



Study on interactions of saccharides and their derivatives with potassium phosphate monobasic (1:1 electrolyte) in aqueous solutions at different temperatures



P.K. Banipal^{*}, Neha Aggarwal, T.S. Banipal

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, Pb, India

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ABSTRACT

The densities (ρ) of monosaccharides, their methyl and deoxy derivatives, disaccharides and trisaccharides have been measured in water and in (0.25, 0.50, 1.00 and 1.25) mol kg⁻¹ aqueous potassium phosphate monobasic (KH₂PO₄) solutions at (288.15, 298.15, 308.15 and 318.15) K and atmospheric pressure. The standard partial molar volumes (V_2°) at infinite dilution and the corresponding volumes of transfer ($\Delta_t V_2^\circ$) of solutes (saccharides and derivatives) from water to aqueous solutions of KH₂PO₄ have been calculated. The interaction coefficients (using the McMillan–Mayer theory) and standard partial molar expansibilities (V_E°) have also been calculated. The results suggested the dominance of hydrophilic–ionic interactions due to the great affinity of phosphate (H₂PO₄⁻) anions for hydrogen bonding with hydrophilic sites of the saccharide molecules.

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1. Introduction

Saccharides and their derivatives, being important organic compounds in life processes, participate in many biological processes such as protein/enzyme stability, cryopreservation of living cells, signaling, cell–cell recognition (immune responses), and cellular communication [1–4]. Deoxy derivatives of saccharides, sugar phosphates, sulfates, carboxylates and amino sugars occur in natural products. L-Rhamnose (6-deoxy mannose) is present as glycosides in plant pigments, gums and mucilages [5–8]. Phosphates present in body as important components of nucleic acids, bones, ADP, ATP etc., also participate in many biochemical processes [9]. The knowledge about solute (saccharide/derivative)–H₂O interactions and packing characteristics of solutes in three dimensional structure of water is helpful in understanding the mechanism of taste chemoreception. Thermodynamic properties are useful tools in studying the hydration behavior of these solutes and solute–solvent interactions [10–16].

The study on interactions of electrolytes with saccharides is important in several fields related to biology, medicine, catalysis and the environment. In view of increasing biological and technological applications, physicochemical properties of saccharides have been studied in a variety of aqueous electrolyte solutions [17–21]. Phosphate-based inorganic salts have stabilizing and salting-out effects on proteins

and macromolecules. To the best of our knowledge, volumetric studies on the interactions between saccharides or their derivatives and KH₂PO₄ are rare in the literature. Therefore, we report systematically the apparent molar volumes ($V_{2,\phi}$) for various monosaccharides, derivatives of monosaccharides, disaccharides and trisaccharides in water and in m_B (molality of KH₂PO₄) = (0.25, 0.50, 1.00 and 1.25) mol kg⁻¹ aqueous potassium phosphate monobasic (KH₂PO₄) solutions at (288.15, 298.15, 308.15, and 318.15) K.

2. Experimental

2.1. Materials

The chemicals along with their abbreviations, mass fraction purity and sources of procurement are given in Table 1. These chemicals with highest available purity were used as received after drying over anhydrous CaCl₂ in a vacuum desiccator for 48 h at room temperature.

2.2. Apparatus

The solutions were freshly prepared by mass using a Mettler balance (Model: AB265-S) with a precision of ± 0.01 mg in double distilled–deionized and degassed water of specific conductance less than 1.29×10^{-4} S m⁻¹. Densities of the solutions were measured using a vibrating–tube digital densimeter (Model: DMA 60/602, Anton Paar, Austria) with a reproducibility better than $\pm 3 \times 10^{-3}$ kg m⁻³ for dilute

^{*} Corresponding author. Tel.: +91 183 2451357; fax: +91 183 2258819/20.
E-mail address: pkbanipal@yahoo.com (P.K. Banipal).

Table 1

The source and mass fraction purity of chemicals used.

Compound	Source	CAS number	Mass fraction purity
(+)-D-Xylose (Xyl)	Sigma Chemical Co.	58-86-6	0.99
(-)-D-Ribose (Rib)	Sigma Chemical Co.	50-69-1	0.99
(-)-D-Fructose (Fru)	Sigma Chemical Co.	57-48-7	0.99
(+)-D-Glucose (Glc)	Sigma Chemical Co.	50-99-7	≥0.99
(+)-D-Mannose (Man)	Fluka	3458-28-4	≥0.99
2-Deoxy-D-ribose (de-Rib)	Sisco Research Lab.	533-67-5	0.99
2-Deoxy-D-glucose (de-Glc)	Sisco Research Lab.	154-17-6	0.99
6-Deoxy-D-mannose (de-Man)	Sisco Research Lab.	6155-35-7	0.99
(+)-Methyl α-D-mannopyranoside (Me α-Man)	Sigma Chemical Co.	617-04-9	≥0.99
(+)-Methyl α-D-glucopyranoside (Me α-Glc)	Sigma Chemical Co.	97-30-3	≥0.99
Sucrose (Suc)	Sigma Chemical Co.	57-50-1	≥0.99
(+)-Cellobiose (Cel)	Sigma Chemical Co.	528-50-7	0.98
(+)-Lactose monohydrate (Lac)	Sigma Chemical Co.	64044-51-5	≥0.98
(+)-Maltose monohydrate (Mal)	Sigma Chemical Co.	6363-53-7	0.95
(+)-Melezitose (Mel)	Sisco Research Lab.	207511-10-2	>0.99
(+)-Raffinose pentahydrate (Raf)	Fluka	17629-30-0	≥0.99
Potassium phosphate monobasic (KH ₂ PO ₄)	Sigma Chemical Co.	7778-77-0	≥0.99

solutions. A constant temperature bath (Julabo F-25) with stability within ± 0.01 K, was used to control the temperature of the densimeter cell. Its working was checked by measuring the densities of aqueous sodium chloride solutions which agreed well with the literature values at 298.15 K [22,23]. Densities for pure water taken from the literature [24] are; $(0.999129, 0.997047, 0.994063, 0.990244) \times 10^3 \text{ kg m}^{-3}$ at (288.15, 298.15, 308.15, and 318.15) K, respectively.

3. Results and discussion

3.1. Apparent molar volumes

The densities (ρ) of various saccharides and derivatives in water and in $m_B = (0.25, 0.50, 1.00, \text{ and } 1.25) \text{ mol kg}^{-1}$ aqueous KH₂PO₄ solutions were determined at (288.15, 298.15, 308.15, and 318.15) K. The ρ values increase with the molality of the saccharide (solute) and KH₂PO₄ (cosolute) while it decreases with rise of temperature. This

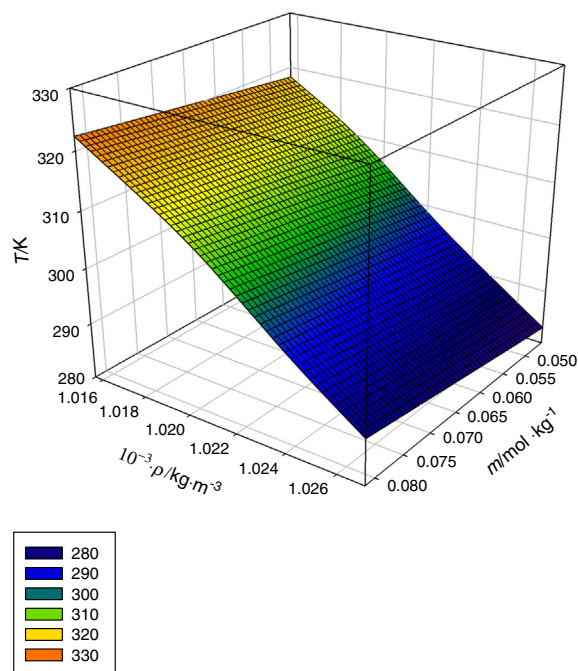


Fig. 1. Density (ρ) vs molality (m) at (288.15, 298.15, 308.15, and 318.15) K for 2-deoxy-D-glucose in aqueous KH₂PO₄ solutions at $m_B = 0.25 \text{ mol kg}^{-1}$. The density, ρ , increases with an increase in molality, m of 2-deoxy-D-glucose and decreases with rise of temperature as evident from the change in color from orange to blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

trend can be observed in the 3-D plot (representative Fig. 1) of ρ vs molality, m (molality of the solute) of 2-deoxy-D-glucose in aqueous KH₂PO₄ solutions at $m_B = 0.25 \text{ mol kg}^{-1}$. These experimentally measured density data were used to calculate apparent molar volumes, $V_{2,\phi}$ (Supplementary Table S1) using the following relation:

$$V_{2,\phi} = [M/\rho - (M/\rho_0)/(m\rho_0)] \quad (1)$$

where M and m are, respectively, the molar mass and molality of the solute (saccharide/derivative) and ρ and ρ_0 are the densities of solution and solvent (pure H₂O or mixed solvent KH₂PO₄ + H₂O), respectively. The $V_{2,\phi}$ values increase with concentration of saccharide and temperature (representative plot of $V_{2,\phi}$ vs molality, m at $T = (288.15 \text{ to } 318.15) \text{ K}$ for lactose monohydrate in water is shown in Fig. 2). The

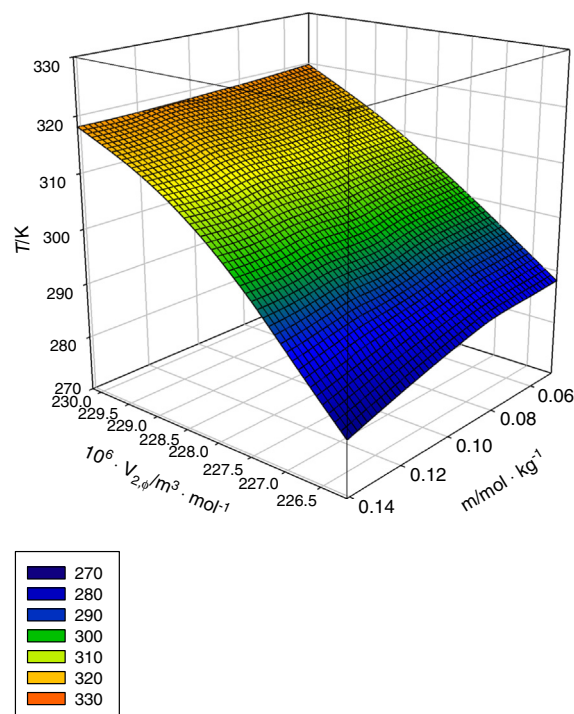


Fig. 2. Plot of apparent molar volume ($V_{2,\phi}$) vs molality (m) at $T = (288.15 \text{ to } 318.15) \text{ K}$ for lactose monohydrate in water. The apparent molar volume ($V_{2,\phi}$) increases with molality (m) and also with temperature. The $V_{2,\phi}$ value is lowest at 288.15 K depicted by the blue region while it increases up to the orange region at higher temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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