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Investigations to explore interactions in (polyhydroxy solute + L-ascorbic acid + H_2O) solutions at different temperatures: Calorimetric and viscometric approach

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ABSTRACT

Isothermal titration micro-calorimeter has been used to measure the enthalpy change (q) of polyhydroxy solutes [(+)-D-xylose, xylitol, (+)-D-glucose, 2-deoxy-D-glucose, (+)-methyl-α-D-glucopyranoside, and (+)-maltose monohydrate] in water and in (0.05, 0.15, and 0.25) mol·kg^{-1} L-ascorbic acid$_{(aq)}$ solutions at (288.15, 298.15, 308.15, and 318.15) K. Limiting enthalpies of dilution ($\Delta_{dil}H^{\circ}$) of these solutes were calculated from heat evolved/absorbed during calorimetric experiments. Further thermodynamic quantities such as limiting enthalpies of dilution of transfer ($\Delta_{tr}\Delta_{dil}H^{\circ}$), change in heat capacity ($\Delta_{dil}C^{\circ}_{p,2,m}$), and pair ($h_{AB}$) and triplet ($h_{ABB}$) enthalpic interaction coefficients were also calculated and used to explore the nature of interactions of solutes with cosolute (L-ascorbic acid). The Jones-Dole viscosity *B*-coefficients for (+)-D-xylose, xylitol, (+)-D-galactose, galactitol, (+)-D-glucose, 2-deoxy-D-glucose, (+)-methyl-α-D-glucopyranoside, and (+)-maltose monohydrate in water and in (0.05, 0.15, 0.25, and 0.35) mol·kg^{-1} L-ascorbic acid$_{(aq)}$ solutions have been determined from viscosity (η) data measured over temperature range (288.15–318.15) K and at pressure, P = 101.3 kPa. The temperature dependence of *B*-coefficients (dB/dT), and viscosity *B*-coefficients of transfer ($\Delta_{tr}B$) of solutes from water to cosolute have also been estimated. These parameters have been discussed in terms of structure-making (kosmotropic) or -breaking (chaotropic) behavior of solutes.

1. Introduction

Saccharides and their derivatives are the most abundant class of biomolecules, known for biological versatility and great diversity of their biological functions [1–4]. Disaccharides can stabilize the labile biomolecules by a combination of kinetic and specific effects in aqueous solutions. During lyophilisation process, disaccharides are used as cryoprotectants against the destabilizing and degradation of drugs and enzymes [5–8]. Sugar alcohols are alternative artificial nutritive sweeteners and have been widely used in food and beverages due to their properties of good taste, low calorie content and no tooth decay. Additionally, they are also applied in many aspects like pharmacy, cosmetics, explosives, and plasticizers, etc [9–14]. As a kind of polyhydroxy compounds, L-ascorbic acid is an ubiquitous and indispensable compound in living systems, required for the metabolism of folic acids and mineral compounds. L-ascorbic acid is essential to synthesize collagen which provides the structure to muscles, bones, and tendon. The most prominent role of L-ascorbic acid is its immune stimulating effect for defense against infections such as common colds. It acts as an inhibitor of histamine released during allergic reactions. As a powerful antioxidant, L-ascorbic acid can neutralize toxins and pollutants. It has an ability to prevent the formation of potentially carcinogenic nitrosamines in the stomach. L-ascorbic acid along with Zn are important for healing the wounds [15–16]. The degradation of L-ascorbic acid is very important and major cause of quality and color changes during storage of food materials [17].

Thermodynamic and transport studies of aqueous solutions of polyhydroxy solutes are significant because of their multidimensional physical, biochemical, and industrially useful properties. Terekhova et al. [18] reported the enthalpies of solutions of few saccharides in L-ascorbic acid at 298.15 K only. Banipal et al. [19] reported the volumetric, isentropic compressibility and viscometric properties of various vitamins; L-ascorbic acid, nicotinic acid, thiamine hydrochloride, and pyridoxine hydrochloride in water at (288.15, 298.15, 308.15 and 318.15) K. Recently, we have reported [20] the volumetric and UV absorption studies in order to understand the solvation behavior of polyhydroxy solutes in L-ascorbic acid$_{(aq)}$ solutions at T = (288.15–318.15) K. In the current

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study, calorimetric and viscometric properties have been exploited to understand the mode of interaction of polyhydroxy solute with L-ascorbic acid. Various quantities such as limiting enthalpy of dilution, heat capacity change, Jones-Dole viscosity *B*-coefficients, and interaction coefficients for solutes have been estimated in water and in different molalities of L-ascorbic acid$_{(aq)}$ solutions. An attempt has been made to examine the concentration and temperature dependence of these outcomes.

2. Experimental

2.1. Materials

The provenances including mass fraction purity, CAS number, source of procurement and abbreviations of the chemicals used are presented in Table 1. The purity of the chemicals used was analyzed with C, H, N, S analysis method using FLASH 2000 Organic Elemental Analyzer, USA. The carbon and hydrogen contents obtained in the analysis are similar to expected values from molecular formula with zero percentage of sulfur and nitrogen (Table 1). These chemicals were used after drying over $CaCl_{2(anhyd)}$ in a vacuum desiccator for 48 h at room temperature. The solutions were prepared fresh on mass basis in air tight glass vials by using Mettler-Toledo balance (*Model: AB 265-S*) having a precision of ±0.01 mg. Pure water with specific conductance less than 1.29×10^{-4} S·m^{-1} was procured from Ultra UV/UF Rions lab water system. It was degassed before use to avoid microbubbles in solutions.

2.2. Isothermal titration calorimetry

The measurement of enthalpy change for the studied systems was carried out on an isothermal titration micro-calorimeter (*MicroCal iTC$_{200}$, USA*) at T = (288.15, 298.15, 308.15 and 318.15) K. The reference cell was filled with pure water and the sample cell with a capacity of 200 μl was filled with water or cosolute solution. Titrations were carried out using a 40 μl syringe filled with 0.25 mol·kg^{-1} solute solution, stirring at a speed of 500 rpm during each run. The titration experiment was consisting of 19 consecutive injections of 2 μl each and having duration 4 s with an interval of 120 s between consecutive injections. The control experiments were also performed and appropriate corrections were made to the main experiment.

2.3. Viscosity

The viscosities (η) of solutes in water and m_B = (0.05, 0.15, 0.25 and 0.35) mol·kg^{-1} L-ascorbic acid$_{(aq)}$ solutions have been determined from efflux time, t measurements at T = (288.15, 298.15, 308.15, and 318.15) K as:

$$\eta/\rho = at - b/t \quad (1)$$

where ρ is the density of solution (reported earlier [20]); a and b are the viscometric constants. The viscosities (η) of solutions were measured by using an Ubbelohde-type capillary viscometer, calibrated by measuring the efflux time of water from T = (288.15–318.15) K. The efflux time was measured with a digital stopwatch with a resolution of ±0.01 s for the average of at least four flow-time readings. The temperature of the experimental solution was controlled within ±0.01 K using an efficient constant temperature bath *(Julabo F-25)*. The measured uncertainty in viscosity is ±0.02 mPa·s which also includes the uncertainty in viscosity of calibrated solvent i.e. water. The viscosities for pure water taken from the literature are (1.1382, 0.8904, 0.7194, 0.5963) mPa·s at (288.15, 298.15, 308.15, and 318.15) K, respectively [21,22].

3. Results and discussion

3.1. Limiting enthalpy of dilution

The enthalpy change (q) was measured for some polyhydroxy solutes in water and in m_B (molality of L-ascorbic acid) = (0.05, 0.15 and 0.25) mol·kg^{-1} L-ascorbic acid$_{(aq)}$ solutions (data are given as supplementary material in Table S1). The process is exothermic and the magnitude of q values decreases with increase in molalities of solute. Overall the enthalpy change was found to be less exothermic with rise of temperature, whereas it increases for Glc, Mal and Xyol in water and for Xyol in $m_B \approx 0.05$ mol·kg^{-1} too. A representative 3-D plot of q versus m_A, molality of 2de-Glc in m_B = 0.15 mol·kg^{-1} L-ascorbic acid$_{(aq)}$ solutions is given in Fig. 1, over the temperature range (288.15–318.15) K. The comparison of data (Fig. 2a) shows that the enthalpy change for derivative; Me α-Glc is more exothermic in water as compared to its parent

Table 1
Specifications of chemicals used.

Compound (abbreviation) [Molecular Formula]	Molar mass (g·mol^{-1})	Mass fraction purity[a]	Source	CAS number	C, H, N, S analysis	
					Calculated%	Observed%
L-Ascorbic Acid [$C_6H_8O_6$]	176.12	⩾0.99	Sigma Chemical Co.	50-81-7	C = 40.88 H = 4.54	C = 40.85 H = 4.57
(+)-D-Xylose (Xyl)[$C_5H_{10}O_5$]	150.13	⩾0.99	Sigma Chemical Co.	58-86-6	C = 40.00 H = 6.71	C = 39.97 H = 6.69
Xylitol (Xyol) [$C_5H_{12}O_5$]	152.15	⩾0.99	Sisco Research Lab.	87–99-0	C = 39.43 H = 7.89	C = 39.45 H = 7.87
(+)-D-Galactose (Gal) [$C_6H_{12}O_6$]	180.16	0.98	Sisco Research Lab.	59-23-4	C = 39.96 H = 6.66	C = 40.03 H = 6.63
Galactitol (Gaol) [$C_6H_{14}O_6$]	182.18	0.99	Sisco Research Lab.	608-66-2	C = 39.52 H = 7.68	C = 39.55 H = 7.65
(+)-D-Glucose (Glc) [$C_6H_{12}O_6$]	180.16	⩾0.99	Sigma Chemical Co.	50–99-7	C = 40.00 H = 6.71	C = 40.03 H = 6.69
2-Deoxy-D-glucose (2de-Glc) [$C_6H_{12}O_5$]	164.16	0.99	Sisco Research Lab.	154-17-6	C = 43.90 H = 7.37	C = 43.88 H = 7.39
(+)-Methyl-α-D-glucopyranoside (Me α-Glc) [$C_7H_{14}O_6$]	194.18	⩾0.99	Sigma Chemical Co.	97-30-3	C = 43.30 H = 7.27	C = 43.27 H = 7.25
(+)-Maltose monohydrate (Mal) [$C_{12}H_{22}O_{11}.H_2O$]	360.31	0.99	Sigma Chemical Co.	6363-53-7	C = 40.00 H = 6.71	C = 40.02 H = 6.69

[a] As reported by the suppliers.