J. Chem. Thermodynamics 113 (2017) 52–63

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Temperature dependence of the volumetric and acoustic behaviour of aqueous mixtures of monosaccharides and trilithium citrate

Harsh Kumar [a,*], Sheetal [a], Isha Behal [a], Sanjay Sharma [b]

[a] Department of Chemistry, Dr. B R Ambedkar National Institute of Technology, Jalandhar 144011, Punjab, India
[b] Department of Chemistry, University College, Kurukshetra University, Kurukshetra 136119, India

ARTICLE INFO

Article history:
Received 13 April 2017
Received in revised form 13 May 2017
Accepted 25 May 2017
Available online 29 May 2017

Keywords:
Saccharides
Apparent molar volume
Apparent molar isentropic compression
Trilithium citrate (TLC)
Ion-ion interaction

ABSTRACT

Densities (ρ) and speeds of sound (c) measurements of D(−)-ribose and D(+)-xylose in (0.2, 0.4, 0.6) $\text{mol}\cdot\text{kg}^{-1}$ aqueous solutions of trilithium citrate (TLC) have been carried out at different temperatures. The experimental results were used to calculate apparent molar and partial molar quantities, partial molar volumes and partial molar isentropic compression of transfer. The pair and triplet interaction coefficients are computed from transfer parameters. The partial molar expansibilities have also been calculated. The results have been interpreted in terms of prevailing interactions and structure making and breaking tendency of the solutes in aqueous solution of TLC.

1. Introduction

The understanding about hydration characteristics of saccharides in aqueous solutions is very important due to the recognition of saccharides in various biological processes like protein/enzyme stability, protective efficacy, cellular interactions, *etc.* [1–4]. With several hydrophilic hydroxyl groups, saccharides are typical non-electrolytes that are responsible for their peculiar hydration characteristics [5–7]. Saccharides, due to their conformational flexibility are suitable models to study the hydration properties of proteins and nucleic acids as these restricts denaturation due to reagents and stabilize the protein confirmations [8–10]. The hydration behaviour of these solutes and solute-solvent interactions [11–14] are studied by means of thermodynamic properties. It is well known that biologically and industrially important citrates [15–17] are used for medicinal purposes as well as in food, pharmaceutical, and cosmetic industries. Citrate is biodegradable and non-toxic and could be discharged into biological waste water treatment plants. Many researchers have done work on the thermochemical properties of saccharides in presence of amino acids [18–24] and different salt-water mixed solvents [25–30]. In continuation to our earlier studies on saccharides with citrate salts [31–34], we report in the present paper, the densities and speeds of sound of D(−)-ribose and D(+)-xylose in aqueous trilithium citrate (TLC) solutions at different temperatures (288.15, 298.15, 308.15, and 318.15) K and experimental pressure, $p = 0.1$ MPa. Further various derived properties like apparent molar properties, partial molar property of transfer, and interactional parameters have also been reported. As per our knowledge no data has been reported for volumetric and acoustic behaviour of D(−)-ribose and D(+)-xylose with aqueous trilithium citrate (TLC) mixtures so far.

2. Experimental

2.1. Chemicals

D(−)-Ribose and D(+)-xylose with mass fraction purities ≥0.99 were obtained from HiMedia laboratories and trilithium citrate (TLC) with mass fraction purity 0.985 was purchased from SD Fine Chem. Ltd. India. All the chemicals were used as received without any further purification. All the chemicals were dried in vacuum and stored in desiccators over P_2O_5 for at least 2 days before their use. The details and specifications of the chemicals used are also reported in Table 1.

2.2. Equipment and procedures

Freshly prepared triple distilled and degassed water (specific conductance $<10^{-6}\ \text{S}\cdot\text{cm}^{-1}$) was used for the preparation of solutions. The solutions were prepared by weighing on a Sartorius CPA225D electronic balance having a precision of ±0.00001 g. The

---

* Corresponding author.
E-mail addresses: h.786.man@gmail.com, manchandah@nitj.ac.in (H. Kumar).

http://dx.doi.org/10.1016/j.jct.2017.05.032
0021-9614/© 2017 Elsevier Ltd.

Table 1
Specification of studied chemicals.

Chemical	CAS No.	Source	Purification method	[a]Mass fraction purity
D(−)-Ribose	50-69-1	Hi Media Chem. Pvt. Ltd., India	Vacuum drying	≥0.99
D(+)-Xylose	58-86-6	Hi Media Chem. Pvt. Ltd., India	Vacuum drying	≥0.99
Trilithium Citrate tetrahydrate (TLC*4H_2O)	6080-58-6	SD Fine Chem. Ltd. India	Vacuum drying	0.985
[b]Trilithium Citrate	919-16-4	SD Fine Chem. Ltd. India	Vacuum drying	0.985

[a] Declared by the supplier.

[b] Anhydrous salt obtained after drying the Trilithium Citrate tetrahydrate mentioned in the table. The water content in the anhydrous salt determined using Karl-Fisher analysis was found to be less than 100 ppm.

standard uncertainty in molality for samples with purity 99% and 98.5% are $u_r(m_A)$ = 1% and $u_r(m_{TLC})$ = 1.5% respectively. After drying the hydrated salt in vacuum and over P_2O_5, the water molecules from trilithium citrate tetrahydrate are dried. The molalities are determined for the anhydrous trilithium citrate salt (TLC) and not for hydrated salt *i.e.* (TLC*4H_2O) as water molecules from hydrated salt are not included in the molality calculations. The solutions have been prepared using anhydrous trilithium citrate. Details regarding calibration and measurement of density and speed of sound using Anton Paar DSA 5000 M densimeter has been described earlier [31]. The speed of sound is measured using a propagation time technique. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample-filled cavity at a frequency of approximately 3 MHz; the second transducer receives those waves. Thus, the speed of sound is obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound wave [35]. The accuracy in the temperature of the instrument corresponds to 0.001 K. The sensitivity of the instrument corresponds to a precision in density and speeds of sound measurements of 1×10^{-3} kg·m^{-3} and 1×10^{-2} m·s^{-1}. The accuracy in the density and speed of sound measurements are 5×10^{-3} kg·m^{-3} and 5×10^{-2} m·s^{-1}. The standard uncertainty of the density and speed of sound are 0.15 kg·m^{-3} and 5 m·s^{-1}, respectively.

3. Results and discussion

3.1. Volumetric properties

3.1.1. Density

The experimental value of solution densities, ρ of D(−)-ribose and D(+)-xylose in (0.2, 0.4, 0.6) mol.kg^{-1} aqueous solutions of TLC were measured at temperatures T = (288.15, 298.15, 308.15, 318.15) K. The values of density of all the solutions at different temperatures are listed in Table 2. From the analysis of table, it is observed that density of solution increases with rise in concentration of saccharides and decreases slightly with increase in temperature of the solution, at a particular concentration of TLC. The density values of D(−)-ribose and D(+)-xylose in (0.2, 0.4, 0.6) mol·kg^{-1} TLC and (0.2, 0.4, 0.6) mol·kg^{-1} trisodium citrate (TSC) at 298.15 K [32] have been plotted in Fig. 1 for the sake of comparison. The comparison of the values shows that TSC has higher values of densities as compared to TLC. Further, the comparison of the densities of the aqueous trilithium citrate solutions was carried out and the same has been given in our earlier paper [33].

3.1.2. Apparent molar volume

From the solution densities (Table 2), the apparent molar volumes, (V_ϕ) of D(−)-ribose and D(+)-xylose in (0.2, 0.4, 0.6) mol·kg^{-1} of aqueous TLC solutions have been obtained using the following relation:

$$V_\phi = (M/\rho) - \{(\rho - \rho_o)/(m_A \rho \rho_o)\} \quad (1)$$

where M is the molar mass of the solute (kg·mol^{-1}), m_A is the molality (mol·kg^{-1}) of saccharides *i.e.* amount of solute (saccharides) per one kilogram of solvent (mixture of water + TLC) and ρ_o and ρ are the densities (kg·m^{-3}) of the solvent and solution, respectively. The values of apparent molar volume are reported in Table 2. The positive values of V_ϕ indicate strong solute-solvent interactions. The values of V_ϕ as function of saccharide concentration and temperature are shown graphically in Figs. 2 and 3. Fig. 2 represents the apparent molar volume for saccharides in 0.2 mol·kg^{-1} aqueous solutions of TLC at different temperatures while Fig. 3 represents the apparent molar volumes for saccharides in aqueous solutions of TLC at 298.15 K. The data reported in Table 2 and represented in Figs. 2 and 3, implies that apparent molar volumes for D(−)-ribose and D(+)-xylose increase with increase in TLC concentration and temperature. For a particular concentration of TLC, apparent molar volume increases with increase in molality of saccharides. It has been also found that V_ϕ^o values for D(−)-Ribose are greater than D(+)-Xylose. The values of V_ϕ increase with increase in temperature. This causes greater affinity for solvent and therefore enhances greater solute–solvent interactions.

3.1.3. Partial molar volume

The V_ϕ values for both saccharides were found to be linear, therefore partial molar volume V_ϕ^o, which is the limiting value of apparent molar volume, is obtained by least squares fitting of apparent molar volume V_ϕ by the following equation:

$$V_\phi = V_\phi^o + S_V^* m_A \quad (2)$$

where S_V^* the experimental slope is the volumetric pair wise interaction coefficient or semi empirical solute-solute interaction parameter and m_A is the molality of saccharides in aqueous TLC solutions. The values of V_ϕ^o and S_V^* together with standard errors derived by least squares fitting of the V_ϕ values to Eq. (2) are indexed in Table 3. Enhanced solute-solvent interactions are expected due to the increase in V_ϕ^o values with an increase in the TLC concentration and temperature for both saccharides as shown in Fig. 4. As per co-sphere overlap model [36,37], an overlap of hydration co-spheres of two ionic species causes an increase in volume, whereas overlap of hydrophobic- hydrophobic groups and ion-hydrophobic groups results in the volume decrease. The observed positive V_ϕ^o values are due to ion-hydrophilic interactions, which dominate over ion-hydrophobic interactions and hydrophobic-hydrophobic interactions. The change in partial molar volume with temperature may involve many reasons such as thermal expansion, weakening of H-bond network, release of molecules from the solvation layers *etc.* The increase in V_ϕ^o values with an increase in temperature for both saccharides may be explained as release of some solvation molecules from the loose solvation layers of the solute in solution. This can also be explained by considering the size of primary and secondary solvation layers around solute. At higher temperatures, the solvent from the secondary solvation layers of solute is released into the bulk of the solvent, resulting into