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Modulation in physico-chemical characteristics of some polyhydroxy solutes in presence of L-glycine: Volumetric and NMR spectroscopic approach

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ABSTRACT

Volumetric and ^{1}H and ^{13}C NMR spectroscopic studies have been exploited to study molecular interactions of some polyhyroxy solutes with L-glycine in aqueous solutions. Apparent molar volumes, $V_{2,\phi}$ for monosaccharides; (+)-D-mannose, (+)-D-glucose, and (−)-L-sorbose, disaccharides; (+)-maltose monohydrate, and (+)-cellobiose, deoxy-derivatives of hexoses; 6-deoxy-D-mannose, 2-deoxy-D-glucose, methyl glycopyranosides; (+)-methyl α-D-mannopyranoside, and (+)-methyl α-D-glucopyranoside, and polyols; D-mannitol, D-sorbitol, and myo-inositol in 0.05, 0.15, 0.25, 0.35 and 0.50 mol kg^{-1} aqueous solutions of L-glycine have been determined from density, ρ data measured at 288.15, 298.15, 308.15 and 318.15 K under atmospheric pressure, $p = 0.1$ MPa. The data were processed to obtain the standard partial molar volumes, V_2° at infinite-dilution and the corresponding volumes of transfer, $\Delta_{tr}V_2^{\circ}$ of solutes from water to aqueous solution of L-glycine. Other parameters such as partial molar expansion coefficients $(\partial V_2^{\circ}/\partial T)_P$ and their second-order derivatives $(\partial^2 V_2^{\circ}/\partial T^2)_P$, and pair and higher-order volumetric interaction coefficients (V_{AB} and V_{ABB}) have also been obtained. These parameters have been utilized to discuss various types of interactions on the basis of co-sphere overlap model. ^{1}H and ^{13}C NMR spectroscopic studies for polyhydroxy solutes were carried out in 0.10 mol kg^{-1} L-glycine prepared in 9:1 (w/w) H_2O–D_2O solvent. NMR results show more downfield shift in ternary system than in pure L-glycine solution, hence suggesting that hydrophilic–ionic interactions predominate over hydrophilic/hydrophobic–hydrophobic interactions occurring between solute and L-glycine molecules.

1. Introduction

Saccharides along with amino acids, lipids, and the nucleotide bases form the chemical building blocks of living matter on the earth. Deoxy-derivatives of saccharides and amino sugars, sugar phosphates, sulphates and carboxylates occur in natural products [1–8]. Saccharides are important due to their hydroxyl (OH) rich periphery, coordinating ability, homo-chirality, stereospecificity and low toxicity. Saccharides and polyhydric alcohols can increase the thermal stability of proteins or reduce the extent of their denaturation by other reagents. The native conformation of the globular proteins under external osmotic stress such as dehydration, temperature, variable pH, freezing, high salinity, and internal stress like high concentration of the protein denaturants can be stabilized by the naturally occurring osmolytes. Polyols and amino acids are considered as naturally occurring protective osmolytes. Sorbitol is widely used as a stabilizing agent in the food industry as well as in pharmaceutical formulations since it is harmless upon ingestion. Myo-inositol is a cyclic polyol and it is an essential nutrient for most living cells including protozoa [9–16]. Disaccharides are well known for their ability to preserve life in cells, organisms, and biomolecules against environmental stresses. Some micro-organisms can survive under extreme conditions of temperature, where saccharide-salt solutions play an important role for their survival by affecting the glass-transition temperature, T_g and ice formation. The molecular mechanisms behind this effect are not yet fully understood and are still matter of debate [17–19].

Physico-chemical properties data characterizing the solvation behavior of saccharides are needed for understanding the protein stabilization, taste chemoreception, and antidesiccation mechanisms. These properties play a pivotal role in study of the reaction conditions such as the feasibility and optimization of currently employed industrial processes [11,20]. In living organisms, interactions of saccharides with proteins play a key role in a wide range of biochemical processes. Saccharides located at cell surfaces are receptors for the bioactive structures of enzymes, hormones,

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Table 1
The specifications of the chemicals used.

Compound/(abbrevation)	Source	CAS number	[a]Mass fraction purity
(+)-D-Mannose/(Man)	Sisco Research Lab.	3458-28-4	≥0.99
6-Deoxy-D-mannose/(6de-Man)	Sisco Research Lab.	3615-41-6	0.99
(+)-Methyl α-D-mannopyranoside/(Me α-Man)	Sigma Chemical Co.	617-04-9	≥0.99
D-Mannitol/(Maol)	Sisco Research Lab.	69-65-8	0.99
(+)-D-Glucose/(Glc)	Sigma Chemical Co.	50-99-7	≥0.99
(+)-Methyl α-D-glucopyranoside/(Me α-Glc)	Sigma Chemical Co.	97-30-3	≥0.99
2-Deoxy-D-glucose/(2de-Glc)	Sisco Research Lab.	154-17-6	0.99
(−)-L-Sorbose/(Sor)	Sigma Chemical Co.	87-79-6	≥0.98
D-Sorbitol/(Srol)	Sisco Research Lab.	50-70-4	0.98
Myo-inositol/(M-inol)	Sisco Research Lab.	87-89-8	0.98
(+)-Maltose monohydrate/(Mal)	Sigma Chemical Co.	6363-53-7	0.95
(+)-Cellobiose/(Cel)	Sigma Chemical Co.	528-50-7	0.98
L-Glycine	Sisco Research Lab.	56-40-6	0.99
Deuterium oxide/(D_2O)	Sigma Chemical Co.	7789-20-0	≥0.999 atom % D

[a] Purity as reported by manufacturer.

antibodies, viruses, etc. Owing to the low threshold for conformational modification of saccharides, the interactions between saccharides and protein are usually specific and multivalent. Therefore, the study of saccharides–protein interactions is very important for immunology, biosynthesis, pharmacology and medicine [21].

Due to complex conformation and configuration of proteins in various solvents, a direct study on proteins is very difficult. Therefore, generally physico-chemical investigations are performed on the protein model compounds such as amino acids [22–24]. We have studied thermodynamic and transport properties of various saccharides, their derivatives, and polyols and their interactions with electrolytes in aqueous media [18,19]. To understand the physico-chemical characterstics of polyhydroxy solutes and how solute–solvent interactions get modified in the presence of amino acids, we have carried out densimetric and ^1H and ^{13}C NMR based spectroscopic studies.

2. Experimental

2.1. Materials and methods

The provenances of chemicals along with their abbreviation, CAS number, mass fraction purity and source of procurement are given in Table 1. These chemicals with highest available purity grade were used as received after drying over $CaCl_{2(anhyd)}$ in a vacuum desiccator for 48 h at room temperature.

2.2. Density measurement

The solutions were freshly prepared on mass basis using a Mettler balance (Model: AB265-S) with a precision of ±0.01 mg in pure water procured from Ultra UV/UF Rions lab water system. The specific conductance was less than 1.29×10^{-4} S m^{-1}. Densities of the solutions were measured using a vibrating-tube digital

Table 2
Standard partial molar volumes, V_2° at infinite-dilution of saccharides, their deoxy and methyl derivatives, and polyols in water and L-glycine$_{(aq)}$ solutions over the temperature range 288.15–318.15 K under atmospheric pressure, p = 0.1 MPa.

[a]m_B/mol kg^{-1}	$V_2^\circ 10^6$/m^3 mol^{-1}			
T/K	288.15	298.15	308.15	318.15
(+)-D-Mannose				
0.00	111.03 (2.82)[b]	111.69 (3.88)	112.30 (2.26)	112.99 (3.37)
0.05	110.03 (3.89)	110.86 (3.32)	111.76 (4.39)	112.53 (3.16)
0.15	110.38 (3.49)	111.23 (3.26)	112.09 (3.48)	112.85 (3.63)
0.25	111.40 (3.50)	112.01 (3.64)	112.55 (3.48)	113.13 (4.04)
0.35	111.49 (3.21)	112.07 (3.11)	112.63 (2.98)	113.18 (3.76)
0.50	111.59 (2.85)	112.16 (3.03)	112.70 (1.70)	113.20 (3.39)
6-Deoxy-D-mannose				
0.00	128.25 (2.02)	128.64 (2.23)	129.65 (2.19)	131.07 (2.12)
0.05	128.66 (2.61)	128.93 (2.90)	129.82 (3.11)	131.14 (2.53)
0.15	128.79 (2.96)	129.05 (3.06)	129.91 (3.16)	131.18 (3.93)
0.25	128.89 (3.34)	129.18 (2.95)	130.03 (2.91)	131.25 (3.22)
0.35	128.97 (3.98)	129.25 (3.16)	130.09 (2.74)	131.30 (3.55)
0.50	129.14 (2.58)	129.38 (2.93)	130.18 (3.00)	131.39 (2.57)
(+)-Methyl-α-D-mannopyranoside				
0.00	132.18 (3.80)	132.58 (3.47)	133.42 (4.16)	134.61 (3.23)
0.05	132.11 (2.95)	132.38 (3.01)	133.06 (4.28)	134.08 (3.80)
0.15	132.97 (2.71)	133.24 (3.13)	133.84 (5.18)	134.76 (3.99)
0.25	133.48 (3.29)	133.80 (3.17)	134.50 (4.33)	135.58 (3.96)
0.35	133.62 (3.00)	133.92 (2.93)	134.61 (4.09)	135.72 (3.13)
0.50	133.82 (3.29)	134.12 (3.11)	134.76 (4.54)	135.84 (3.45)
D-Mannitol				
0.00	117.05 (3.87)	119.07 (3.58)	120.45 (3.15)	121.30 (3.59)
0.05	117.84 (2.35)	119.70 (2.63)	120.92 (2.82)	121.51 (2.61)