



Hydration Numbers of Carbohydrates in Dilute Aqueous Solutions at Different Temperatures

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Hydration numbers (n_h) of glucose, fructose, galactose, sucrose, lactose, α -methyl glucoside and, β -methyl glucoside have been computed at 278.15, 288.15 and 298.15 K by Shii's method using density and speed of sound data. It has been observed that at 298.15 K hydration numbers of glucose and fructose are of the same order the value which is less for galactose. In the case of disaccharides the value is very high for lactose than sucrose while, α -methyl glucoside seems to be more hydrated than β -methyl glucoside. The behaviour at 278.15 K and 288.15 K was found to be different. Galactose shows very high values as compared to glucose and fructose, whereas, other carbohydrates show the same trends. These results have been interpreted in terms of stereo specificity of carbohydrates in interactions with water as observed in volumetric and compressibility studies.

Key Words: Carbohydrates, Hydration numbers, Stereo specificity.

INTRODUCTION

The study of interactions of carbohydrates with water has always found a foremost place as they are essential components of all living organisms and are in fact, the most abundant class of biological molecules. The carbohydrates or sugars are important in metabolism in the animal body. Carbohydrate metabolism in the animal body is essentially the metabolism of glucose and of substances related to glucose in their metabolic processes¹. Normally, carbohydrate metabolism supplies more than half of the requirements of the body. Thus carbohydrates play an important role in the life of animals as well as in nature. Understanding the behaviour of these in dilute aqueous solutions is then of utmost importance in the field of biology as well as medicine. The aqueous solutions of carbohydrates have been studied extensively at different concentrations and at various temperatures²⁻⁹. The dissolution of sugar molecules in water has been of more interest due to the unique properties of water and the biological and technological importance of both sugar as well as water. Moreover, the main features that set water apart from other liquids are its spatial and orientational intermolecular correlations, which are dominated by labile hydrogen-bond interactions and its time-averaged tetrahedral geometry. It has been observed that a particular carbohydrate can be an effective substituent for water if the majority of hydroxyl groups occupy equatorial positions and the hydration of the carbohydrates depends on the detailed

stereochemistry of the solute and the way the solute molecule fits into the water structure^{8, 9-12}. In the sugar molecule, the spacing of oxygen atoms linked to next-nearest carbon neighbours is of the order of 0.485 nm, which is also the distance between next-nearest neighboring oxygen atoms in liquid water¹³. It has also been observed that the physical properties of the isomers of carbohydrates are different. Thus it was thought to be worthwhile to study the hydration behaviour of some of the carbohydrates. We report in this communication, the hydration numbers (n_h), *i.e.* the number of water molecules associated with one molecule of solute. Hydration numbers (n_h) of glucose, fructose, galactose, sucrose, lactose, α -methyl glucoside, β -methyl glucoside have been computed at 278.15, 288.15 and 298.15 K by Shii's method¹⁴ using density and speed of sound data from the literature⁸. The results obtained have been interpreted in terms of compatibility of solute molecules with water and stereo-specificity of carbohydrates.

EXPERIMENTAL

Procurement and processing of data: The hydration numbers (n_h) have been calculated by Shii's method¹⁴ using relation:

$$\lim_{c \rightarrow 0} \frac{\Delta}{c} = \frac{\left(\frac{\beta}{\beta_0} - v_0 \right)}{c} = - \frac{v_0 \left(1 - \frac{\beta_2}{\beta_0} \right)}{c} \quad (1)$$

where, β - isentropic compressibility of solution, β_0 - isentropic compressibility of solvent, β_2 - isentropic compressibility of bound water, v_0 - specific volume fraction of bound water, V_0 - apparent specific volume fraction of total solvent used

$$i.e. V_0 = \frac{d-c}{d_0}, d_0 - \text{density of solvent (water), } d - \text{density of}$$

solution, c - concentration of solute in g. cm^{-3} of solution.

The adiabatic compressibility (β) is calculated by using the relation:

$$\beta = \frac{1}{u^2 \cdot d} \quad (2)$$

where, d is density and u is the speed of sound of solution.

The values of density and speed of sound of aqueous solutions of carbohydrates at different concentrations and at different temperatures *i.e.* 278.15, 288.15 and 298.15 K were used to calculate adiabatic compressibility (β) from data of Kaulgud and Dhondge⁸. The error in density measurements was of the order of $\pm 0.003 \text{ kg m}^{-3}$. The error in speed of sound measurements was of the order of $\pm 0.025 \text{ m.s}^{-1}$. Thus considering error in density and speed of sound, the uncertainty in β is of the order of $\pm 0.0016 \times 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$. By knowing β , β_0 and v_0 , the values of Δ/c are obtained at various concentrations

of a solute and the value of $\lim_{c \rightarrow 0} \frac{\Delta}{c}$ is obtained graphically by the extrapolation of graph of Δ/c against c to zero concentration.

From eqn. 1 it is seen that the value of $\lim_{c \rightarrow 0} \frac{\Delta}{c}$ is proportional to the specific volume fraction of bound (v_0) water. In this method, the compressibility of solute is neglected and the bound water to solute is considered to be a solid like structure and it loses the freedom of mobility and the free volume contained in free water is decreased. Thus the compressibility of bound water may be considerably smaller than the normal state (compressibility of water and ice are about 45 and $18 \times 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$ respectively). Thus the value of (β_2/β_0) is taken as 18/45. Using this value of (β_2/β_0) the hydration numbers (n_h) of different carbohydrates have been obtained.

RESULTS AND DISCUSSION

Table-1 listed the hydration numbers (n_h) of different carbohydrates obtained in aqueous solutions at different temperatures by using data of Kaulgud and Dhondge⁸ in this work by Shiiio's method. Table-2 collected the hydration numbers for some carbohydrates calculated by other researchers using different methods for the sake of comparison. It is observed from these Tables that the hydration numbers calculated by Shiiio's method are higher than the hydration numbers calculated by viscosity measurements. This is because of the fact that in volumetric or compressibility measurements, the hydrated water is in equilibrium with the surrounding water, whereas, in viscometric measurements, the hydrated water is permanently attached to solute molecule and it becomes a non-equilibrium process.

The hydration numbers calculated by Shiiio⁴ are in good agreement with our values. But hydration numbers calculated

by other methods are comparatively lower than that of values obtained in this work. However, the hydration numbers calculated in this work from the data of Kaulgud and Dhondge⁸ are more reliable as they have been obtained from the extrapolation of lower concentrations.

TABLE-1
HYDRATION NUMBERS OF CARBOHYDRATES
AT DIFFERENT TEMPERATURES, OBTAINED
IN THIS WORK BY SHIIIO'S METHOD

Compound	n_h /(mol/mol)			Mol/OH radical		
	278.15	288.15	298.15	278.15	288.15	298.15
	K	K	K	K	K	K
Glucose	8.6	8.0	4.2	1.7	1.6	0.8
Fructose	8.1	6.3	4.1	1.6	1.3	0.8
Galactose	17.1	12.0	3.3	3.4	2.4	0.7
Sucrose	8.9	8.2	6.0	1.1	1.0	0.8
Lactose	25.0	13.6	13.1	3.1	1.7	1.6
α -Methyl glucoside	9.0	-	2.5	2.3	-	0.6
β -Methyl glucoside	7.2	-	2.1	1.8	-	0.5

TABLE-2
HYDRATION NUMBERS OF CARBOHYDRATES AT
DIFFERENT TEMPERATURES, REPORTED BY IN THE
LITERATURE BY DIFFERENT METHODS

Compound	n_h /(mol/mol)			Method
	278.15 K	288.15 K	298.15 K	
Glucose			3.5 ^a	Shiiio's method
	2.3 ^b , 3.7 ^c		1.8 ^b	Dielectric relaxation
	2.2 ^b			NMR
		2.8 ^c , 3.4 ^f	2.5 ^e , 2.5 ^f	Viscosity measurements
Fructose			3.8 ^a	Shiiio's method
Sucrose			3.8 ^a	Shiiio's method
	6.6 ^c			Dielectric relaxation
Lactose			5.6 ^d	Viscosity measurements
α -Methyl glucoside			2.5 ^a	Shiiio's Method

a) Ref. 14; b) Ref. 15; c) Ref.16; d) Ref.17; e) Ref.18; f) Ref.19

It is observed from Table-1 that the hydration numbers at 298.15 K of glucose and fructose are of the same order and it is less for galactose than for these two. In case of disaccharides, lactose has high hydration number than that of sucrose. α -methyl glucoside seems to be more hydrated than β -methyl glucoside. At 278.15 and 288.15 K the behaviour seems to be very different. Galactose shows high values of hydration numbers and order of increase is fructose < glucose < galactose. Sucrose and lactose and α -methyl glucoside and β -methyl glucoside show the same trends. Thus it is seen that hydration of carbohydrates is stereospecific in nature. This specificity is due to subtle differences in the structure of these compounds. Glucose, fructose and galactose are isomers. Glucose and galactose, when present in pyranose form, possess C1 conformation. The only difference in glucose and galactose is that in galactose the position of OH group at 4th carbon atom is different than that of glucose. In α -glucose all OH groups except at carbon atom number 1 are in equatorial positions, whereas in α -galactose the OH groups at position 1 and 4 are axial and other two OH groups are in equatorial position. Thus α -galactose has two axial OH groups and α -glucose has only

one axial OH group. In β -glucose all OH groups are equatorial, whereas, in β -galactose all OH groups are equatorial except at position 4. Since these carbohydrates are present in the form of anomeric mixture, galactose has more percentage of axial OH groups than that of glucose. When fructose is present in furanose form, it has also five OH groups but out of these five, two are attached to $-\text{CH}_2$ groups and not to the ring. In case of disaccharides, sucrose is compound of glucose and fructose while, lactose is that of glucose and galactose.

It is seen from Table-1 that glucose, sucrose and galactose are more hydrated at 278.15 and 288.15 K and hydration suddenly decreases at 298.15 K. In case of fructose, hydration decreases gradually as the temperature is increased. It is observed that lactose is highly hydrated at 278.15 K; with increase in temperature to 288.15 K hydration decreases sharply and with further increase in temperature to 298.15 K, it remain almost constant. Kaulgud and Dhondge⁸ observed that in case of all the carbohydrates studied in this work, the limiting apparent molar isentropic compressibilities of solutes in aqueous solutions (ϕ_{KS}^0) are highly negative at 278.15 K and the magnitude decreases with increase in temperature. It has been shown that the ϕ_{KS}^0 is the measure of protection a solute molecule gives to the water structure around the solute molecule¹¹. This corroborates well with the results obtained by us for hydration numbers. The decrease in values of hydration numbers for lactose from 278.15 to 288.15 K is explained on the basis that here a chain of water-water bonds is formed and is attached to solute molecule. On increasing the temperature, the water-water bonds are broken resulting in decrease in a hydration number. It is also seen from Table-2 that the hydration number for lactose is quite higher than that of sucrose at 298.15 K. It clearly indicates that the nature of hydration and hydrated water for lactose must be different than that of other carbohydrates. In case of α -methyl glucoside and β -methyl glucoside the hydration numbers decrease almost 4 times as the temperature increased from 278.15 K to 298.15 K. This may be due the fact that the hydration of α -methyl glucoside and β -methyl glucoside is of hydrophobic hydration type.

It seems that OH groups of carbohydrates interact with water like OH group of alcohols. This fact is supported by the viscosity B coefficients of alcohols and carbohydrates. The viscosity B coefficient at 298.15 K for methanol²⁰ (one OH group) is $0.087 \text{ dm}^3 \text{ mol}^{-1}$, that of ethylene glycol²⁰ (two OH groups) is $0.143 \text{ dm}^3 \text{ mol}^{-1}$, for Glycerol²⁰ (three OH groups) it is $0.225 \text{ dm}^3 \text{ mol}^{-1}$, for glucose¹⁹ (five OH groups) it is $0.45 \text{ dm}^3 \text{ mol}^{-1}$, for sucrose³³ (8 OH groups) it is $0.878 \text{ dm}^3 \text{ mol}^{-1}$

and for lactose²¹ (8 OH groups) it is $1.144 \text{ dm}^3 \text{ mol}^{-1}$. It is observed that B-coefficient increases almost linearly with increase of number of OH groups. B-coefficient gives direct idea about the amount of water attached permanently to the solute molecule when molecule is in dynamic motion. However, lactose is an exception to this. It shows quite high value of B-coefficient as compared to sucrose. To support our notion, we have calculated the number of water molecules per OH radical attached to a sugar molecule at different temperatures. These are depicted in Table-1. At 298.15 K the values for glucose, fructose, galactose and sucrose are almost of same magnitude; however, lactose shows quite higher value as expected. α -Methyl glucoside and β -methyl glucoside show smaller values because of hydrophobic hydration type. As the temperature is lowered these values increase and show an effect similar to observed in case of hydration numbers. Thus it can be concluded that the sugars interact with water just like alcohols with the exception of lactose. Thus the nature of hydration and hydrated water for lactose is different than that of other carbohydrates.

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