



Osmotic properties of carbohydrate aqueous solutions



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ARTICLE INFO

Article history:

Received 8 January 2016
 Received in revised form
 14 February 2016
 Accepted 17 February 2016
 Available online 20 February 2016

Keywords:

Vapor pressure osmometry
 Osmotic coefficient
 Activity
 Carbohydrate
 Aqueous solutions

ABSTRACT

Precise systematic osmotic coefficient measurements have been carried out for aqueous solutions of different carbohydrates and polyols by using vapor pressure osmometry (VPO) method. Herein, in order to investigate the effect of structure and stereochemistry of solutes on the vapor–liquid equilibria behavior of aqueous solutions, we studied the osmotic properties of binary aqueous sugar solutions containing pentose monosaccharides (xylose, ribose and arabinose), hexose monosaccharides (glucose, fructose, galactose and mannose), disaccharides (sucrose, maltose and lactose), trisaccharide (raffinose) and polyols (sorbitol, xylitol and maltitol) at 308.15 K and in the extended concentration range. From the experimental osmotic coefficient data, the values of water activity and vapor pressure of the investigated solutions were obtained.

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1. Introduction

Carbohydrates which are a large natural resource have long interested chemists and biochemists because of their predominant role in biological and industrial applications. An important fraction of carbohydrates is made up of the smaller building units, namely sugar monomers and oligomers, and their aqueous solutions are mainly associated with the processing and the preservation of foods [1]. Thermodynamics investigations of aqueous carbohydrate solutions will be helpful in the precise design of operations and equipment used in food industries including chemical feed stocks, food production, and preservation of processed foods as well as in the study of the reaction conditions (e.g. feasibility and optimization) of currently employed industrial processes such as enzymatic conversion of biomass to useful chemicals [2]. As an example, water activity of solutions can be controlled by freeze drying and evaporation processes in order to reduce microorganism's growth and osmotic pressure caused by high concentrations of sugars that also inhibit food contaminations [3]. Although, a systematic and extensive study of water activities could contribute to a better understanding of the sugars hydration mode, which is a topic of considerable importance, a comprehensive understanding in this respect is yet to emerge.

In the present work, for the first time, systematic vapor pressure

osmometry (VPO) measurements have been carried out for several binary aqueous sugar solutions containing pentose monosaccharides, hexose monosaccharides, disaccharides, trisaccharide and polyols, at 308.15 K and in the extended concentration range in order to comprehensive study of vapor–liquid equilibrium of these systems and precise determination of water activity and osmotic coefficients of them. Although previously water activity and osmotic coefficient data have been reported in the literature for some aqueous carbohydrate solutions from isopiestic [4–12], hygrometry [13–15], freezing point depression [16,17] and manometry [18,19] methods, but these techniques aren't precise as VPO, the number of data reported in the dilute concentration region is limited, none of them is an extensive study, and besides those data have often been reported at 298.15 K (except water activity obtained from the freezing point depression method which is the activity at the corresponding freezing point temperature and may be had considerable difference with water activity at room temperature (298.15 K) or human body temperature (310.15 K)).

2. Experimental section

2.1. Materials

The properties of the chemicals used in this work have been listed in Table 1 and their structures have been presented in Scheme 1. Given that in aqueous solutions pyranose conformation of the investigated monosaccharides is more favored than furanose conformation, in Scheme 1 only pyranose form have been drawn

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Table 1
Specification of chemical samples.

Chemical name	$10^3 \cdot$ Molecular weight ($\text{kg} \cdot \text{mol}^{-1}$)	Source	Purification method	Final mass fraction purity
D (+) – Xylose	150.13	Merck	none	≥ 0.99
D (–) – Ribose	150.13	Acros	none	≥ 0.99
L (+) – Arabinose	150.13	Merck	none	≥ 0.99
D (+) – Glucose	180.16	Merck	none	≥ 0.995
D (+) – Galactose	180.16	Merck	none	≥ 0.98
D (+) – Mannose	180.16	Merck	none	≥ 0.98
D (–) – Fructose	180.16	Merck	none	≥ 0.99
Sucrose	342.29	Merck	none	≥ 0.98
Maltose monohydrate	360.32	Merck	none	0.99
Lactose monohydrate	360.32	Merck	none	≥ 0.98
Raffinose pentahydrate	594.52	Merck	none	≥ 0.97
Xylitol	152.15	Alfa Aesar	none	0.99
D (–) – Sorbitol	182.17	Merck	none	≥ 0.99
Maltitol	344.32	Alfa Aesar	none	0.97
NaCl	58.44	Merck	was dried in an electrical oven at about 110 °C for 24 h prior to use	≥ 0.995

for all the monosaccharides. The chemicals were used without further purification and double distilled and deionized water was used.

2.2. Methods

All the solutions were prepared by mass on a Sartorius CP124S balance precise to within $\pm 1 \cdot 10^{-7}$ kg. The VPO measurements were performed using an Osmomat K-7000 (Knauer Inc.) at 308.15 K. The cell temperature was controlled electronically within $\pm 1 \cdot 10^{-3}$ K. The instrument consists of two thermistors (1 and 2) placed in an airtight cell (its gas phase is saturated by solvent vapor) which measure resistance changes caused by changes in temperature. Initially, a droplet of pure water is attached to both thermistors with the help of a microsyringe, and after equilibration (~5 min), the reading is adjusted to zero. After that, the pure water on thermistor 1 is replaced by the carbohydrate solution. Because of the condensation of water from the vapor phase into the carbohydrate solution, the thermistor 1 will be warmed and vapor pressure rises. This condensation process continues until the vapor pressure of the carbohydrate solution equals to the vapor pressure of pure water. In this steady state (a time of 4–8 min suffices to reach it), the thermistors measure the resistance differences (ΔR) due to the change of temperature (ΔT) between the two thermistors. ΔT is proportional to ΔR , when ΔT is small. Initially, the instrument was calibrated using aqueous NaCl solutions as reference and from which a correlation between the panel readings and the corresponding concentrations of the NaCl solutions (and therefore their osmotic coefficients) was obtained. After that, the measurements for the different aqueous carbohydrates solutions were carried out in the same conditions. In this work, we performed experiments with three different modes of instrument setting, hence the instrument was calibrated with aqueous NaCl solutions at three conditions: (bridge voltage = 100%, gain = 16), (bridge voltage = 52.1%, gain = 16) and (bridge voltage = 100% and gain = 1) for dilute, middle and concentrated regions, respectively. The following relation was used to correlate instrument panel reading (signal, SI) and NaCl molality (m_{NaCl}):

$$m_{\text{NaCl}} = b_0 + b_1 SI + b_2 SI^2 + b_3 SI^3 \quad (1)$$

where b_0 , b_1 , b_2 and b_3 are calibration constants and their values are reported in Table 2.

The osmotic coefficient, ϕ , of a carbohydrate solution with molality m which has a same instrument reading as a sodium chloride solution with molality m_{NaCl} , was obtained according to:

$$\phi = \frac{\nu_{\text{NaCl}} m_{\text{NaCl}} \Phi_{\text{NaCl}}}{m} \quad (2)$$

where ν_{NaCl} is the stoichiometric number of NaCl. Φ_{NaCl} is the osmotic coefficient for aqueous solutions of NaCl with molality m_{NaCl} calculated from the correlation of Colin et al. [20] The uncertainty in the measurement of osmotic coefficient was found to be better than $\pm 1 \cdot 10^{-3}$.

3. Result and discussion

The osmotic coefficients of the systems investigated at 308.15 K are given in Table 3. From the experimental osmotic coefficient data, the values of water activity and vapor pressure for the solutions were determined through the following equations [21]:

$$a_w = \exp\left(-\frac{mM_w\phi}{1000}\right) \quad (3)$$

$$\ln a_w = \ln\left(\frac{p}{p_w^*}\right) + \frac{(B_w^* - V_w^*)(p - p_w^*)}{RT} \quad (4)$$

where M_w is the molecular weight of the solvent, B_w^* is the second virial coefficient of water vapor, V_w^* is the molar volume of liquid water, and p_w^* is the vapor pressure of pure water. The value of B_w^* at 308.15 K equals $-1016.75 \text{ cm}^3 \text{ mol}^{-1}$, where calculated using the equation provided by Rard and Platford [22]. The obtained water activities and vapor pressures data of the systems investigated at 308.15 K are also given in Table 3.

Fig. 1 shows the experimental osmotic coefficients and water activities for monosaccharides: D-xylose, D-ribose, L-arabinose, D-mannose, D-fructose, D-galactose and D-glucose. As can be seen, the values of the osmotic coefficients follow the order: (D-Glucose \geq D-galactose) > (D-fructose \geq L-arabinose) > (D-xylose \geq D-mannose) > D-ribose. Although the differences between the values of the water activities (and also vapor pressures) are very small, close examination of Fig. 1b indicates the reverse order to that observed for the osmotic coefficients. As can be seen, except for D-mannose, water activities of aqueous solutions of hexose monosaccharides are smaller than those of pentose monosaccharides. This is because the hexose monosaccharides have more hydroxyl groups (hydrophilic group) in their structures than the pentose monosaccharides. The hydration of a carbohydrate is mostly dependent on the axial and equatorial arrangements of its hydroxyl groups. Equatorial hydroxyl substituents are more easily hydrated than axial. In Table 4, the arrangements of the hydroxyl groups

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