compressibility to increase. Also dβ/dC is negative through the solute is a neutral molecules. The straight lines obtained in the plot of β vs coventration of galactose for four temperatures. A number of workers [15] have postulated the existence of two structural types of water aggregates at a given temperature (a structured form and a non structured or less structured form). The dβ/dC term for the structured form is negative while it is positive for the structured type. The term is negative for galactose which, being a neutral molecule, does not influence the water structure like an ion or a dipolar ion. However, the formation of clathrate like structure of water molecule around the hydrophobic molecule is possible. The apparent molar compressibility, øk in Table (2), decreases with increasing in concentration and decreases of temperature, $øk^0$ values are obtained from the linear plots of øk Vs C. These values are negative with rising temperature. S_k parameters are all positive and increase with temperature. It is well known that the electrolyte solution becauses of the electrostrication caused by the solute shows negative values of øk. Hydrophobic solutes often show negative compressibility as well, due to the ordering, which is induced by them in the water structure [16,17]. The order parameters, which inform about-solvent interaction, are intermolecular free length (Lf), the specific acoustic impedance (Z) and the relative association (R_A). These are obtained by the equation

$$Lf = K\sqrt{\beta}$$

$$Z = U.d$$

$$R_A = \frac{d}{d0}\left[\frac{U0}{U}\right]^{1/3}$$

K, β, U, U_0, d, and d_0 are Jacobson constant, adiabatic compressibility, ultrasonic velocity of solute and solvent, density of solute and solvent. Values of $K \times 10^4$ are taken as 6.25, 6.31, 6.37 and 6.42 at 25, 30, 35 and 40^0C. The mathematically derived values are shown in Tables (3).

The variation in ultrasonic velocity depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed by Eyring and Kincaid [18] ultrasonic velocity increases on decrease of free length and vice versa. In the present investigation it has been observed that the intermolecular free length decreases linearly with the concentration of galactose for four temperatures. The magnitude of Lf, however, does not show a measurable change with temperature. Genrally, values of acoustic impedance increase while β decreases, if ultrasonic velocity increase with temperature [19]. The trend observed as the variation in U and Z with temperature is in line with genrally accepted principals. Relative association is influenced by two factors. i) Breaking of the solvent molecule on addition of slute molecule on addition of solute and ii) Solvation of ions that are simultaneously present.

In the present study R_A increase with concentration and temperature. The increase of RA with concentration suggests that salvation of solute predominates over the breaking up of the solvent aggregates, resulting in increased salvation of solute by free solvent molecule and there by increase in RA with increase in temperature.

Table 1: Density(d), Apparent molar volume (Øv) Partial molar volumes ($Øv^0$) and Sv of galactose at four temperatures

Temp. ^0C	Conc.Mol. dm^3	Apparent molar volumes Øv dm^3 mol^{-1}	Partial molar volumes $Øv^0$ dm^3 mol^{-1}	Sv
25	0.00		111.98	0.935
	0.20	112.19		
	0.40	112.37		
	0.60	112.49		
	0.80	112.75		
	1.00	112.93		
30	0.00		112.81	0.865
	0.20	112.90		
	0.40	113.23		
	0.60	113.40		
	0.80	113.53		
	1.00	113.61		
35	0.00		114.15	0.610
	0.20	114.24		
	0.40	114.42		
	0.60	114.56		
	0.80	114.63		
	1.00	114.74		
40	0.00		114.51	0.565
	0.20	114.60		
	0.40	114.75		
	0.60	114.89		
	0.80	114.97		
	1.00	115.06		

The viscosity B- coefficient (Table 4) originally introduced as an empirical term has been found to depend upon solvent solute interaction, and on the relative size of the solute and solvent molecules. B- coefficient values for galactose are positive and large than B values of simple inorganic ions[20] which may be to the size effect. Large B values indicate structure making capacity of the solute which in proved by negative values for dB/dT.

It is observed that B- coefficient values decreases with increasing temperature [21,22]. The salvation of any solute can be judged from the magnitude of $B/Øv^0$. These values are important indicators [23-25] as to whether a particular solute is solvated or unsolvated. Since a value between 0-2.5 points to unsolvated species and any higher values to solvated ones.

The $B/Øk^0$ of galactose are set out in Table (4). The $B/Øk^0$ depends on viscosity and density. In the present system $B/Øk^0$ is larger than 2.5, showing a distinct hydration. $B/øk^0$ decreases with

temperature, the trend is similar to the trend shown by B but dissimilar to the trend shown by$Øv^0$.

At high temperature B is less and $Øv^0$ is higher, than at lower temperature. dB/dT is negative, emphasizing the greater hydration at higher temperature [21]. Higher B and negative dB/dT reveal the structure making capacity of galactose.

Table 2: Ultrasonic velocity (U), Adiabatic compressibility (*β*), Apparent molar compressibility (Øk) and Partial molar compressibility ($Øk^0$) for galactose at four temperatures

Temp. ^0C	Conc. (mol. dm^3)	Ultrasonic velocity $m.s^{-1}$	Adiabatic compressibility $\beta \times 10^{14}$ pa^{-1}	Apparent molar compressibility $Øk \times 10^{14}$ ($m^3\,mol^{-1}\,pa^{-1}$)	Partial molar compressibility $Øk^0 \times 10^{14}$ ($m^3\,mol^{-1}\,pa^{-1}$)
25	0.00	1497.07	44.75		26.05
	0.20	1512.20	43.27	25.75	
	0.40	1528.00	41.81	27.15	
	0.60	1558.60	40.46	27.25	
	0.80	1574.50		27.55	
	1.00	1574.50	37.89	28.09	
30	0.00	1509.57	44.07		22.25
	0.20	1525.00	42.61	25.50	
	0.40	1538.50	41.31	23.09	
	0.60	1553.00	40.02	23.56	
	0.80	1567.25	38.80	23.82	
	1.00	1581.90	37.60	24.35	
35	0.00	1520.37	43.52		22.00
	0.20	1535.20	42.12	21.05	
	0.40	1550.05	40.78	22.84	
	0.60	1564.90	39.50	23.31	
	0.80	1578.10	38.35	222.68	
	1.00	1593.80	37.17	23.74	
40	0.00	1529.76	43.07		21.65
	0.20	1544.10	41.71	20.49	
	0.40	1559.70	40.35	22.74	
	0.60	1574.25	39.10	22.83	
	0.80	1589.15	37.89	2333	
	1.00	1603.40	36.76	23.41	

Table 3: Intermolecular free length (Lf), Specfic acoustic impedance (Z) and relative association (R_A) at four temperature

Temp. ^0C	Conc. mol. dm^3	Intermolecular Free Length Lf $\times 10^6$	Specfic Acoustic Impedance (Z) Kg s^{-1} m^{-2}	Relative association (Rv)
25	0.00	4.181	14.92	
	0.20	4.111	15.28	1.0103
	0.40	4.041	15.65	1.0203
	0.60	3.975	16.01	1.0304
	0.80	3.911	16.38	1.0403
	1.00	3.847	16.76	1.0468

30	0.00	4.189	15.02	
	0.20	4.119	15.39	1.0101
	0.40	4.055	15.73	1.0206
	0.60	3.991	16.08	1.0307
	0.80	3.930	16.44	1.0408
	1.00	3.869	16.81	1.0508
35	0.00	4.202	15.11	
	0.20	4.134	15.41	1.0101
	0.40	4.068	15.82	1.0201
	0.60	4.003	16.17	1.0300
	0.80	3.945	16.52	1.0403
	1.00	3.883	16.89	1.0498
40	0.00	4.213	15.17	
	0.20	4.146	15.52	1.0102
	0.40	4.078	15.89	1.0201
	0.60	4.014	16.24	1.0301
	0.80	3.952	16.60	1.0400
	1.00	3.892	16.96	1.0499

Table 4: Viscosity B-coefficent and ($\beta/\emptyset v^0$) for galactose at four temperatures

Temp ^{0}C	Viscosity B-coefficent	$\beta/\emptyset v^0$
25	0.532	4.750
30	0.490	4.343
35	0.460	4.029
40	0.440	3.842

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REFERENCES

[1] F. Franks, *Pure Appl. Chem.*, **1987,** 79, 1189.
[2] F.J. Millero, A.L. Surdo, C. Shin, *J. Phys Chem.*, **1978,** 82, 784.
[3] G. Jones and M.J. Dole, *Am. Chem. Soc.*, **1929,** 51, 2950.
[4] F.J. Millero, Water and aqueous solution: Structure, Thermodynamics and transport processes, edited by R. A. Horne, Wiley Interscience, New York **1971.**
[5] F.J. Millero, Structure and transport processes n water and aqueous solution, edited by R.A. Horne, Chapter 15, Wiley Interscience, New York **1971.**
[6] F.J Millero, *Chem. Rev.***, 1971,** 71, 147.
[7] F.J. Millero and D. Drost Housen, *J. Phys. Chem Rev.*, **1968**, 72, 1758.
[8] L.G. Hepler, *Can.J.Chem.*, **1969,** 47, 4613.
[9] F. Shahidi, P.G. Farrell, J.T. Edward, *J. Sol. Chem.*, **1976,** 5, 807.
[10] K.S. Palij, C. Klofular, and M. Kac, *J. Chem. Eng. Data.*, **1990,**35, 41.
[11] H. Hoiland, H. Holvik, *J. Sol. Chem.*, 1982 7, 325.
[12] R.V. Jasra, J. C. Ahluwalia, *J. Sol. Chem.*, **1982,** 11, 325.
[13] P.J. Bernal. W.A.Vanhook, *J. Chem. Thermodynamics.*, **1986,** 18, 955.
[14] B.B. Owen and P.K. Kronick, *J. Phy. Chem.*, **1961,** 65, 81.

[15] F. Hirata and K. Arakawa, *Bull. Chem. Soc. Japan.*, **1972,** 45, 2715.
[16] M. Iqubal and R.E. Verrall, *Can J. Chem.*, **1989,** 67, 727.
[17] P.S. Nikam and A.R. Hiray, *Indian J. Pure and Appl. Phys.*, **1991,** 29, 601.
[18] H. Eyring and J.F. Kimcaid, *J. Chem. Phys.*, **1938,** 6, 620.
[19] Pankaj and C. Sharma, *Indian J. Pure and Aool. Phys.*, **1989,** 27, 32.
[20] M. Kaminsky, *Disc. Faraday Soc.*, **1957,** 171.
[21] B. Behre and R.K. Mishra, *Ind. J. of Chem.*, **1979,** 17, 445.
[22] M.J. Lee and T.K Lin, *J. Chem. Eng. Data.*, **1995,** 40, 336.
[23] S. Nishikawa, N. Kuramoto and T. Uchiyama, *Bull. Chem. Soc. Japan.*, **1994,** 67, 2870.
[24] A.G. Shankarwar, V.A. Shelke, S.G. Shankarwar, *Advances in Applied Science Research*, **2011,** 2 (4), 426-430.
[25] A. G. Shankarwar, V.A. Shelke, S. G. Shankarwar, B.R. Arbad, *Der Chemica Sinica.*, **2011,** 2 (4), 59-63.