



Investigation of carbohydrates as non-charged, non-toxic and renewable soluting-out agent for polymer based aqueous biphasic systems implementation



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ABSTRACT

In order to obtain new insights into the molecular-level mechanisms behind the polymer based aqueous biphasic systems (ABS) formation, phase equilibria including both liquid–liquid and vapor–liquid equilibria of different aqueous polymer–carbohydrate systems was deeply scrutinized in this work. For this purpose, the relative ability of a large range of mono-, di- and trisaccharides, as well as polyols to form ABS with different water soluble polymers PPG400, PPG725, PEG400, PEG4000 and PEG10000 was investigated at different temperatures. It was found that, the ABS formation seems to be controlled by the interplay of the relative strength of the carbohydrate–water, polymer–water and carbohydrate–polymer interactions. In the case of aqueous PPG + carbohydrates systems, because of the unfavorable PPG–carbohydrate interactions, the solutes exclude themselves from the vicinity of each other and therefore ABS are entropically formed when PPG and carbohydrate are mixed above a given concentration in an aqueous media. These systems show the negative deviation from the semi-ideal behavior. By increasing temperature and PPG molecular weight (PPG–water interactions become weaker) and increasing hydrophilicity of the carbohydrate (stronger carbohydrate–water interactions) the immiscibility region increases. However, in the case of PEG + carbohydrate aqueous systems which not capable of inducing phase separation, because of the favorable PEG–carbohydrate interactions, the interaction of each solute with water molecules becomes weaker in the presence of the other solute. Therefore the vapor–liquid equilibria behavior of these systems shows the positive deviations from the semi-ideal behavior. By increasing the PEG molar mass as well as the hydrophobicity of carbohydrate, the carbohydrate–PEG interaction increases and then the positive deviations from the semi-ideal behavior increase.

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1. Introduction

Aqueous biphasic systems (ABS) are formed when pair of solutes such as, two polymers, a polymer and salt or two salts are mixed above their critical concentrations in an aqueous medium. As both phases are aqueous-rich, when biomolecules are added to these systems they are partitioned unequally between the two phases formed, while maintaining the native biological activity and conformation of the diverse biomaterials due to the high water content of the equilibrium phases (*ca.* 60–80% on a weight fraction basis) [1–3]. ABS have been investigated in the extraction and

purification of diverse biomolecules such as proteins, enzymes, nucleic acids, flavor compounds, antioxidants, antibiotics and alkaloids [4]. The main advantages of ABS in the recovery and purification of biomolecules are their versatility, low cost, high efficiency, improved purification factor, fast mass transfer rates, high yield and selectivity [5,6].

The first report of an ABS dates back from as early as the late 19th century, when Beijerinck [7] mixed the aqueous solutions of gelatin and agar to obtain an aqueous biphasic system. Since the first observation by Beijerinck in 1886, many other pairs of phase-forming constituents including polymer–polymer [1–3,8], polymer–salt [1–3,9], polymer–amino acid [10] and ionic liquid-different solutes (such as: salt, polymer, amino acid and carbohydrate) [11] have been explored. Carbohydrates have been used as soluting-out agents in the ionic liquid-based ABS [11–15].

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Carbohydrates can have a soluting-out effect on polypropylene glycol in aqueous solutions with the advantages that such compounds are of common occurrence in the food chemistry. As far as we know very limited information have been reported in the literature about the phase behavior of polymer–carbohydrate ABS [16,17]. The use of carbohydrates to induce ABS can be visualized as a step towards the usage of a broad spectrum of valuable bio-compounds available from biomass. Since carbohydrates are non-charged, biodegradable, nontoxic, and a renewable feedstock, greener processes involving ABS can be immediately envisaged [11]. The soluting-effects of carbohydrates on the aqueous solutions of different solutes and in turn their position in the Hofmeister series have rarely been studied. Although ABS formation is well documented and has been extensively investigated in the literature, its mechanism at the molecular level is still unclear. Furthermore, carbohydrates are good candidates for studying the effect of structurally and stereochemically isomers on the phase behavior of polymer-based ABS and therefore to obtain further information about the mechanism of solute-effect in aqueous polymer solutions. It was found that low molecular weight carbohydrates cause soluting-in of hydrophilic polymers and gels [18], but soluting-out of macromolecules having a partial hydrophobic character [17,19,20] in aqueous solutions. However, the mechanism of soluting-effect and the reasons for the differences between effects of various saccharides are still obscure.

Polymer–carbohydrate ABS may offer greener extraction procedures as compared to polymer–salt and polymer–ionic liquid 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 medium created by salts may be deleterious to a number of biomolecules or microorganisms. Meanwhile, in comparison with imidazolium or pyridinium based ionic liquids which have been widely used for ABS formation [11], carbohydrates are more eco-friendly and less expensive substances. In order to investigation of carbohydrate–polymer ABS and obtain further details about the mechanisms of polymer-based ABS formation, this work is, thus, systematically focused on the isopiestic and liquid–liquid equilibria measurements of a large series of aqueous polymer–carbohydrate solutions capable or not of inducing phase separation at different temperatures. In order to cover a range of hydrophilic and hydrophobic behaviors, the polymers polyethylene glycol 400 (PEG400), polyethylene glycol 4000 (PEG4000), polyethylene glycol 10000 (PEG10000), polypropylene glycol 400 (PPG400) and polypropylene glycol 725 (PPG725) and carbohydrates 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) were investigated.

2. Experimental section

2.1. Materials

PPG400 and PPG725 were obtained respectively from Fluka and Aldrich. D (+)-Xylose ($\geq 99.0\%$ w/w), L (+)-Arabinose ($\geq 99.0\%$ w/w), D (+)-Glucose ($\geq 99.5\%$ w/w), D (+)-Galactose ($\geq 98.0\%$ w/w), D (+)-Mannose ($\geq 98.0\%$ w/w), D (-)-Fructose ($\geq 99.0\%$ w/w), Sucrose ($\geq 98.0\%$ w/w), Maltose monohydrate ($\geq 99.0\%$ w/w), Lactose monohydrate ($\geq 98.0\%$ w/w), Raffinose pentahydrate ($\geq 97.0\%$ w/w), D (-)-Sorbitol ($\geq 99.0\%$ w/w), NaCl ($\geq 99.5\%$ w/w) and PEGs were obtained from Merck. D (-)-Ribose ($\geq 99.0\%$ w/w) was obtained from Acros. Xylitol ($\geq 99.0\%$ w/w) and Maltitol ($\geq 97.0\%$ w/w) were obtained from Alfa Aesar. The PPGs, PEGs and carbohydrates were

used without further purification. NaCl was dried in an electrical oven at about 383.15 K for 24 h prior to use. Double-distilled and deionized water was used. The chemical structures of the carbohydrates under study 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 for all the monosaccharides.

2.2. Experimental procedures

The ternary phase diagrams (binodal curves) for the ABS composed of carbohydrate, PPG and water were determined by the cloud point titration method at different temperatures and atmospheric pressure, as previously described [21]. Briefly, stock solutions of carbohydrates with known concentrations were previously prepared on a weight basis using an analytical balance (Sartorius CP124S) with an accuracy of $\pm 1 \times 10^{-7}$ kg. In a glass vessel (provided with an external jacket in which water circulated at the certain temperature), repetitive drop-wise addition of the polymer to the aqueous solution of carbohydrate, or *vice versa*, was carried out until the appearance of a cloudy solution (biphasic region), followed by the drop-wise addition of water to make the mixture clear and limpid (monophasic region). All these additions were carried out under constant stirring. The compositions were determined by weight within $\pm 10^{-7}$ kg at each point of turbidity and clear solution.

Isopiestic measurements of the investigated carbohydrate + polymer + water systems were carried out by the procedure described previously [9]. The used isopiestic chambers have 7 or 8 sample cups uniformly distributed at the bottom. The appropriate known amounts of pure anhydrous NaCl (two cups), pure carbohydrate (one cup), pure polymer (one cup), and carbohydrate + polymer mixture with a certain composition (two or three cups) were added to each weighed cup and the central cup served as a water reservoir. After all of the sample cups were placed in the isopiestic chamber, the chamber was closed and slowly evacuated to remove the air and was held in a constant-temperature bath at a certain temperature to within ± 0.05 K for the necessary time to achieve equilibrium. The samples reached equilibrium between 7 and 14 days; the longer times correspond to the lower concentrations and temperatures. The volatile component (water) is transported from the central cup into the other cups containing the dry samples through the vapor phase until the solutions reach equilibrium and the central cup is dried. Equilibrium was assumed to have been reached when the reference aqueous NaCl solutions in the duplicate cups arrived at the same molality (within 0.1%). When the equilibrium is reached, the isopiestic chamber is removed from the bath and each cup is removed from the chamber. The weight fractions of each solution were determined by weighing the cups after equilibration and the initial weight of the solutes. At equilibrium, the activity of water in each of the solutions within the isopiestic apparatus is identical. For the calculation of water activity of the standard NaCl + water solutions, the relation reported in the literature was used [22]. The estimated uncertainty in the measurement of water activity was estimated to be $\pm 5 \cdot 10^{-4}$.

3. Results and discussion

In the present study, the following systematic experimental works were carried out on a large range of aqueous polymer–carbohydrate solutions at different temperatures:

(i) isopiestic measurements of ternary aqueous polymer (PEG400, PEG4000, PEG10000, PPG400) + carbohydrate (glucose,

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