Soluting-in and Soluting-out of Water-Soluble Polymers in Aqueous Carbohydrate Solutions Studied by Vapor Pressure Osmometry

Nosaibah Ebrahimi, Rahmat Sadeghi*

Department of Chemistry, University of Kurdistan, Sanandaj, Iran

ABSTRACT

Precise vapor pressure osmometry measurements at 308.15 K have been performed for ternary systems of carbohydrate in aqueous 0.2 w/w polymer solutions. The polymers are polyethylene glycol 400 (PEG400), polyethylene glycol 10000 (PEG10000) and polypropylene glycol 400 (PPG400), and the carbohydrates are xylose, xylitol, glucose, fructose, sucrose and raffinose. In order to study the soluting-out and soluting-in effects occurring in the polymer-carbohydrate aqueous systems, deviations of vapor-liquid equilibria behavior of these systems from the semi-ideal state have been evaluated. In the case of PPG + carbohydrates aqueous systems, because of unfavorable PPG-carbohydrate interactions, the solutes exclude themselves from the vicinity of each other and therefore aqueous biphasic systems are entropically formed above a critical concentration. The monophasic and biphasic regions of these systems show, respectively, negative and positive deviations from the semi-ideal behavior, which become more negative and more positive with increasing hydrophilicity of the carbohydrates. However, in the case of PEG + carbohydrate aqueous systems, which are completely miscible because of favorable PEG-carbohydrate interactions, the interaction of each solute with water molecules becomes weaker in the presence of the other solute. These systems show positive deviations from the semi-ideal behavior. By increasing the PEG molar mass and decreasing the hydrophilicity of carbohydrates,

* Corresponding author. *E-mail address:* rahsadeghi@yahoo.com and rsadeghi@uok.ac.ir

the carbohydrate-PEG interactions increase and then the positive deviations from the semi-ideal state increase.

Keywords

Vapor pressure osmometry, Water-soluble polymer, Carbohydrate, Semi-ideal behavior, Soluting-out effect, Soluting-in effect

1. Introduction

Carbohydrates are the most abundant class of organic compounds found in living organisms which are very important in maintenance life as main source of energy, basic component of tissue cells, and informative molecules [1]. They have received a huge interest for delivery of macromolecular drugs, vaccine development and cosmetic industry [2,3]. Carbohydrates may exert significant influence on the stability and behavior of aqueous polymeric systems in foods and in other fields of application [4-6]. For instance, polyethylene glycols (PEGs) are used as plasticizers in film-coating formulations for food supplements and pharmaceutical products (tablets and capsules) [7]. In this respect, it is important to investigate the effects of PEGs and sugars on each other in aqueous media. Moreover, the addition of sufficient amounts of sugars to aqueous solutions of polypropylene glycols (PPGs) or block copolymers of ethylene oxide and propylene oxide units leads to the formation of aqueous biphasic systems (ABS) [8,9]. Since the bulk of the two phases consists mainly of water, ABS are environmentally friendly and provide a biocompatible media for biomaterials. ABS have been utilized in the extraction and purification of diverse biomolecules such as proteins, enzymes, nucleic acids, flavor compounds, antioxidants and antibiotics [10,11]. It is interesting to note that polymer-carbohydrate ABS offer greener extraction procedures than polymer-ionic liquid and traditional polymer-salt ABS. The substitution of high charge density salts by carbohydrates for implementation of polymer based ABS can lead to improved biotechnological routes, because high ionic strength or alkaline media created by salts may be deleterious to a

number of biomolecules. Also, carbohydrates are more eco-friendly and less expensive than imidazolium or pyridinium based ionic liquids which have been widely used for ABS formation. This fact merits accurate thermodynamic properties investigations of different ternary polymer-carbohydrate aqueous solutions, as these properties are necessary for elucidating phase forming behavior and also for optimum design of industrial separation process dealing with polymer-carbohydrate ABS.

The water activity of aqueous solutions is an important thermodynamic property which provides valuable information about the relative strength of the different interactions in solution. Although several papers have been published regarding the water activity of binary (sugar + water) [12-15] and (PPG/PEG + water) [16-19] solutions, despite its importance, there are no water activity data for ternary (sugar + PPG/PEG + water) systems. In this work, a precise vapor pressure osmometry method is used to determine water activities of different ternary aqueous solutions containing both polymers (PEG400, PEG10000 and PPG400) and sugars (xylose, xylitol, glucose, fructose, sucrose and raffinose) at 308.15 K. According to deviations of vapor-liquid equilibria behavior of the studied systems from the semi-ideal state, soluting-out and soluting-in phenomena occurring in carbohydrates-polymer aqueous solutions are scrutinized. The influences of carbohydrate structure, type and molar mass of polymer on the soluting effects are discussed.

2. Experimental

2.1 Materials

The specifications of used chemicals have been summarized in Table 1. Double distilled and deionized water was used. The chemical structures of the under study compounds have been presented in Scheme 1. Given that in aqueous solutions, the pyranose conformation of the investigated monosaccharides is more favored than the furanose conformation, in Scheme 1 only pyranose forms have been drawn for monosaccharides.

2.2. Apparatus and procedure

Solutions were prepared by mass with the use of a Sartorius CP124S balance precisely within $\pm 1.10^{-7}$ kg. The vapor pressure osmometry (VPO) measurements were carried out with a Knauer vapor pressure osmometer (model K-7000). The details of the unit and relevant procedure for determination of water activity were reported earlier [17]. In this method, the water activity is determined indirectly by using thermistors to measure voltage changes caused by changes in temperature. The osmometer has two thermistors, placed in a chamber which contains a reservoir of water and paper wicks to provide a saturated water atmosphere. The cell temperature is electronically controlled and maintained with an accuracy of $\pm 1.10^{-3}$ K. Firstly, a droplet of pure water is located on both thermistor, and after equilibration the instrumental reading is adjusted to zero. After that, the pure water on one thermistor is replaced by the sample solution. Since the vapor pressure of any binary or ternary sample solution is lower than that of pure water, this replacement leads to a vapor pressure difference between the two droplets. Hence, some water vapor that saturated the gas phase condenses on the sample droplet until the vapor pressures are balanced. This process warms the thermistor containing sample aqueous solution due to the heat of condensation. The temperature difference (ΔT) between the two thermistors is always proportional to the vapor pressure of the sample solution. The thermistors measure the resistance difference (ΔR) due to the change of temperature (ΔT) between the two thermistors. Once equilibrium is reached a constant measurement value is achieved (generally a time of 4 to 8 min suffices to reach it). The osmometer was calibrated by obtaining a relation between the panel readings of the osmometer and the concentrations of the aqueous NaCl solutions. Then, under the same conditions, the panel readings were specified for the aqueous solutions under investigation. For each solution, 10 determinations (zero-point adjustment after 5 determinations and repeating) were performed and the mean value was calculated. Generally, the relative deviations from the mean value were less than 1%, otherwise the measurements were repeated. At the end of measurements, the calibration was controlled again to exclude any base-line drifts of the apparatus. The water activity (a_w) for a certain

aqueous carbohydrate-polymer solution which has a same instrument reading as a sodium chloride solution with molality m_{NaCl} , was obtained through the following equation:

$$a_w = \exp(-0.001\nu_{\text{NaCl}}m_{\text{NaCl}}\Phi_{\text{NaCl}}M_w) \quad (1)$$

where ν_{NaCl} is the stoichiometric number of sodium chloride and equals 2, M_w is the molar mass of water, Φ_{NaCl} is the osmotic coefficient for aqueous solution of NaCl with molality m_{NaCl} calculated from the correlation of Clarke and Glew [20]. The uncertainty in the measurement of water activity was estimated to be better than $\pm 2.10^{-4}$. From the water activity values, the vapor pressures of aqueous solutions, p , were determined according to [21]:

$$\ln(a_w) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_w^*)(p - p^*)}{RT} \quad (2)$$

where B is the second virial coefficient of water vapor that calculated using the equation provided by Rard and Platford [22]. p^* is the vapor pressure of pure water which calculated using the state equation of Saul and Wagner [23]. V_w^* , R and T are the molar volume of liquid water, gas constant and absolute temperature, respectively.

3. Results and discussion

In the present study, vapor pressure osmometry measurements have been performed for different ternary systems of carbohydrate in aqueous 0.2 w/w polymer solutions. Table 2 shows the water activity and vapor pressure data. Based on our visual observations, the aqueous solutions of carbohydrate + PEG400 and carbohydrate + PEG10000 are completely homogenous and clear over the whole concentration range, while the aqueous solutions of carbohydrate + PPG become cloudy above certain concentrations and form ABS.

Fig. 1 depicts the concentration dependence of the water activity for systems of carbohydrate in aqueous 0.2 w/w polymer solutions. Fig. 1a shows that water activity in carbohydrate-PEG10000 aqueous solutions in the whole concentrations range increases in the order: raffinose < sucrose < glucose < fructose $\cong$ xylitol < xylose. Also, the measured water activities for systems of

carbohydrate in aqueous 0.2 w/w PEG400 solutions obey the same order. The values of water activity in the binary carbohydrate + water solutions [12] follow the order: raffinose < sucrose < glucose < xylitol < fructose < xylose, which is similar to that in carbohydrate-PEG aqueous solutions, with the exception of xylitol and fructose. From Fig. 1b, it is possible to observe two different and quite reverse orders for water activities in the one-phase and two-phase regions of carbohydrates in aqueous 0.2 w/w PPG400 solutions: raffinose < sucrose < glucose < fructose < xylitol < xylose, in the one-phase region, and sucrose > glucose > fructose > xylitol > xylose, in the two-phase region. As can be seen, for each of the carbohydrate + PPG400 aqueous systems, the slope of the plot of water activity against carbohydrate molality (a_w vs. m_c) in the two-phase region is less than that in the one-phase region. This is because of partial dehydration of solutes occurring by ABS formation [24,25]. In addition, the interesting order observed for water activities in the two-phase region indicates that in the case of more hydrophilic carbohydrates, more partial dehydration occurs by phase separation. The concentration point at which the slope of a_w vs. m_c changes and phase separation achieves is 1.17, 1.35, 1.48, 1.62 and 2.04 mol.kg⁻¹ for sucrose, glucose, fructose, xylitol and xylose, respectively. These values increase in the same order of water activity in the one-phase region. Furthermore, these observations are in good agreement with liquid-liquid equilibria phase diagrams (binodal curves) for these systems [26]. The more hydrated the carbohydrate (the lower a_w), the higher soluting-out strength of the carbohydrate and then the lower required carbohydrate concentration for phase separation. The trend of water activity for the PPG400-carbohydrate aqueous solutions in the one-phase region, with the exception of xylitol and fructose, is the same as that for the PEG- carbohydrate aqueous solutions. In the case of raffinose in the aqueous 0.2 w/w PPG400 solutions, because of the low water solubility of raffinose which is lowered in the presence of PPG, we are not able to obtain water activity data in the biphasic region. The trend of water activity in the investigated polymer-sugar aqueous systems is controlled by the interplay of the relative strength of the carbohydrate-water, polymer-water and carbohydrate-polymer interactions. The number and orientation of hydroxyl groups present in each carbohydrate,

and also the alkyl chain length and monomer hydrocarbon proportion of each polymer, affect the interactions of solutes with water and with each other. For elucidating soluting effects exerted by the addition of sugars to aqueous polymer solutions, the comparative study of water activity in the ternary sugar + polymer + water and its corresponding binary sugar + water and polymer + water solutions has been accomplished.

In order to investigate the salting effect occurring in a ternary A + B + water solution, here, we scrutinize deviations from the following equations (see Scheme 2) [27,28]:

$$(a_w + 1) - (a_{wA}^\circ + a_{wB}^\circ) = 0 \quad (3)$$

or

$$\Delta p - (\Delta p_A^\circ + \Delta p_B^\circ) = 0 \quad (4)$$

where a_{wA}° and a_{wB}° are, respectively, the water activities in binary A + water and B + water solutions with solute molalities m_A and m_B , and a_w is the water activity in ternary A + B + water solution with the same solute concentrations as the constituent binary aqueous solutions. Also, $\Delta p = p - p^*$ and $\Delta p_i^\circ = p_i^\circ - p^*$ are, respectively, the vapor pressure depressions for ternary A + B + water and binary i + water solutions with the same solute molalities. These equations (Eqs. 3 and 4) are established for the semi-ideal solutions in which the A-B interactions are negligible and the A-water and B-water interactions in the ternary solutions are the same as those in the corresponding binary solutions. Therefore, departures from Eqs. 3 and 4 may be taken as evidence for specific A-B interactions. If in a ternary A + B aqueous system, the A-B interactions are more favorable than the A-water and B-water interactions, the water molecules are allowed to relax to the bulk state and therefore $a_w + 1 > a_{wA}^\circ + a_{wB}^\circ$ and Δp is less negative than $\Delta p_A^\circ + \Delta p_B^\circ$ (positive deviation from the semi-ideal behavior). This is an example of soluting-in phenomenon in which the mutual solubilities of A/water and B/water increase. In other words, each solute acts as cosolvent for another solute. For instance, it was observed that in ternary amino acid + $(\text{NH}_4)_2\text{HCit}$ + water solutions [29] which are completely miscible and there are desirable interactions between salt ions

and amino acid zwitterions, vapor pressure depression values for the ternary solutions are less negative than the sum of those for the corresponding binary solutions with the same solute molalities. However, if in a ternary A + B aqueous system, the A-B interactions are unfavorable, the interactions of each solute with water (A-water and B-water interactions) are strengthened in the presence of the other solute. In these systems, unfavorable interactions between two solutes decrease the amount of free water molecules with respect to the semi-ideal state, thus $a_w + 1 < a_{wA}^\circ + a_{wB}^\circ$ and Δp is more negative than $\Delta p_A^\circ + \Delta p_B^\circ$ (negative deviation from the semi-ideal behavior). This is an example of soluting-out phenomenon in which solutes A and B exclude themselves from the vicinity of each other and compete for water molecules. In this case, the quality of solvent for each solute is lowered by the addition of another solute to solution and ultimately above the critical concentration because of entropic reasons ABS formation is favorable [24,25]. For instance, it has been shown that in the PPG-amino acid [28], PEG-salt [30], PPG-salt [31] and ionic liquid-salt [27] aqueous systems which are capable of inducing phase separation, vapor pressure depression values for the ternary solutions are more negative than the sum of those for the corresponding binary solutions at the same solute concentration.

The plots of $(a_w + 1) - (a_{w,p}^\circ + a_{w,c}^\circ)$ against carbohydrate molality for the investigated systems are depicted in Fig. 2. a_w is the water activity in ternary systems of carbohydrates in the aqueous 0.2 w/w polymer solutions with carbohydrate molality m_c . $a_{w,p}^\circ$ is the water activity in the binary aqueous polymer solutions which is equal to 0.9849, 0.9960 and 0.9915 for aqueous 0.2 w/w PEG400, PEG10000 and PPG400 solutions, respectively (see Table 2). $a_{w,c}^\circ$ is the water activity in the binary aqueous carbohydrates solutions with molality m_c , which was taken from our previous paper [12]. In Fig. 2, half-filled symbols represent biphasic mixtures. According to these plots, in the case of carbohydrate + PPG400 + water systems which can produce ABS, the negative and positive departures from Eq. 3, that become more negative and more positive with increasing carbohydrate concentration, are seen in the one-phase and two-phase regions, respectively.

However, in the carbohydrate + PEG10000 + water solutions which soluting-in phenomenon occurs, positive deviation from Eq. 3, that becomes more positive with increasing carbohydrate concentration is observed. Carbohydrate + PEG400 + water solutions don't show phase separation, and have very small deviations from the semi-ideal behavior. This indicates that favorable sugar-PEG interactions are increased by increasing the PEG molar mass. The raffinose + PEG aqueous solutions are the sole exception of the investigated systems and show clear negative deviations from the semi-ideal behavior, although the negative deviations in these solutions are much smaller than those in raffinose + PPG aqueous solutions which can induce ABS formation (Fig. 2f). Raffinose is a trisaccharide composed of a galactose, a glucose and a fructose unit (Scheme 1). Because it has the most hydroxyl groups, it is the most hydrophilic of the investigated sugars. As discussed later (Fig. 3), the polymer-sugar interaction becomes weaker by increasing the hydrophilicity of sugars. The hydrophilicity order of PEG is larger than that of PPG [19]. This is because PPG contains a greater proportion of hydrocarbon in its segments. Furthermore, the side chain methyl groups in the PPG segments hinder the PPG-water hydrogen bonding (Scheme 1). In the carbohydrate + PEG + water solutions as a result of preferential carbohydrate-PEG interactions, the PEG-water interactions become less favorable in the presence of the carbohydrate. Hence, for these solutions the values of $(a_w + 1)$ are larger than $(a_{w,p}^\circ + a_{w,c}^\circ)$. These positive deviations from the semi-ideality suggest that the investigated carbohydrates are good cosolvents for PEG and have a soluting-in effect on the aqueous PEG solutions. As we observed visually, the carbohydrate + PEG + water solutions are monophasic over the whole investigated concentration range. The more positive deviations from the semi-ideal behavior for carbohydrate + PEG10000 + water solutions compared to carbohydrate + PEG400 + water solutions, indicates the more favorable carbohydrate-PEG10000 interactions compared to carbohydrate-PEG400 interactions. This may be attributed to the more appreciable dispersion forces between hydrocarbon portions of PEG and carbohydrates. In the carbohydrate + PPG400 + water systems, because of unfavorable carbohydrate-PPG interactions, the solutes exclude themselves from the vicinity of each other and their interactions with water

molecules become more stable. Therefore, in these ternary systems less free water molecules would be available with respect to the semi-ideal behavior, and so $(a_w + 1) < (a_{w,p}^\circ + a_{w,c}^\circ)$. Due to the fact that the binding of carbohydrates to PPG is a highly unfavorable process, the carbohydrate molecules in aqueous PPG solutions are strongly hydrated. The strongly hydrated carbohydrate molecules imply that their hydration water has lower entropy compared with bulk water. By increasing the concentration of the solutes, the carbohydrate solution becomes a worse solvent for PPG and ultimately the system reaches a state where the ABS formation becomes entropically favorable. The solute-water interaction, which is stronger in the presence of the other solute, become weaker by ABS formation. Hence, by phase separation partial dehydration of solutes occurs and then, in the two-phase region $(a_w + 1)$ is larger than $(a_{w,p}^\circ + a_{w,c}^\circ)$. Silva and Loh [32], from calorimetric measurements showed that phase separation in aqueous polymer + salt solutions is an endothermic process, indicating that entropy increase is the driving force for ABS formation. Livney *et al.* [4,6] studied the effect of carbohydrates on the swelling of polyacrylamide and poly(N-isopropylacrylamide) gels. They observed that the swelling of polyacrylamide gels, which are hydrophilic polymers as PEGs, increases with rising glucose concentrations and there is an enthalpically favorable interaction between glucose and polyacrylamide [4]. However, based on their results, sugars exert shrinkage and soluting-out effects on poly(N-isopropylacrylamide) gels, which are hydrophobic polymers as PPG [6]. These observations are in close agreement with the results of the present study of the carbohydrates soluting effects on aqueous polymer solutions.

Fig. 3 compares departures from the semi-ideal state for different carbohydrate + PEG10000 + water (3a) and carbohydrate + PPG400 + water (3b) systems. Fig. 3a shows that positive deviation from Eq. 3 increases by decreasing the hydrophilic nature of the sugar, and follows the order: raffinose < sucrose < glucose < fructose < xylitol < xylose, which is similar to the trend observed in Fig. 1a for the water activity of these solutions. This means that the carbohydrate-PEG interactions increase with increasing hydrophobic nature of carbohydrates. It should be pointed out that although the water activity values for ternary PEG + xylitol and PEG + fructose aqueous solutions

are equal (Fig. 1a), the water activities for binary fructose + water solutions are larger than those for xylitol + water solutions [12]. This accounts for the more positive deviations for PEG + xylitol aqueous solutions compared to PEG + fructose aqueous solutions. As can be seen from Fig. 3b, the magnitude of negative deviations from Eq. 3 in the one-phase region of carbohydrate + PPG + water systems increases by increasing the hydrophilic nature of the carbohydrates and obey the order: raffinose > sucrose > glucose > fructose > xylitol > xylose. The liquid-liquid equilibria behavior (binodal curves) of carbohydrate-PPG400 aqueous systems [26] ascertains that the soluting-out strength of carbohydrates decreases in the order: raffinose > sucrose > glucose > fructose > xylitol > xylose, which is quite in agreement with the extent of negative deviations from Eq. 3. In fact, the mutual exclusion of PPG and carbohydrate from the vicinity of each other is intensified by increasing the carbohydrate hydrophilicity. This is the main reason for more negative deviations from the semi-ideal behavior for the more hydrophilic sugars. Furthermore, Fig. 3b shows that the positive deviations from Eq. 3 in the two phase region of carbohydrate + PPG + water systems increase in the same order of the water activities in this region (Fig. 1b). The extent of partial dehydration due to phase separation, increases with increasing hydrophilicity of carbohydrate. This explains the order observed for positive deviation in the biphasic region of Fig. 3b. The values of $(a_w + 1) - (a_{w,p}^\circ + a_{w,c}^\circ)$ and $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$ obtained for all the investigated systems are reported in Table 3. As expected, the investigation of the studied systems based on deviations from $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ) = 0$, provides the same results as those obtained based on deviations from $(a_w + 1) - (a_{w,p}^\circ + a_{w,c}^\circ) = 0$. The plots of $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$ against carbohydrate molality are given in Figs. 4 and 5.

The Gibbs free energy change of water during the process that a solution of m_c moles of carbohydrate in 1 kg of water is mixed isothermally with a solution of m_p moles of polymer in 1 kg of water and 1 kg of water is then isothermally separated via an osmotic membrane can be defined as [15]:

$$\Delta G = 55.51 RT \ln\left(\frac{a_w}{a_{w,p} \cdot a_{w,c}}\right) \quad (5)$$

The values of ΔG for the investigated systems are also given in Table 3. As Fig. 6 depicts, the plots of ΔG against carbohydrate molality have the same behavior as those observed in Figs. 2 and 4 for $(a_w + 1) - (a_{w,p}^\circ + a_{w,c}^\circ)$ and $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$. In the case of PEG10000 + carbohydrate + water solutions ΔG is positive. The magnitude of ΔG in the PEG400 + carbohydrate + water solutions is very small and for PPG400 + carbohydrate + water systems the values of ΔG are negative and positive in the one-phase and two-phase regions, respectively. The values of ΔG reported in Table 3 for different carbohydrates in aqueous polymer solutions follow the same trends as those observed in Figs. 3 and 5 for deviations from Eqs. 3 and 4.

4. Conclusions

Vapor-liquid equilibria behavior of different ternary polymer (PPG400, PEG400 or PEG10000) + carbohydrate (xylose, xylitol, glucose, fructose, sucrose or raffinose) aqueous solutions was studied at 308.15 K by the VPO method. Carbohydrate + PEG + water solutions are completely miscible. In these systems, because of preferential carbohydrate-PEG interactions, the interactions of each solute with water become less favorable compared to the semi-ideal behavior. Therefore, under the same solute concentration (solute concentrations in the ternary solution are the same as those in the corresponding binary solutions), the vapor pressure depression for PEG + carbohydrate + water solutions is less negative than the sum of those for carbohydrate + water and PEG + water solutions and $a_w + 1$ is larger than $a_{w,p}^\circ + a_{w,c}^\circ$. This indicates that carbohydrates are good cosolvents for PEG and have a soluting-in effect on the aqueous PEG solutions. By increasing the PEG molar mass and decreasing hydrophilicity of the carbohydrate, the PEG-carbohydrate interactions become more favorable, and then the positive deviations from the semi-ideal behavior increase. However, carbohydrate + PPG + water systems have limited miscibility. In these systems, because of unfavorable carbohydrate-PPG interactions, the interactions of each solutes with water molecules

become more stable in the presence of the other solute. Therefore, at the same solute concentration, the vapor pressure depression for carbohydrate + PPG + water systems is more negative than the sum of those for carbohydrate + water and PPG + water solutions and $a_w + 1$ is smaller than $a_{w,p}^\circ + a_{w,c}^\circ$. This means that aqueous carbohydrate solutions are worse solvents for PPG compared to pure water. In other words, carbohydrates exert soluting-out effect on the aqueous PPG solutions and above critical concentrations induce phase separation which leads to the formation of ABS composed of PPG-rich and carbohydrate-rich phases. Since, by ABS formation partial dehydration of solutes occurs, in the biphasic region of PPG-carbohydrate aqueous systems, positive departure from the semi-ideality was observed. Based on deviations from the semi-ideal behavior, it was found that the mutual exclusion of PPG and carbohydrates from the vicinity of each other is intensified by increasing hydrophilic degree of carbohydrates.

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Scheme 1. Chemical structures of the studied carbohydrates and polymers.

Scheme 2. Description of soluting-out and soluting-in effects based on deviations from the semi-ideal behavior for a ternary A + B aqueous solution (A and B are nonvolatile solutes) under condition that solute molalities in the ternary solution are the same as those in the corresponding binary solutions.

Table 1. Sample Description of the Used Chemicals.

Chemical name	$10^3 \cdot$ Molecular weight ($\text{kg} \cdot \text{mol}^{-1}$)	Source	Lot number	Purification method	Final mass fraction purity ^a
D (+) - Xylose	150.13	Merck		none	≥ 0.99
D (+) - Glucose	180.16	Merck		none	≥ 0.995
D (-) - Fructose	180.16	Merck		none	≥ 0.99
Sucrose	342.29	Merck		none	≥ 0.98
Raffinose pentahydrate	594.52	Merck		none	≥ 0.97
Xylitol	152.15	Alfa Aesar		none	0.99
PPG400	400	Fluka	1252304 20206282	none	
PEG400	400	Merck	S6041783 019	none	
PEG10000	10000	Merck	S5190581 835	none	
NaCl	58.44	Merck		was dried in an electrical oven at about 110 °C for 24 h prior to use	≥ 0.995

^a Declared by supplier.

Table 2. Experimental Water Activity, a_w , and Vapor Pressure, p / (kPa), Data of the Investigated Aqueous Solutions as a Function of Carbohydrate Molality, m_c / (mol.kg⁻¹), Obtained via Vapor Pressure Osmometric Measurements at $T = 308.15$ K.

m_c / mol.kg ⁻¹	a_w	p / kPa	m_c / mol.kg ⁻¹	a_w	p / kPa	m_c / mol.kg ⁻¹	a_w	p / kPa
Aqueous 0.2 w/w PPG400 Solution			Aqueous 0.2 w/w PEG400 Solution			Aqueous 0.2 w/w PEG10000 Solution		
Xylose in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.5015	0.9816	5.5226	0.4989	0.9765	5.4936	0.4997	0.9878	5.5574
0.7530	0.9765	5.4936	0.7474	0.9722	5.4694	0.7555	0.9836	5.5338
1.0006	0.9714	5.4648	1.0031	0.9679	5.4453	1.0025	0.9796	5.5113
1.2483	0.9666	5.4379	1.2523	0.9638	5.4222	1.2451	0.9756	5.4890
1.4961	0.9618	5.4111	1.4883	0.9597	5.3991	1.4973	0.9715	5.4657
1.8739	0.9547	5.3707	1.8662	0.9534	5.3633	1.8643	0.9654	5.4314
2.4997	0.9453	5.3177	2.5018	0.9424	5.3014	2.4643	0.9555	5.3752
3.1327	0.9377	5.2752	3.1108	0.9315	5.2402	3.0839	0.9449	5.3159
3.7524	0.9304	5.2339	3.7344	0.9200	5.1755	3.6965	0.9344	5.2563
4.3724	0.9221	5.1869						
Xylitol in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.5008	0.9808	5.5179	0.4987	0.9761	5.4918	0.5023	0.9874	5.5554
0.7528	0.9756	5.4890	0.7519	0.9717	5.4666	0.7432	0.9831	5.5310
1.0033	0.9704	5.4592	1.0034	0.9672	5.4416	0.9968	0.9788	5.5067
1.2507	0.9653	5.4305	1.2336	0.9631	5.4185	1.2519	0.9743	5.4815
1.5015	0.9604	5.4028	1.5693	0.9571	5.3844	1.4749	0.9705	5.4601
1.8589	0.9551	5.3734	1.8776	0.9516	5.3532	1.8674	0.9640	5.4231
2.5073	0.9461	5.3222	2.4739	0.9409	5.2932	2.4819	0.9532	5.3624
3.1211	0.9382	5.2779	3.1527	0.9288	5.2250	3.1577	0.9416	5.2968
3.7876	0.9307	5.2357	3.7584	0.9182	5.1650	3.6951	0.9326	5.2464
Glucose in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.5015	0.9801	5.5142	0.4990	0.9756	5.4890	0.4979	0.9871	5.5536
0.7542	0.9742	5.4806	0.7544	0.9710	5.4629	0.7498	0.9826	5.5282
1.0063	0.9687	5.4499	1.0024	0.9666	5.4379	1.0008	0.9781	5.5029
1.2573	0.9636	5.4212	1.2542	0.9620	5.4121	1.2421	0.9738	5.4787
1.4771	0.9597	5.3991	1.4944	0.9574	5.3862	1.4903	0.9694	5.4537

1.8853	0.9556	5.3761	1.8944	0.9500	5.3441	1.8294	0.9633	5.4194
2.5205	0.9477	5.3314	2.4933	0.9385	5.2797	2.4755	0.9516	5.3532
3.1352	0.9404	5.2905	3.1349	0.9263	5.2108	3.1204	0.9396	5.2860
3.7758	0.9333	5.2500	3.7783	0.9140	5.1415	3.7664	0.9277	5.2188
Fructose in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.5026	0.9806	5.5170	0.5020	0.9760	5.4908	0.5000	0.9873	5.5545
0.7538	0.9753	5.4871	0.7493	0.9715	5.4657	0.7531	0.9829	5.5301
1.0028	0.9697	5.4555	0.9984	0.9671	5.4407	0.9933	0.9788	5.5067
1.2468	0.9649	5.4286	1.2474	0.9627	5.4157	1.2532	0.9743	5.4815
1.5076	0.9609	5.4056	1.4971	0.9582	5.3909	1.4680	0.9707	5.4610
1.8786	0.9558	5.3771	1.8626	0.9517	5.3541	1.8853	0.9636	5.4212
2.4981	0.9477	5.3314	2.4907	0.9406	5.2914	2.5003	0.9532	5.3624
3.1293	0.9396	5.2860	3.1490	0.9288	5.2250	3.0963	0.9430	5.3050
3.7340	0.9328	5.2473	3.7501	0.9180	5.1641			
Sucrose in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.2509	0.9854	5.5442	0.5004	0.9751	5.4861	0.5015	0.9866	5.5508
0.5026	0.9794	5.5104	0.7466	0.9704	5.4592	0.7438	0.9819	5.5244
0.7528	0.9732	5.4750	1.0048	0.9651	5.4296	0.9889	0.9773	5.4983
1.0064	0.9671	5.4407	1.2541	0.9600	5.4009	1.2608	0.9717	5.4666
1.2358	0.9633	5.4194	1.5074	0.9547	5.3707	1.4926	0.9669	5.4397
1.5113	0.9600	5.4009	1.8612	0.9469	5.3268	1.8616	0.9591	5.3955
1.8547	0.9566	5.3817	2.4870	0.9326	5.2464	2.5081	0.9448	5.3150
2.5016	0.9485	5.3359	3.1179	0.9177	5.1624	3.0893	0.9314	5.2393
3.1192	0.9417	5.2977	3.7039	0.9035	5.0825	3.6934	0.9171	5.1589
3.8043	0.9344	5.2563						
Raffinose in Aqueous Polymer Solutions								
0.0000	0.9915	5.5782	0.0000	0.9849	5.5413	0.0000	0.9960	5.6040
0.1254	0.9868	5.5517	0.1206	0.9823	5.5263	0.1244	0.9935	5.5896
0.2465	0.9829	5.5301	0.2489	0.9794	5.5104	0.2486	0.9910	5.5753
0.3757	0.9796	5.5113	0.3731	0.9766	5.4945	0.3766	0.9881	5.5592
0.5025	0.9761	5.4918	0.4853	0.9740	5.4797	0.5027	0.9853	5.5432

The uncertainty in m_c , a_w and T was $\pm 2.10^{-4}$ mol.kg⁻¹, $\pm 2.10^{-4}$ and $\pm 1.10^{-3}$ K, respectively.

Table 3. Values of $a_w + 1 - (a_{w,p}^\circ + a_{w,c}^\circ)$, $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$ and ΔG against Carbohydrate Molality, m_c , For the Systems Investigated at $T = 308.15$ K.

$m_c /$ mol.kg ⁻¹	$a_w + 1 -$ $(a_{w,p}^\circ + a_{w,c}^\circ)$	$[\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)]$ / kPa	$\Delta G /$ J.kg ⁻¹	$m_c /$ mol.kg ⁻¹	$a_w + 1 -$ $(a_{w,p}^\circ + a_{w,c}^\circ)$	$[\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)]$ / kPa	$\Delta G /$ J.kg ⁻¹	$m_c /$ mol.kg ⁻¹	$a_w + 1 -$ $(a_{w,p}^\circ + a_{w,c}^\circ)$	$[\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)]$ / kPa	$\Delta G /$ J.kg ⁻¹
Aqueous 0.2 w/w PPG400 Solution				Aqueous 0.2 w/w PEG400 Solution				Aqueous 0.2 w/w PEG10000 Solution			
Xylose in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5015	-0.0010	-0.0055	-10.2088	0.4989	0.0004	0.0021	2.2853	0.4997	0.0006	0.0033	5.2414
0.7530	-0.0017	-0.0096	-17.6756	0.7474	0.0004	0.0024	2.3259	0.7555	0.0009	0.0050	8.1540
1.0006	-0.0025	-0.0140	-25.8072	1.0031	0.0006	0.0036	3.5650	1.0025	0.0012	0.0069	11.2334
1.2483	-0.0029	-0.0166	-30.6543	1.2523	0.0009	0.0050	5.3797	1.2451	0.0015	0.0084	13.6680
1.4961	-0.0034	-0.0190	-35.3637	1.4883	0.0009	0.0051	5.0852	1.4973	0.0018	0.0100	16.2793
1.8739	-0.0039	-0.0221	-41.7576	1.8662	0.0012	0.0066	6.7623	1.8643	0.0021	0.0119	19.5288
2.4997	-0.0022*	-0.0126*	-26.2206*	2.5018	0.0014	0.0081	7.7775	2.4643	0.0028	0.0156	25.8020
3.1327	0.0017*	0.0096*	12.4165*	3.1108	0.0016	0.0091	8.0105	3.0839	0.0034	0.0194	32.5620
3.7524	0.0060*	0.0339*	55.7206*	3.7344	0.0018	0.0104	8.6043	3.6965	0.0043	0.0244	41.5320
4.3724	0.0098*	0.0555*	94.8591*								
Xylitol in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5008	-0.0017	-0.0096	-17.2205	0.4987	0.0002	0.0009	0.1694	0.5023	0.0004	0.0023	3.5980
0.7528	-0.0023	-0.0128	-23.2732	0.7519	0.0003	0.0016	0.7227	0.7432	0.0004	0.0024	3.6658
1.0033	-0.0030	-0.0169	-30.8449	1.0034	0.0004	0.0023	1.3259	0.9968	0.0007	0.0040	6.3456
1.2507	-0.0036	-0.0202	-37.0836	1.2336	0.0005	0.0029	1.6837	1.2519	0.0009	0.0051	8.0259
1.5015	-0.0039	-0.0220	-40.8677	1.5693	0.0006	0.0034	1.7047	1.4749	0.0012	0.0067	10.6889
1.8589	-0.0026*	-0.0146*	-28.4661*	1.8776	0.0007	0.0041	2.0785	1.8674	0.0018	0.0102	16.6117
2.5073	0.0002*	0.0013*	-1.6537*	2.4739	0.0010	0.0056	3.1977	2.4819	0.0023	0.0130	21.2582
3.1211	0.0035*	0.0200*	31.0395*	3.1527	0.0013	0.0072	4.1431	3.1577	0.0030	0.0169	27.9968
3.7876	0.0081*	0.0456*	76.8772*	3.7584	0.0016	0.0088	5.4469	3.6951	0.0038	0.0212	35.6358
Fructose in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5026	-0.0019	-0.0107	-19.1938	0.5020	-0.0000	-0.0001	-1.5421	0.5000	0.0001	0.0007	0.9288
0.7538	-0.0028	-0.0155	-27.8842	0.7493	-0.0001	-0.0005	-2.8827	0.7531	0.0003	0.0016	2.2265
1.0028	-0.0039	-0.0222	-40.0889	0.9984	-0.0001	-0.0007	-3.8465	0.9933	0.0004	0.0021	3.0741
1.2468	-0.0044	-0.0248	-45.0238	1.2474	-0.0001	-0.0008	-4.7332	1.2532	0.0005	0.0029	4.2192
1.5076	-0.0039	-0.0218	-40.4566	1.4971	-0.0001	-0.0008	-5.3393	1.4680	0.0007	0.0039	5.7856
1.8786	-0.0024*	-0.0132*	-26.1856*	1.8626	-0.0002	-0.0010	-6.6460	1.8853	0.0010	0.0058	8.8421
2.4981	0.0006*	0.0033*	1.95220*	2.4907	-0.0001	-0.0006	-7.8875	2.5003	0.0015	0.0087	13.6657
3.1293	0.0039*	0.0220*	34.6686*	3.1490	0.0000	-0.0002	-8.9936	3.0963	0.0021	0.0118	18.9132

3.7340	0.0081*	0.0457*	77.1032*	3.7501	0.0002	0.0010	-8.5946				
Glucose in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5015	-0.0023	-0.0132	-23.4239	0.4990	-0.0003	-0.0018	-4.4833	0.4979	0.0000	0.0000	-0.2587
0.7542	-0.0037	-0.0210	-37.2807	0.7544	-0.0003	-0.0018	-5.0634	0.7498	0.0001	0.0004	0.2288
1.0063	-0.0045	-0.0256	-46.0189	1.0024	-0.0002	-0.0013	-4.8787	1.0008	0.0002	0.0010	1.0379
1.2573	-0.0050	-0.0283	-51.2999	1.2542	-0.0002	-0.0010	-5.2126	1.2421	0.0003	0.0017	2.1943
1.4771	-0.0049	-0.0275	-50.4673	1.4944	-0.0003	-0.0018	-7.1754	1.4903	0.0005	0.0026	3.4247
1.8853	-0.0013*	-0.0076*	-16.2907*	1.8944	-0.0003	-0.0018	-8.4963	1.8294	0.0007	0.0040	5.6376
2.5205	0.0027*	0.0154*	23.3336*	2.4933	-0.0004	-0.0024	-11.4179	2.4755	0.0012	0.0066	9.9155
3.1352	0.0073*	0.0412*	69.0554*	3.1349	-0.0003	-0.0017	-12.1787	3.1204	0.0016	0.0093	14.3088
3.7758	0.0127*	0.0715*	123.7544*	3.7783	0.0000	0.0001	-10.9253	3.7664	0.0024	0.0134	21.5329
Sucrose in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.2509	-0.0015	-0.0086	-15.1201	0.5004	-0.0006	-0.0035	-7.4320	0.5015	-0.0003	-0.0015	-2.7987
0.5026	-0.0028	-0.0158	-27.9884	0.7466	-0.0006	-0.0036	-8.2495	0.7438	-0.0002	-0.0013	-2.6666
0.7528	-0.0042	-0.0239	-42.4647	1.0048	-0.0007	-0.0040	-9.8096	0.9889	0.0000	0.0002	-0.2628
1.0064	-0.0052	-0.0295	-52.9283	1.2541	-0.0006	-0.0035	-9.7895	1.2608	0.0001	0.0003	-0.3835
1.2358	-0.0043	-0.0240	-44.0008	1.5074	-0.0006	-0.0034	-10.5555	1.4926	0.0002	0.0012	0.9938
1.5113	-0.0017*	-0.0095*	-19.1413*	1.8612	-0.0006	-0.0036	-12.0939	1.8616	0.0004	0.0025	2.8804
1.8547	0.0024*	0.0136*	20.8648*	2.4870	-0.0006	-0.0035	-14.3197	2.5081	0.0009	0.0052	7.1820
2.5016	0.0091*	0.0511*	86.6876*	3.1179	-0.0006	-0.0032	-16.2751	3.0893	0.0013	0.0072	10.3453
3.1192	0.0169*	0.0955*	166.6858*	3.7039	-0.0005	-0.0026	-17.7436	3.6934	0.0017	0.0097	14.5293
3.8043	0.0263*	0.1483*	263.8215*								
Raffinose in Aqueous Polymer Solutions											
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1254	-0.0024	-0.0134	-23.1145	0.1206	-0.0004	-0.0025	-4.6058	0.1244	-0.0003	-0.0015	-2.5524
0.2465	-0.0038	-0.0217	-37.4570	0.2489	-0.0007	-0.0042	-7.9572	0.2486	-0.0004	-0.0020	-3.5642
0.3757	-0.0045	-0.0252	-43.8061	0.3731	-0.0010	-0.0055	-10.5045	0.3766	-0.0005	-0.0030	-5.3479

* This is a biphasic solution

Figure Caption

Fig. 1. Plot of water activity, a_w , against carbohydrate molality, m_c , for (a) systems of carbohydrate in aqueous 0.2 w/w PEG10000 solutions and (b) systems of carbohydrate in aqueous 0.2 w/w PPG400 solutions: +, raffinose; ○, sucrose; Δ, glucose; ×, fructose; ◇, xylitol; □, xylose.

Fig. 2. Plot of $a_w + 1 - (a_{w,p}^\circ + a_{w,c}^\circ)$ against carbohydrate molality for systems of carbohydrate in aqueous polymer solutions: ○, carbohydrate in aqueous 0.2 w/w PPG400 solutions (monophasic region); ◐, carbohydrate in aqueous 0.2 w/w PPG400 solutions (biphasic region); Δ, carbohydrate in aqueous 0.2 w/w PEG400 solutions; ◇, carbohydrate in aqueous 0.2 w/w PEG10000 solutions.

Fig. 3. Plot of $a_w + 1 - (a_{w,p}^\circ + a_{w,c}^\circ)$ against carbohydrate molality for (a) systems of carbohydrate in aqueous 0.2 w/w PEG10000 solutions and (b) systems of carbohydrate in aqueous 0.2 w/w PPG400 solutions. In these plots the empty symbols represent monophasic mixtures and half-filled symbols represent biphasic ones: (plus), raffinose; (pentagone), sucrose; (diamond), glucose; (circle), fructose; (triangle), xylitol; (square), xylose.

Fig. 4. Plot of $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$ against carbohydrate molality for systems of carbohydrate in aqueous polymer solutions: ○, carbohydrate in aqueous 0.2 w/w PPG400 solutions (monophasic region); ◐, carbohydrate in aqueous 0.2 w/w PPG400 solutions (biphasic region); Δ, carbohydrate in aqueous 0.2 w/w PEG400 solutions; ◇, carbohydrate in aqueous 0.2 w/w PEG10000 solutions.

Fig. 5. Plot of $\Delta p - (\Delta p_p^\circ + \Delta p_c^\circ)$ against carbohydrate molality for (a) systems of carbohydrate in aqueous 0.2 w/w PEG10000 solutions and (b) systems of carbohydrate in aqueous 0.2 w/w PPG400 solutions. In these plots the empty symbols represent monophasic mixtures and half-filled symbols represent biphasic ones: (plus), raffinose; (pentagone), sucrose; (diamond), glucose; (circle), fructose; (triangle), xylitol; (square), xylose.

Fig. 6. Plot of ΔG against carbohydrate molality for systems of carbohydrate in aqueous polymer solutions: ○, carbohydrate in aqueous 0.2 w/w PPG400 solutions (monophasic region); ◐, carbohydrate in aqueous 0.2 w/w PPG400 solutions (biphasic region); Δ, carbohydrate in aqueous 0.2 w/w PEG400 solutions; ◇, carbohydrate in aqueous 0.2 w/w PEG10000 solutions.

Fig. 1a

Fig. 1b

Fig. 2

Fig. 3a

Fig. 3b

Fig. 4

Fig. 5a

Fig. 5b

Fig. 6