



Energy-Volume Coefficient and Limiting Excess Molar Volume Studies of Some Carbohydrates in Dilute Aqueous Solutions at 288.15 K

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In this work, we report the determination of energy volume coefficient $\left(P_{\text{int}} = \left(\frac{\partial U}{\partial V} \right)_T \right)$ also called as an internal pressure (P_{int}) in the dilute concentration region for the basic carbohydrates *i.e.*, glucose, fructose, sucrose, galactose and lactose in aqueous solutions at 288.15 K in the concentration range 0-0.05 mol kg⁻¹. To obtain this one requires precise isothermal compressibility and expansivity data. We used earlier reported data of density (ρ) and speed of sound (u) obtained at 278.15, 288.15 and 298.15 K; assuming specific heat (C_p) is nearly the same in the studied concentration region. The internal pressure for solutions is found to increase with concentration of solute linearly and the increase depends upon the number of polar hydroxyl groups and conformational characteristics of the carbohydrate molecules. It is well known that apparent molar volumes (ϕ_v) of these compounds do not vary with concentration in dilute solution region (almost ideal solutions), while the conformational specificity is reflected only in limiting partial molar volumes because of solute-solvent interactions. We applied Gibson-Tait equation of state to internal pressure data and obtained limiting excess molar volumes (\bar{V}_2^{OE}) and found that values of excess molar volume of these compounds are highly negative (-31×10^{-6} to -62×10^{-6} m³ mol⁻¹) at 288.15 K. These are large negative when compared with the molar volume data of solid carbohydrates. The differences are attributed to void volume and cage volume contribution to the total volume of solute molecule. It is invoked that when carbohydrates are dissolved in water, almost all free and void volumes are being used up due to dipole (-OH) and water molecular interactions through hydrogen bonding and retaining water structural characteristics intact in solution phase.

Key Words: Isothermal compressibility, Internal pressure, Excess partial molar volume, Carbohydrates.

INTRODUCTION

The chemistry of polyhydroxy compounds (PHCs) is very important for life processes. One of the most important characteristics is their ability to interact with water by means of their hydrogen bonding potential¹. Several properties of aqueous polyhydroxy compound solutions have been studied². It has been discussed that the polyhydroxy compound solutions can be treated as semi-ideal and apparent derivation could be accounted for in terms of simple hydration equilibrium, each -OH group being associated with one water molecule³. Of all chemical species, the polyhydroxy compounds most closely resemble water in their properties. Stokes and Robinson using the concept of ideal solution suggested that the observed concentration dependence of the thermodynamic quantities is

due to solute-water interaction in terms of hydration equilibria. It has been shown that for carbohydrates-water systems free energies, as a result of enthalpy-entropy compensation effects^{2,4} may be fairly insensitive to the hydration model chosen⁵. Franks *et al.*⁵ have developed specific hydration model for aqueous carbohydrate solutions using calorimetric and dielectric measurements. According to them the nature and extent of hydration is a function of relative compatibility of the solute conformation with the aqueous environment as well as by the intermolecular order through hydrogen bonding interaction. Warner and Ann⁶ has discussed the correlation between the stereochemistry of sugar and their hydration behaviour with reference to biological specificity and cryoprotective action. It has been noted that no reliable data of free energy changes are available in dilute concentration range; it may be because

of complication due to mutarotation at lower temperature. However, the recent results of osmotic coefficient and excess free energy changes have shown the hydration number of 10–12, compatible with clathrate hydrate structure (class I) in solution phase. Franks¹ has stressed the importance of specific heat data to find hydration details. However, the results are not conclusive because of the complications due to changes in the internal degrees of freedom of the solute molecule when it is removed from its crystalline environment⁷. Similar problems occur when one deals with volumetric properties of sugars. The limiting partial molar volume of solute (\bar{V}_2^0) is mainly a function of molecular weight. However, the concentration dependence of apparent molar volume is also nil or negligible showing the absence of solute-solute interaction^{8,9}. The excess partial volume (\bar{V}_2^E) data cannot be used with ease to draw meaningful information (for comparison with other solutes or conformers), as V_2^0 (molar volume) of sugars calculated from van der Waals radii or of solids as reference states do not corroborate.

It is known from the literature that the limiting excess partial molar volumes (\bar{V}_2^{0E}) of electrolytes can be obtained by application of Gibson-Tait equation of state which can further be analyzed in terms of electrostatic, void volume, cage volume and intrinsic volume components^{10–13}. This treatment needs fine data of internal pressure which can be evaluated if isothermal compressibility, expansivity and specific heat data in limiting concentration range is available. In recent years, the fine data became available for dilute aqueous solutions and we were successful in obtaining reliable excess volumes for alcohols in aqueous solutions which can be accounted satisfactorily in terms of water-structure making effect and hydrophobic interaction¹⁴. We now extend this treatment to aqueous-carbohydrate solutions for which fine data of adiabatic compressibility and volume are available at 278.15, 288.15 and 298.15 K in dilute concentration range (0–0.05 mol kg⁻¹)⁸. The methodology of obtaining isothermal compressibility, expansivity and internal pressure at various concentrations is described and finally the excess limiting volume evaluation using Gibson-Tait equation is presented. The details of all these and possible interpretation are described in this study.

Methodology to obtain isothermal compressibility (β_T) and internal pressure data (P_{int}): The isentropic compressibility (β_S) was calculated by using data of density (ρ) and speed of sound (u) reported earlier⁸ by using the eqn. 1.

$$k_S = \frac{1}{u^2 \rho} \quad (1)$$

where, ρ is density of solution and u is speed of sound in solution. Our speed of sound data (u) were obtained by phase comparison interferometry⁸ having accuracy of ± 0.02 to 0.03 m/s.

The coefficient of expansion (α_p) is determined at 288.15 K by variation of ρ with varying temperature at 278.15, 288.15 and 298.15 K at specified molalities using the relation:

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (2)$$

The calculations of isothermal compressibility (k_T) were made by using, k_S , α_p and the specific heat at constant pressure (C_p) data and using the equation:

$$k_T - k_S = \delta = \frac{\alpha_p^2 T}{\alpha} = \frac{\alpha_p^2 T}{C_p \rho} \quad (3)$$

C_p values for the solution are assumed to be the same as that of the solvent (water). The values for u , β_S , β_T and C_p for pure water were 1466.4 m s⁻¹, 46.5464×10^{-11} Pa⁻¹, 46.7039×10^{-11} Pa⁻¹ and 0.99976 Cal g⁻¹ K⁻¹, respectively at 288.15 K. The variation of δ is the main contributing factor in obtaining values which in turn depend upon the accuracy of expansivity coefficient¹⁵. Our data of isothermal compressibility (β_T) having an accuracy of $\pm 0.01 \times 10^{-11}$ Pa⁻¹ at 288.15 K for various aqueous solutions are depicted in Fig. 1.

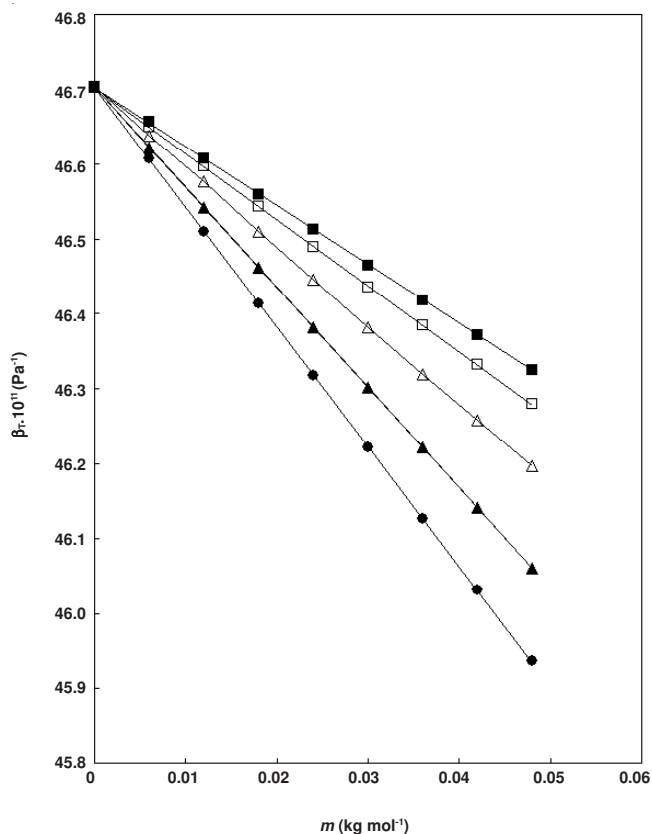


Fig. 1. Plot of isothermal compressibility (β_T) of aqueous solution of carbohydrates at 288.15 K: \square - \square , glucose; \blacksquare - \blacksquare , fructose; \triangle - \triangle , galactose; \blacktriangle - \blacktriangle , sucrose; \bullet - \bullet , lactose

The energy volume coefficient (internal pressure) *i.e.*, P_{int} values for aqueous solutions of carbohydrates at different concentrations were evaluated using the equation of state:

$$P_{int} = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P = T\beta_V - P \quad (4)$$

where, β_V is thermal pressure coefficient. Assuming P (1 atm

= 101325 Pa) is negligible and using $\left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha_p}{k_T}$, equation 4 becomes

$$P_{int} = P \left(\frac{\partial P}{\partial T} \right)_V = T\beta_V = \frac{\alpha_p T}{k_T} \quad (5)$$

The variation of internal pressure (P_{int}) as a function of molality (m) of carbohydrates at 288.15 K is shown in Fig. 2.

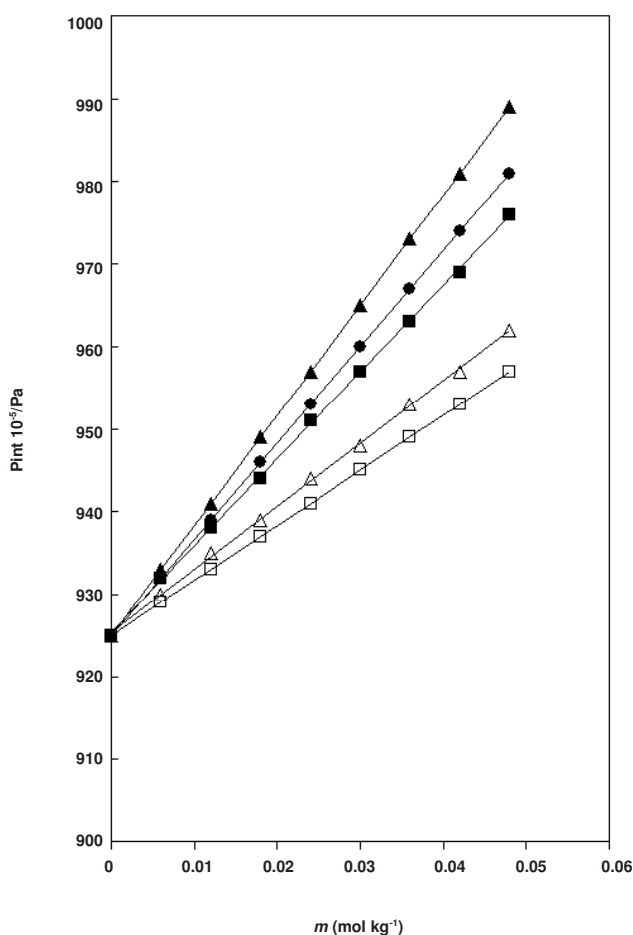


Fig. 2. Plot of Internal pressure (P_{int}) of aqueous solution of carbohydrates at 288.15 K: \square - \square , glucose; \blacksquare - \blacksquare , fructose; \triangle - \triangle , galactose; \blacktriangle - \blacktriangle , sucrose; \bullet - \bullet , lactose

The details about Gibson-Tait equation are given elsewhere¹¹. The useful equation is:

$$\bar{V}_2^{(p)} - M_2 v_2 = -\frac{434.3C}{v_o(B + P_{int} + P)} \frac{\partial(B + P_{int})}{\partial m} \quad (6)$$

where C and B are positive constants. The $\frac{C}{v_o}$ (v_o being the

apparent specific volume of solvent) term having a value of 0.3150 while the B is 2996×10^5 Pa at 298.15 K. The v_2 is specific volume of pure solute (as a liquid). We can call P_{int} as the effective internal pressure created in solution due to dipole-dipole (H bonding) and hydrophobic interaction between the solute molecules. The equation shows that the magnitude of the partial molar volume of solute is governed

by two factors. The term $\frac{\partial(B + P_{int})}{\partial m}$ is the rate of change of total internal pressure with concentration and is a function of

both solvent and solute. The term $\frac{434.3C}{v_o(B + P_{int} + P)}$ is related

to the compressibility of the solvent at the pressure ($P_{int} + P$) and is independent of solute. P_{int} is considered to have constant characteristics for a given system at constant composition and temperature.

Gibson¹⁰ derived the equation:

$$\bar{V}_2^0 - V_2^0 = \frac{-1000}{(B + P_{int} + P)} \frac{\partial(B + P_{int})}{\partial m} \quad (7)$$

where m is the molality of solution and V_2^0 is taken to be the hypothetical molar volume of the pure solute in the liquid state at the temperature and pressure of the experiment. The volume change $\bar{V}_2^0 - V_2^0$ is therefore the change in the volume on mixing this hypothetical pure liquid solute and the solvent. To obtain the value of excess partial molar volume ($\bar{V}_2^0 - V_2^0$) at infinite dilution, we must take the limiting case of eqn. 7. The

term $\frac{1000}{v_o(B + P_{int} + P)}$ represents the compressibility of solvent at an external pressure ($P_{int} + P$). At infinite dilution of the solute this can be replaced by the compressibility of pure water k_T at 1 atm (46.70×10^{-11} Pa⁻¹ at 288.15 K). eqn. 7, then reduces to

$$\bar{V}_2^0 - V_2^0 = \frac{k_T}{\rho_o} \lim_{m \rightarrow 0} \frac{d}{dm} (B + P_{int}) \quad (8)$$

The density data of pure solids at 293.15 K are used to estimate molar volume of solids¹⁶. We assume that there will be no appreciable error for V_2^0 at 15 °C due to this. These values are used to estimate excess partial molar volume at infinite dilution $\bar{V}_2^{0E} (= \bar{V}_2^0 - V_2^0)$ based on solid as standard state.

RESULTS AND DISCUSSION

Fig. 1 reveals that β_T decreases with concentration of solute in solution (m) in all studied systems. The relative decrease is lowest for fructose while it is highest for lactose. These small differences can be attributed to conformational differences in carbohydrate structures. It may be due to the fact that equatorial -OH group is hydrated more than the axial one. The same observation was made by Kaulgud and Dhondge⁸ and Franks *et al.*⁹.

It is observed from Fig. 2 that the internal pressure parameter (P_{int}) increases linearly in all the systems. The $\frac{\partial P_{int}}{\partial m}$

value is highest for sucrose while it is lowest for glucose. The number of -OH groups (in sucrose it is 8, while in glucose it is 4) decides this rise because of dipole-dipole hydrogen bonding interaction between -OH and water molecule interaction.

There is no appreciable difference in the densities of solids studied in this work and so excess volumes do not show a trend when solid state is taken as a standard state (Table-1). Lactose shows the highest volume loss. We observed earlier⁸ that the limiting apparent molar compressibility (ϕ_{KS}^0) of lactose is highly negative meaning strong dipole-solvent interaction similar to that of electrostriction. Lactose is a combination of glucose and galactose (both are in pyranose form). Therefore the pyranose and furanose form (sucrose) do cause solute-solvent interaction but the extent of hydration is more for pyranose form. The magnitude of \bar{V}_2^{0E} for

TABLE-1
 DENSITY (ρ), THE COEFFICIENT OF THERMAL EXPANSION (α), ISOTHERMAL COMPRESSIBILITY (β_T),
 INTERNAL PRESSURE (P_{int}) SOLUTIONS AND LIMITING APPARENT MOLAR EXCESS VOLUME OF
 SOLUTES (\bar{V}_2^{0E}) IN AQUEOUS SOLUTIONS OF CARBOHYDRATES AT 288.15 K

m (mol kg ⁻¹)	$\rho \times 10^{-3}$ (kg m ⁻³)	$\alpha \times 10^4$ (K ⁻¹)	$\beta_T \times 10^{11}$ (Pa ⁻¹)	$P_{int} \times 10^{-5}$ (Pa)	$\bar{V}_2^{0E} \times 10^6$ (m ³ mol ⁻¹)	
					Eqn. 8	Using solid as standard state
Glucose						
0	0.999098	1.5013	46.7039	925		
0.006	0.99952	1.5063	46.6496	929		
0.012	0.999941	1.511	46.597	933		
0.018	1.000361	1.5157	46.543	937		
0.024	1.00078	1.5204	46.4898	941	-31	7
0.03	1.001196	1.525	46.4355	945		
0.036	1.001618	1.5297	46.384	949		
0.042	1.002021	1.5344	46.3314	953		
0.048	1.002429	1.539	46.279	957		
Fructose						
0	0.999098	1.5013	46.7039	925		
0.006	0.999516	1.5102	46.6565	932		
0.012	0.999938	1.5188	46.6082	938		
0.018	1.000361	1.5274	46.56	944		
0.024	1.000786	1.5359	46.5124	951	-49	-3.3
0.03	1.001211	1.5445	46.4648	957		
0.036	1.001635	1.5533	46.4817	963		
0.042	1.002057	1.5616	46.372	969		
0.048	1.002478	1.5701	46.3255	976		
Galactose						
0	0.999098	1.5013	46.7039	925		
0.006	0.99952	1.5069	46.6385	930		
0.012	0.999944	1.5122	46.5763	935		
0.018	1.00037	1.5175	46.5102	939		
0.024	1.000796	1.5228	46.446	944	-36	-2.5
0.03	1.001222	1.5281	46.3821	948		
0.036	1.001647	1.5334	46.3183	953		
0.042	1.002071	1.5386	46.2572	957		
0.048	1.002492	1.5439	46.1964	962		
Sucrose						
0	0.999098	1.5013	46.7039	925		
0.006	0.999887	1.5117	46.6224	933		
0.012	1.000679	1.5217	46.5421	941		
0.018	1.001471	1.5318	46.462	949		
0.024	1.002271	1.5418	46.3814	957	-62	-6.1
0.03	1.003081	1.5518	46.3012	965		
0.036	1.003888	1.5618	46.2211	973		
0.042	1.004699	1.5718	46.1409	981		
0.048	1.005513	1.5818	46.0607	989		
Lactose						
0	0.999098	1.5013	46.7039	925		
0.006	0.999908	1.5096	46.6071	932		
0.012	1.000717	1.5176	46.5104	939		
0.018	1.001586	1.5257	46.4141	946		
0.024	1.002332	1.5336	46.3169	953	-55	-17.7
0.03	1.003126	1.5415	46.2212	960		
0.036	1.003938	1.5494	46.126	967		
0.042	1.004736	1.5573	46.0312	974		
0.048	1.005531	1.5652	45.9369	981		

monosaccharide is similar to that of alcohols; however the details of interactions are different. In alcohols the volume loss is due to hydrophobic interaction¹⁷ (dissolution with economy of space), while for monosaccharides it is due to dipole-dipole interaction.

When this excess volume based on solid as a standard state is compared with those obtained with Gibson-Tait

equation, we find that in the latter case, these are highly negative (-31 to -62 cm³ mol⁻¹). It is now certain, that solid as standard state is inadequate to account for interaction. Edward¹⁸ has tried to understand molecular volumes of various molecules. He estimated van der Waals volumes and divided into atomic increment as well as calculated free volume due to empty space. At 0 K, a crystal made of closed-packed spheres

has only 74 % of its total volume occupied by the spheres. In view of this, our excess volume for carbohydrates indicate large negative volume ranging from -31 to -62 cm³ mol⁻¹. Since these calculations are based on best equation of state, it is concluded that so much free space is available for these molecules. Thus, the empty volume associated with these molecules in aqueous solutions is roughly the same as the empty volume associated with carbohydrate molecules in the

solid or liquid state $\left(\frac{\bar{V}_M}{V_w} = 1.38\right)$. We found no evidence of

solute-solute association for these solutes; hence it is clear that the empty volume is all available for H-bonding (dipole-dipole) interaction with water molecules. The detailed numerical agreement of course would depend on the stereochemical/conformational specificity of the molecules. The empty volume will be reduced by hydrogen bonding between solute and solvent water, which will bring them closer together yielding the negative excess molar volumes.

Following the treatment advanced for ionic solution by Millero¹³, the solute molecules at infinite dilution are far away from each other, each interacting with the surrounding water molecules in its own unique way. The \bar{V}_2 of glucose can be represented by four major components:

$$\bar{V}_2^0 = V_{2\text{cryst}}^0 + \bar{V}_{\text{elect}}^0 + \bar{V}_{\text{disord(viod)}}^0 + \bar{V}_{\text{cage}}^0 \quad (9)$$

Since there are no ions, \bar{V}_{elect}^0 will be zero but will be replaced by -H bonding and dipole-dipole interaction contribution. Therefore, the excess partial molar volume will correspond to

$$\bar{V}_2^0 - V_{2\text{cryst}}^0 = V_{\text{dipole interaction}}^0 + \bar{V}_{\text{disord(viod)}}^0 + \bar{V}_{\text{cage}}^0 \quad (10)$$

We obtained directly by application of Gibson-Tait equation which corresponds to the effects due to sum of H-bonding and \bar{V}_{cage}^0 (water structural effects) subtly. The values obtained are shown in Table-1. Therefore, it is concluded that the availability of hydroxyl grouping, the number of intermolecular hydrogen bonds per molecule in the crystal and free space available determine the thermodynamic properties of aqueous-carbohydrate solutions. The remarkable loss of apparent volume observed demonstrates the resemblance between water molecules and -OH groups in carbohydrate. Polyhydroxy

compounds are well known for their ability to protect native proteins and nucleotides against the denaturing effects of dehydration¹⁹. Polyhydroxy compounds are also employed by living organism as protestants against physiological water stress, whether due to low temperature, drought or solubility²⁰.

Conclusion

The interactions between polyhydroxy compounds and water, like those between water molecules, are governed by hydrogen bonding. The large negative excess volumes reported, signify large free volume associated with these molecules. The detailed manifestation in thermodynamic properties seems to depend on solute-solvent interactions and are very sensitive to spacing and orientation of the -OH groups on the solute molecule. Where, different conformers can coexist in solution, the aqueous solvent acts so as to favour the conformers with largest number of equatorial -OH groups because of their special compatibility with water.

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