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Evaluation of the effect of carbohydrates as renewable, none-charged and non-toxic soluting-out agents on the ionic-liquid-based ABS implementation

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ABSTRACT

In order to study the effects of number of hydroxyl groups and stereochemical properties of sugar molecules, as well as temperature on the phase separation capability and vapor-liquid equilibria behavior of the carbohydrate + IL aqueous systems, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and seven carbohydrates including monosaccharides (L-(+)-arabinose, D-(+)-xylose, D-(+)-glucose and D-(−)-fructose), disaccharides (maltose and sucrose), and a polyol (maltitol) were selected and their vapor-liquid equilibria and phase diagram behaviors were studied. For these systems, the constant water activity lines in mono- and biphasic regions show large negative deviations from the linear isopiestic relation ($\Delta_0 < 0$) and these deviations in monophasic region are larger than biphasic region. The values of Δ_0 as well as the phase separation capability of the investigated ternary systems were increased with decreasing temperature and increasing hydrophilicity of the carbohydrates.

1. Introduction

Bioseparation is a fundamental part of the modern biotechnology and therefore there is a commercial interest in inexpensive methods that can purify and separate bioproducts and be easily scaled-up. In some types of liquid–liquid extraction (LLE) and solid phase extraction (SPE), hazardous organic solvents are used which are harmful for the environment and health safety. Therefore, in the recent decades the design and development of new and "greener" bioseparation methods for the improvement of clean manufacturing processes have extensively been investigated. In 1956, Albertsson [1] introduced the aqueous biphasic systems (ABS), which have been recognized as a mild, economical, and effective downstream processing method [2]. These systems have two immiscible aqueous phases based on polymer/salt, polymer/amino acid, polymer/carbohydrate, ionic liquid/salt, ionic liquid/polymer, or ionic liquid/amino acid compositions [3,4]. Since the bulk of both phases are composed of water, ABS forms a gentle ambience for bioproducts. These systems can be used for the extraction of products from biomolecules to metal ions [2,5–11]. In recent years, a pile of works have been devoted to ABS composed of a novel group of compounds: ionic liquids. After introducing the topic by Rogers and coworkers in 2003 [12], a large number of researchers have been working on ionic liquid-based ABS [3–5,13]. In this regard, many studies have been done either for providing thermodynamic information or studying capability of these systems to extract value-added compounds. Ionic liquids have the potential that act both as a soluting-out agent (for example in aqueous IL-polymer systems [14]) and as a component that soluted-out from aqueous solution (for example in aqueous IL-electrolyte systems [15]). Recently, carbohydrates were investigated as soluting-out agent in IL-based ABSs [16–18]. The use of carbohydrates (which are nontoxic, renewable feedstock and biodegradable organic molecules) for the extraction processes have several advantages such as easy recycling ionic liquid from phases in compared to the systems containing electrolytes, and eliminate the effect of change in pH on the biological activity of some of biomolecules such as proteins [18]. Therefore studying thermodynamic properties of aqueous solutions containing ionic liquids and carbohydrates for understanding of molecular mechanism of phase separation is very important. In this work, for performing a comprehensive thermodynamic study about soluting effect phenomenon in aqueous IL/carbohydrate systems two experiments including phase diagram and vapor – liquid equilibria (VLE) were carried out. In order to study the effects of some parameters such as number of hydroxyl groups and stereochemical properties of sugar molecules, and temperature on the phase separation capability and vapor-liquid equilibria behavior of these systems, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), and seven carbohydrates including monosaccharides (L-(+)-arabinose, D-(+)-xylose, D-(+)-glucose, D-(−)-fructose), disaccharides (maltose and sucrose), and a polyol (maltitol) were selected and the

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thermodynamic properties of their ternary aqueous systems were studied at different temperatures.

2. Experimental section

2.1. Materials

D-(+)-xylose (≥0.99 w/w), L-(+)-arabinose (≥0.99 w/w), D-(+)-glucose (≥0.99 w/w), D-(−)-fructose (≥0.99 w/w), maltose (≥0.99 w/w), sucrose (≥0.98 w/w), NaCl (≥0.995 w/w), 1-methylimidazole (≥0.99 w/w), 1-bromobutane (≥0.98 w/w), and sodium tetrafluoroborate (≥0.97 w/w) were obtained from Merck. Maltitol (≥0.97 w/w) was purchased from Alfa Aesar. NaCl was dried in an electric oven at 383.15 K for 24 h prior to use. Double distilled and deionized water was used for the preparation of the solutions. The structures of studied carbohydrates have been presented in Scheme 1. [Bmim][BF_4] was synthesized and purified according to the procedures described in the literature [19]. The synthesized [Bmim][BF_4] was analyzed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The FT-IR spectrum of [Bmim][BF_4] contains the peaks at; ν/cm^{-1} 2938 and 2876 (aliphatic asymmetric and symmetric (C—H) stretching vibrations), 1171 and 1059 (inplane bending vibrations for methyl groups), a broad peak at 3122–3162 (for quaternary amine salt formation with tetrafluoroborate), 1657 (stretching C═C), 1466 (stretching C═N), 757 and 623 (stretching vibration C—N). ^{1}H NMR spectrum contains peaks at δ(ppm): 0.89 (t, $J = 7.1$, 3H), 1.25–1.36 (m, 2H), 1.77–1.89 (m, 2H), 3.91 (s, 3H), 4.17 (t, $J = 7.3$, 2H), 7.44 (s, 2H), 8.67 (s, 1H); ^{13}C NMR: 13, 19, 31.6, 35.8, 49.4, 122.3, 123.6, 135.8.

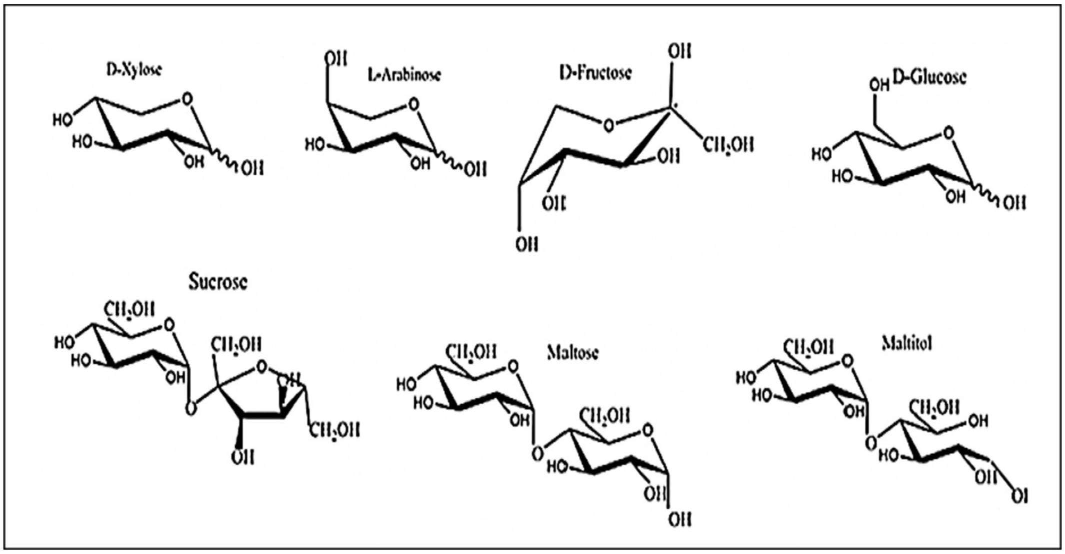
Before using, the ionic liquid was dried under reduced pressure around 5 Pa at 120 °C for 3 h to remove the water. The water content in the purified ionic liquid measured with Karl Fischer titrator was <1000 ppm and it was accounted upon solution preparation.

2.2. Vapor-liquid equilibrium measurements

Vapor-liquid equilibria properties of the investigated systems such as osmotic coefficient, water activity and vapor pressure data were obtained by the improved isopiestic method. The basis of this method is that a number of solutions within a closed system are correlated with each other through the vapor phase. The solvent (which is the only volatile compound in the system) mass is transferred between the solutions by distillation and the solutions approach equilibrium. All solutions have a common solvent (here water) and the equilibrium condition in constant pressure and temperature is that the chemical potential of the solvent and thereby activity of solvent in all the systems becomes equal. The mass transfer of the solvent between the solutions continues until the concentration gradients become zero in the same binary solutions. From the solvent activity of a standard solution (in this work NaCl solution), the activity of solvent for all the solutions within the isopiestic system can be determined. The isopiestic device used in this work has a glass multileg manifold attached to several flasks. Known amounts of pure NaCl (two flasks), pure carbohydrate (one flask), pure IL (one flask) and carbohydrate + IL with different ratios (two or three flasks) were added to different flasks and the central one was used as a solvent reservoir. The measurements were performed in a constant-temperature water bath at three temperatures: 298.15, 303.15 and 308.15 K. Each equilibrium system was held at least for 3 days at a constant temperature. After reaching the equilibrium, the isopiestic apparatus was removed from the water bath, and the flasks were dried and then weighed. From the weight of each solution after equilibrium and the initial weight of the solutes, the molalities of solutions were calculated. At the equilibrium, the solvent activities of all the solutions are equal and therefore the solvent activity can be determined from the standard NaCl solution. The uncertainty in the measurement of the water activity was estimated to be ±0.0005.

2.3. Phase diagram measurements

The binodal curves for aqueous [Bmim][BF_4] + carbohydrate systems were obtained at the 298.15–318.15 K temperature range at 5 K intervals by the cloud-point titration method. This experimental setup includes a water jacketed glass vessel that temperature in which was kept constant by circulating water from a water bath. The temperature was controlled to within ±0.05 K. The binodal curves were obtained by titrating a homogeneous mixture of the (water + carbohydrate) solution of a known concentration with an (IL + water) solution until a heterogeneous solution (biphasic system) was detected. Then this cloudy solution was titrated with water until the turbidity was disappeared. The composition of this clear mixture, which is a point of binodal curve, was determined by its mass measured using an analytical balance with a precision of $\pm 1 \times 10^{-4}$ g. These visual experiments (transition from homogeneity to heterogeneity by adding the aqueous IL solution to the obtained clear mixture, followed by the dropwise addition of water until the formation of a clear solution) were repeated until a complete binodal curve was obtained.



Scheme 1. Chemical structures of the carbohydrates.