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Poly(vinyl alcohol) as a novel constituent to form aqueous two-phase systems with acetonitrile: Phase diagrams and partitioning experiments

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ABSTRACT

In this work it is shown, for the first time, that aqueous solutions of poly(vinyl alcohol) (PVA) and acetonitrile (ACN) undergo liquid–liquid demixing and form aqueous two-phase systems (ATPS). The ternary phase diagrams composed of PVA of different molecular weights, namely 9000–10,000, 13,000–23,000, 31,000–50,000 g mol^{-1} and 85,000–124,000 g mol^{-1} , acetonitrile and water, and the respective tie-lines were determined at 25 °C. In all the systems investigated, ACN is enriched in the top phase while PVA is found in the bottom phase. To explore the potentiality of these ATPS for extraction strategies, the partitioning of vanillin among the coexisting phases was further evaluated. The effects of ACN and PVA concentrations and temperature toward the vanillin partitioning were also investigated. An increased vanillin partitioning to the top phase was verified with the increase of the ACN concentration; however, the partition coefficient of vanillin for the ACN-rich phase decreases with the increase on both the PVA concentration and temperature. The highest partition coefficient of vanillin for the ACN-rich phase (2.24) was found with the system composed of 49 wt% of ACN + 9 wt% of PVA 9000–10,000 g mol^{-1} at 5 °C, with a recovery of 79%. The vanillin migration to the top phase is spontaneous and an exothermic process.

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Keywords: Aqueous two-phase system; Acetonitrile; Poly(vinyl alcohol); Vanillin; Partition; Extraction

1. Introduction

Poly(vinyl alcohol) (PVA) is a non-toxic, amorphous and biodegradable synthetic high- κ -polymer presenting, in addition, a randomly coiled and highly flexible chain when in solution (Senga and Sankhala, 2007). This polymer is obtained by hydrolysis of polyvinyl acetate and its properties depend on the polymerization and hydrolysis conditions, as well as on the drying and grinding (Krumova et al., 2000). PVA is a relatively water soluble polymer with interesting

properties, such as a low cost, good surface alignment effects, and an excellent film forming, emulsifying and adhesive properties (Chou, 2010). Due to these features, PVA is broadly used as a thickening, emulsifying or film-forming agent or as an adhesive in many household and industrial applications, especially in the paper, textile and chemical industries (Marusincová et al., 2013). In addition, PVA is usually employed as a phase forming-component in aqueous two-phase systems (ATPS) when combined with inorganic salts (Wu et al., 2001).

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Acetonitrile, CH₃CN, also known as cyanomethane or methyl cyanide, is an aprotic and polar organic solvent miscible with water in all proportions (Mandal et al., 2011). The ACN molecules do not strongly interact with themselves and leave a hydrogen-bond network formed by water (Takamuku et al., 1998). ACN is also a by-product from the manufacture of acrylonitrile (Pollak et al., 2000), which is widely used by industry in the production of perfumes, rubber products, pesticides or pharmaceuticals (Zhang et al., 2011), or as a mobile phase in reverse phase high performance liquid chromatography (HPLC) (Taha et al., 2012; Gu and Shih, 2004).

ATPS have been divided into two major categories: those which contain two polymers, such as polyethylene glycol (PEG) + dextran (Karakatsanis and Liakopoulou-Kyriakides, 2007; Chen and Lee, 1995) and PEG + maltodextrin (Silva and Meirelles, 2000) systems, and those formed by a polymer and a salt, such as PEG-phosphate-based (Silva et al., 2013; Lima et al., 2002; Köhler et al., 1991) and PEG-citrate-based salts (Neves et al., 2012; Porto et al., 2008). However, many other pairs of compounds can be used to form ATPS, especially alcohol + salt (Reis et al., 2012), ionic liquid + salt (Ventura et al., 2012b; Neves et al., 2009; Gutowski et al., 2003), ionic liquid + PEG (Pereira et al., 2013a; Freire et al., 2012) and ionic liquid + carbohydrate (Freire et al., 2011) mixtures. Recently, it was demonstrated that acetonitrile (ACN) can also form ATPS when combined with carbohydrates (Cardoso et al., 2013) or polyols (Cardoso et al., 2014).

ATPS can be seen as an alternative option for extraction, separation and purification purposes over conventional systems which usually require organic solvents (Martínez-Aragón et al., 2009). Moreover, ATPS are easy to scale up, present low cost and typically lead to a high product purity as well as to a high yield, while maintaining the biological activity of the molecules due to their water-rich environment (Lu et al., 2013; Rito-Palomares et al., 2000). These systems have been used in the recovery and purification of many biomolecules, namely enzymes (lipase – Ventura et al., 2012a; Barbosa et al., 2011; Souza et al., 2010), antioxidants (rutin – Reis et al., 2014; gallic acid – Cláudio et al., 2012), alkaloids (caffeine – Cláudio et al., 2013; theobromine, theophylline, nicotine and caffeine – Passos et al., 2013), antibiotics (tetracycline – Pereira et al., 2013b; Wang et al., 2010) and antibodies (Azevedo et al., 2009; Samatou et al., 2007).

This work addresses novel ATPS based on acetonitrile and poly(vinyl alcohol) of different molecular weight. The corresponding ternary phase diagrams, tie-lines and tie-line lengths at 25 °C were firstly determined. Further, their potential application to extract or separate a model antioxidant – vanillin (3-methoxy-4-hydroxybenzaldehyde) – was evaluated. This biomolecule is used here as a standard biomolecule and representative of the phenolic compounds with antioxidant properties. Vanillin is the major component of natural vanilla and it is widely used as a flavoring material in confectionery, food products, beverages, perfumes and in pharmaceutical preparations (Walton et al., 2003).

2. Materials and methods

2.1. Materials

The ATPS studied in this work are formed by water, poly(vinyl alcohol) of different molecular weights ($M_w = 9000\text{--}10,000\text{ g mol}^{-1}$; $13,000\text{--}23,000\text{ g mol}^{-1}$; $31,000\text{--}50,000\text{ g mol}^{-1}$; $85,000\text{--}124,000\text{ g mol}^{-1}$) and acetonitrile. All

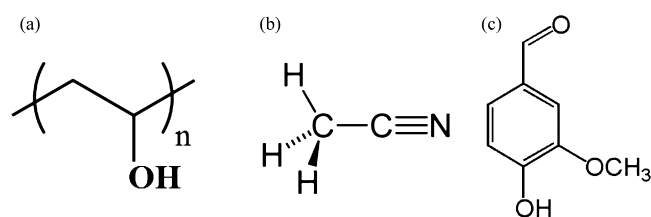


Fig. 1 – Chemical structures of the phase-forming components used in the ATPS formation and of the biomolecule used as a partitioning solute: (a) poly(vinyl alcohol); (b) acetonitrile; (c) vanillin.

reagents were purchased from Sigma–Aldrich: poly(vinyl alcohol) 9000–10,000 g mol⁻¹ 80% hydrolysed (>99.5 wt% pure), poly(vinyl alcohol) 13,000–23,000 g mol⁻¹ 87–89% hydrolysed, poly(vinyl alcohol) 31,000–50,000 g mol⁻¹ 98–99% hydrolysed, poly(vinyl alcohol) 85,000–124,000 g mol⁻¹ >99 wt% hydrolysed, acetonitrile (HPLC grade with a purity of 99.9 wt%) and vanillin (>99 wt% pure). The chemical structures of the phase-forming components of the ATPS investigated and of the target biomolecule used in the partitioning experiments are shown in Fig. 1. Distilled and deionized water was used in all experiments.

2.2. Phase diagrams and tie-lines

The ternary phase diagrams for poly(vinyl alcohol) and acetonitrile were determined at $(25 \pm 1)^\circ\text{C}$ and atmospheric pressure by the cloud point titration method. Stock solutions of poly(vinyl alcohol) ($\approx 5\text{ wt}\%$) and acetonitrile ($\approx 80\text{ wt}\%$) were previously prepared and used for the determination of the phase diagrams. Repetitive drop-wise addition of the ACN solution to the aqueous solution of each PVA was carried out until the detection of a cloudy solution, followed by the drop-wise addition of ultra-pure water until the detection of a monophasic region (clear and limpid solution). These additions were carried out under continuous stirring and the saturation curves were determined gravimetrically within $\pm 10^{-5}\text{ g}$.

The tie-lines (TLs) were obtained through a gravimetric method originally described by Merchuck et al. (1998). Several mixtures at the biphasic region of the ternary systems were prepared, vigorously stirred, and allowed to reach equilibrium and phase separation, for a minimum of 18 h at $(25 \pm 1)^\circ\text{C}$. Initial soluble aqueous solutions of each PVA were prepared followed by the subsequent addition of pure ACN. After the equilibration step, the top and bottom phases were carefully separated and weighted within $\pm 10^{-5}\text{ g}$. Each individual TL was determined by the application of the lever-arm rule, which describes the relationship between the weight of the top phase and the overall system weight and composition. For that purpose, the binodal curves were correlated using Eq. (1),

$$Y = A \exp\{(B \times X^{0.5} - (C \times X^3))\} \quad (1)$$

where Y and X are the acetonitrile and poly(vinyl alcohol) weight fraction percentages, respectively, and A, B and C are constants parameters obtained by the regression of the experimental binodal data.

The determination of the TLs (Y_T , Y_B , X_T and X_B) was then accomplished by solving the a system of four equations based

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