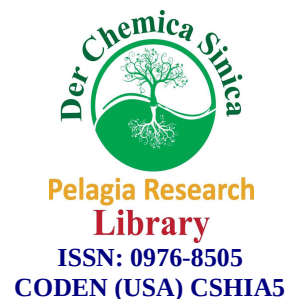




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Apparent molar volume and viscometric study of carbohydrate in aqueous solution

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ABSTRACT

Densities and viscosities of Carbohydrates at different temperature (293.15, 303.15, and 313.15K) have been measured from experimental data. The apparent molar volume, limiting APPARENT molar volume, Jones-doles A and B coefficients were calculated. The results show strong solute -solvent interaction that indicates all selecting Carbohydrates are structure builder in aqueous solution.

Key Words: Limiting Apparent Molar Volume, Hepler Constant, Jones Dole Coefficient, stereo chemical effects

INTRODUCTION

Partial molar volume provided useful information about various types of interactions occurring in solutions .these studies are help us to characterize the structure and properties of the solutions. The structure of solution is imported to understand the nature of action of bio-molecules in body system (1-3). The study of such interactions of non electrolyte in solution is very significant &useful for investigate their physicochemical behavior.

Carbohydrates are the most abundant class of organic compounds found in living organism. They form numerous roles in living system from the storage and transport of energy to participation in immune-system. The study of carbohydrate has become subject of increasing interest, because of its, multidimensional physical, biomedical& industrial useful properties (4-5). Carbohydrate are not only biochemically important, but also non-electrolytes with hydrophilic hydroxyl group which having high affinity to water and salting out aptitude that are involving in intra-molecular hydrogen bonding with water.

MATERIALS AND METHODS

All the Chemical D-glucose, D-fructose, sucrose and maltose were used in the present study of analytical grade. .Freshly distilled water with specific conductance of $\sim 10^{-6} \Omega \text{ cm}^{-1}$ was used to preparing solution throughout the experiment. The aqueous solution of glucose was made by weight and molalities were converted in to molarities using the standard expression (6). The densities of solutions were measured at 293.15, 303.15, and 313.15 k using a single stem pycnometer made of borosil glass. The mass measurement were done on digital electronic balance (Sartorius GC103).Viscosity determines with calibrated U shaped Ostwald viscometer with sufficiently long reflux

time more than 100sec. to avoid kinetic energy correction. The viscometer was averaged from three readings for each solution. The calibration of density bottle and viscometer (6-7) was done by using doubly distilled water. An average of triplet measurement was taken in to account. Temperature was controlled by thermostatic water-bath.

Theory

The apparent molar volume can be calculated from density data using the following equation (7)

$$\Phi_v = M/d_0 - 1000(d-d_0)/d_0c$$

Where d_0 and d are the densities of solvent and solution respectively; c is the molar concentration in gram/liter and M is molecular weight of solute. The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecules and changes that occur in to the solution due to its interaction with solvent. The data are fitted to Masson (8) equation & calculate limiting partial molar volume and experimental slope by least square method.

$$\Phi_v = \Phi_{v0} + S_v \sqrt{c}$$

Time of flow were determined for carbohydrate under study at chosen concentration and temperature from 20-40°C. the viscosity were determined from the formula $\eta/\eta_0 = t/t_0 d_0$ where η , t , d are the absolute viscosity, time of flow & density of solution, while η_0 , t_0 , d_0 are same quantities for the solvent water. The viscosity data was analyzed according to Jones- dole (9) equation

$$\eta/\eta_0 = \eta_r = 1 + A c^{1/2} + Bc$$

Where η_r is relative viscosity, c is molar concentration the constant A is the Falkenhagen coefficient and B is the Jones- dole coefficient related to solute solvent & solute- solute interaction respectively. Viscosity data has been analyzed with the help of Jones-dole equation from the linear plots of $[(\eta/\eta_0)-1]/c^{1/2}$ versus $c^{1/2}$ by computerized least square method.

RESULTS AND DISCUSSION

The value of apparent molar volume of carbohydrates at different temperature (293.15, 303.15 & 313.15) given in Table 1. It shows that Φ_v is linear function of concentration. Apparent molar volume of solute varies with the square root of the molar concentration and obeys Masson's equation.

Perusal of table 2. shows that The value of Φ_{v0} for all carbohydrates is positive in water & increase with increasing temperatures again since Φ_{v0} is a measure of solute solvent interaction, the positive value indicates strong solute solvent interaction which suggests that the overall structural order is enhanced in aqueous solution. The presence of ion solvent interaction between the molecules promotes the structure making effect of solutes in water. Φ_{v0} is a limiting apparent molar volume of the solute also called the apparent molar volume at infinite dilution. It is evident from table that the values of S_v are small and less positive for all carbohydrates in aqueous solution at different temperature. Since S_v is a measure of ion- ion interaction so the results indicate the presence of weak ion- ion interaction. The Φ_v value in water in present investigation has good agreement with reported value of Dey (10) et al 2003, Hoiland (11) 1991, Jasra Alhuwalia (12-13) 1997, 1983 Kulgud and Dhondgre (14) 1988. According to Gurney co-sphere overlap model the always produce overlap of the co-spheres of two ions or polar group or an ion with hydrophilic group positive volume change. On the other hand overlap of the co-spheres of an ion with that of hydrophobic groups result a negative volume change. Results indicate that ion-hydrophilic and hydrophilic-hydrophilic interactions predominate over the ion-hydrophobic and hydrophobic-hydrophobic interactions.

The temperature dependence of limiting apparent molar volume, Φ_{v0} for carbohydrates in aqueous solution can be represented by following expression.

$$\Phi_{v0} = a_0 + a_1 T + a_2 T^2$$

Where T is temperature in Kelvin. The value of coefficient a_0 , a_1 and a_2 are given in table 4, calculated by differentiating above equation with respect to temperature.

$$\Phi_{E0} = (\partial \Phi_{v0} / \partial T)_p = a_1 + 2a_2T$$

The limiting apparent molar expansibilities for carbohydrates in aqueous solution obtained at different temperature are calculated. It is found that Φ_{E0} value increase with rise in temperature, this increase Φ_{E0} with temperature ascribed to the presence of caging effect (15).

The structure making/breaking capacity of solute in aqueous solution may be interpreted with the help of Helper (16) equation on the basis of sign of giving expression.

$$(\partial \Phi_{E0} / \partial T)_p = (\partial^2 \Phi_{v0} / \partial T^2)_p = -a_2$$

The sign of $(\partial^2 \Phi_{v0} / \partial T^2)_p$ second derivative of limiting apparent molar volume of solution with respect to temperature at constant pressure, which correspond to structure making or breaking properties of solution was determined. The determined value of $(\partial^2 \Phi_{v0} / \partial T^2)_p$ has been found to be positive for all four carbohydrates suggesting structure making properties.

The value of viscosity of all studied four carbohydrates at different temperature (293.15, 303.15 & 313.15) given in Table 2. Viscosity of aqueous solution of carbohydrates has been determined as a function of their concentrations. The values of coefficients A & B of the Jones- Dole equation have been determined by computerized least square method and the result has been showed in Table (3). 'A' and 'B' coefficients are constant and characteristics of ion-ion and ion-solvent interaction respectively. The value of A coefficients are negative and very small for all the four carbohydrates indicating the presence of weak ion- ion interaction.

Perusal of table 3 shows that the value of B-coefficient for all carbohydrates in aqueous solution is positive; since B is measure of solute- solvent interaction & its value depend on size and shape of solute. Positive B value indicates the existence of ion solvent interaction. A decrease in the value of B- coefficient with the rise of temperature represents structure promoting effect. This is due to ordering and a sort of enforcement of hydrogen bonded structure around the solute. At higher temperature, the surrounded sheath of solvent molecule around the water is broken and ion -solvent interaction is weakened. That further supporting earlier conclusion drawn from Φ_{v0} and S_v . Recently it has been emphasized by many workers (17) that (dB/dT) is a better decisive factor for determine structure making/breaking nature of any solute rather than the B-coefficient. The values of (dB/dT) were calculated from the slope of the curve obtained by plotting B- coefficient value against temperatures and these values given in Table 3. Table 3 shows at higher temperature B is less and Φ_v is higher than at low temperature. (dB/dT) is negative underline the greater hydration at higher temperature (18-19). Higher B and negative (dB/dT) disclose the structure making capacity of carbohydrates. These are in identical agreement with the conclusion drawn from Helper equation as discussed earlier.

According to volumetric & viscometric behavior these non electrolyte solutes act overall as water structure builder due to hydrophobic hydration and hydrogen bonding between solute and water molecules. Similar explanation had drawn from stereo chemical, kinetic & thermo dynamical studies (20-22) of carbohydrates. Hydrophobic hydration of carbohydrate depends on their confirmation and configuration of hydroxy group. The hydration of carbohydrate has been explained with the help of concept of compatibility through specific hydration model (23-25).

Table (1) Apparent molar volume Φ_v of carbohydrates in water at different temperature

conc.	Apparent molar volume Φ_v (cm ³ mol ⁻¹)											
	293.15K				303.15K				313.15K			
gm.dm ⁻³	glucose	fructose	sucrose	maltose	glucose	fructose	sucrose	maltose	glucose	fructose	sucrose	maltose
0.05	111.31	109.92	210.90	222.60	113.63	111.62	212.8626	223.36	115.65	113.73	214.85	225.36
0.10	111.52	110.14	211.23	222.81	113.79	111.80	212.9284	223.61	115.79	113.97	215.12	225.62
0.15	111.71	110.29	211.43	223.32	113.93	111.98	213.2727	223.88	115.93	114.05	215.36	225.86
0.20	111.87	110.45	211.75	223.62	114.02	112.07	213.5959	224.17	116.07	114.13	215.56	226.12
0.25	112.02	110.62	212.06	223.77	114.20	112.13	213.8583	224.39	116.16	114.22	215.84	226.31

Table (2) Viscosities η (cp) of carbohydrates in water at different temperature

Viscosities η (cp) of carbohydrates												
gm.dm ⁻³	293.15K				303.15K				313.15K			
	glucose	fructose	sucrose	maltose	glucose	fructose	sucrose	maltose	glucose	fructose	sucrose	maltose
0.050	1.007	1.0068	1.009	1.020	0.829	0.821	0.836	0.852	0.688	0.682	0.703	0.712
0.100	1.03	1.0262	1.059	1.071	0.878	0.860	0.864	0.905	0.722	0.719	0.743	0.751
0.150	1.073	1.054	1.119	1.144	0.917	0.890	0.911	0.957	0.757	0.746	0.773	0.792
0.200	1.122	1.116	1.178	1.205	0.956	0.915	0.946	1.010	0.791	0.774	0.795	0.836
0.250	1.195	1.1502	1.238	1.270	0.995	0.969	.983	1.062	0.826	0.808	0.830	0.884

Table (3) Partial molar volumes at infinite dilution Φ_{V_0} , experimental slope Sv, A, B and Temperature B coefficient of carbohydrates in water at different temperature

Carbohydrate	Φ_{V_0} cm ³ mol ⁻¹			Sv(cm ³ lit ^{1/2} mol ^{-3/2})			B m ³ mol ⁻¹		
	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
Glucose	110.8	113	115.23	2.37	2.3	1.82	1.31	1.15	1.07
Fructose	109.35	111.2	113.39	1.69	1.31	1.13	1.06	1.01	0.986
Sucrose	209.94	211.88	214.29	4.1	3.77	2.74	1.61	1.12	1.09
Maltose	221.5	222.41	224.54	4.57	3.976	3.499	1.69	1.32	1.13

Table (4) values of various coefficients a_0 , a_1 and a_2 Hepler constants and dB/dT for studied carbohydrates

Carbohydrate	a_0	a_1	a_2	HEPLER CONSTANT	dB/dT
Glucose	50.64	0.1899	0.000052	0.000104	- 0.01194
Fructose	206.19	- 0.828	0.0017	0.0034	- 0.0037
Sucrose	361.1	- 1.20	0.0023	0.0046	- 0.0256
Maltose	736.92	- 3.54	0.0061	0.00122	- 0.03

CONCLUSION

Different thermodynamic and spectroscopic study(20-22) showed that the hydration of carbohydrate did not depend only on hydroxyl group & potential site of hydrogen bonding, but also depend on their relative orientation .The number of hydroxyl group results a higher number of potential hydrogen bonding sites with water Furthermore, from the comparison between the structural isomers glucose and fructose, it is evident that pyranose (six sided ring) are more efficient salting –out agents than furanoses (five sided ring). Maltose is made up of two units of glucose whereas sucrose is made of one molecule of glucose and one molecule of fructose. Six member pyranose ring in maltose is more favorable for interaction with water than the five member furanose ring in sucrose. Among two disaccharides reveals that maltose can fold (25) together readily to screen hydrophobic surfaces while the sucrose molecule cannot .Thus the results in keeping with the expected behavior of the two disaccharides and indicate the presence of intermolecular hydrophobic bonding. According to frank & Evan this nonpolar solutes in water promotes in its surrounding and enhanced hydrogen bond network of water. Consequently, the water molecules rearranges toward formation of a local cage like (clathrates) structure surrounding each solute molecule. On according to further discussion these all carbohydrates are structure promoter solute & their capacity lie in the order of Fructose < Glucose < Sucrose < Maltose

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