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Extraction of dimethyl sulfoxide using ionic-liquid-based aqueous biphasic systems

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ABSTRACT

To combine ionic liquid (IL) recovery with cosolvent separation in biomass processing, the quaternary aqueous biphasic systems (ABSs) formed by IL, kosmotropic salt and water in the presence of dimethyl sulfoxide (DMSO) are herein proposed. Three main parameters were evaluated through the phase diagrams and the DMSO partitioning process: the IL cation and anion structure, the salt anion, and the temperature. In all systems and conditions texted, DMSO preferentially dissolves in the IL-rich phase. The results obtained indicate that, the partitioning process is essentially controlled by the IL cation interactions with DMSO. The partition coefficients (K_{DMSO}) displays a maximum for the system formed by [C_6mim]Cl. The K_{DMSO} value increases monotonically with the initial concentration of DMSO, and it decreases in the systems with different salts: $K_3PO_4 > K_2HPO_4 > K_2CO_3 > KOH$. The increase of temperature reduces the partition coefficients. Moreover, densities and pH of both aqueous phases were measured at 298.15 K to evaluate the properties of the systems. The results gathered indicate that the densities and pH values of the two phases can be affected by the nature of IL and its initial concentrations, and the smaller density differences between the fluids, the lower the partition coefficients of DMSO.

1. Introduction

Liquid–liquid extraction processes are important techniques used for the recovery and purification steps [1,2]. Aiming at avoiding the use of organic solvents as the extractive phase in traditional liquid–liquid extraction techniques, aqueous biphasic systems (ABSs) which essentially composed of water in both phases were introduced by Albertsson [3]. The ABS formed by mixing of polymer/polymer, polymer/salt or salt/salt in water above critical concentrations can be used for separation of biomolecules [4]. However, most of the aqueous solutions of the phase-forming polymers present high viscosities, and also may alter the kinetics or interfere with the enzyme reaction in some other way [5–7].

In 2003, Rogers and co-workers [8] reported the pioneering research pointing to the possible creation of ABS by the addition of inorganic salts to aqueous solutions of ionic liquids (ILs). Consequently, a wide variety of IL-based ABSs in the presence of inorganic salt [9–12], organic salt [13,14], carbohydrate [15–17], polymer [18–20], amino acid [21], and anionic surfactant [22] have been presented. ILs are salts with a large array of fascinating properties, such as a negligible vapor pressure, low viscosity and high thermal and chemical stability [23]. As "designer solvents", the main advantage of the applicability of IL-based ABSs is the ability to tailor their polarities and affinities by a proper manipulation of the cation/anion and their combinations in ILs [24,25]. Therefore, these systems have been extensively studied as successful separation/extraction methods of different compounds and molecules, such as biomolecules [11,26], antibiotics [27], polar solutes [28–31], and biocatalysis [32–34]. Meanwhile, the influence of the IL structure [5,35–40], temperature [20,41,42], pH [34,43], viscosity [22,44], and density [44] on the phase behavior or partition coefficient have been extensively studied.

Generally, the use of IL-organic solvent mixtures offers a lower viscosity, provides higher biomass loading, and reduces cost by using less IL [45,46]. Dimethyl sulfoxide (DMSO), a dipolar aprotic solvent, has been widely used as IL's cosolvent to dissolve starch [47], cellulose [48,49], and lignocellulosic biomass [50]. The previous applications of the mixture of IL and DMSO have been reported, yet, to minimize environmental impacts the recovery of IL together with DMSO has been a problem to solve. Recent advances have shown that the mixed solvents of IL and DMSO which were used as pretreated solvents of lignocellulosic biomass for biogas production were successfully recovered together by forming ABS with K_3PO_4, and the recovery rates of IL and DMSO were all over 90% [51]. Subsequently, the influence of these dipolar aprotic solvents on the phase behavior of IL-based ABS was further evaluated, and it was shown that biphasic area increases when the concentrations of the dipolar aprotic solvent increase [52]. These literatures deserve further attention of the research community

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working with IL-based ABSs in the presence of dipolar aprotic solvent.

Attempting at developing the understanding on the partition of dipolar aprotic solvents in ABSs containing ILs (Fig. 1), and to recovery ILs along with the extraction of its cosolvents, in this work an extensive study was conducted using DMSO as the partitioning molecule. For that purpose, several extraction parameters were studied in quaternary systems composed by imidazolium-based ILs, DMSO, water and inorganic salts, namely the influence of the IL cation, the salt, the temperature of extraction and the concentration of DMSO. Moreover, densities and pH of both monophasic region and biphasic region were measured at 298.15 K to evaluate the properties of the systems.

2. Experimental

2.1. Materials

The ionic liquids used in this work to study the formation of ABSs in the presence of dipolar aprotic solvent were the following: 1-ethyl-3-methylimidazolium chloride, [C_2mim]Cl; 1-butyl-3-methylimidazolium chloride, [C_4mim]Cl; 1-hexyl-3-methylimidazolium chloride, [C_6mim]Cl; 1-octyl-3-methylimidazolium chloride, [C_8mim]Cl; 1-allyl-3-methylimidazolium chloride, [Amim]Cl; 1-butyl-2,3-dimethylimidazolium chloride, [BDmim]Cl; 1-ethyl-3-methylimidazolium bromide, [C_2mim]Br; 1-butyl-3-methylimidazolium bromide, [C_4mim]Br; 1-hexyl-3-methylimidazolium bromide, [C_6mim]Br; 1-octyl-3-methylimidazolium bromide, [C_8mim]Br. All ionic liquids were supplied by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, China (purity > 99.0 wt%). Dimethyl sulfoxide, DMSO (purity > 99.0 wt%) was acquired at Sigma Aldrich. The inorganic salts used were $K_3PO_4{\cdot}3H_2O$ > 96.0 wt%, $K_2HPO_4{\cdot}3H_2O$ > 97.0 wt%, KH_2PO_4 > 99.5%, K_2CO_3 ⩾ 99.5 wt%, KOH ⩾ 99.5 wt%, and KCl ⩾ 98 wt%, all from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was double-distilled and passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus.

2.2. Phase diagrams

Aqueous solutions of each salt with variable mass fractions in a range between 40 and 60 wt%, and aqueous solutions of ionic liquid with mass fraction at 80 wt% (the concentration of DMSO in IL was from 0 and 20 wt%) were prepared and used for the determination of the corresponding binodal curves. The phase diagrams were determined through the cloud point titration method at

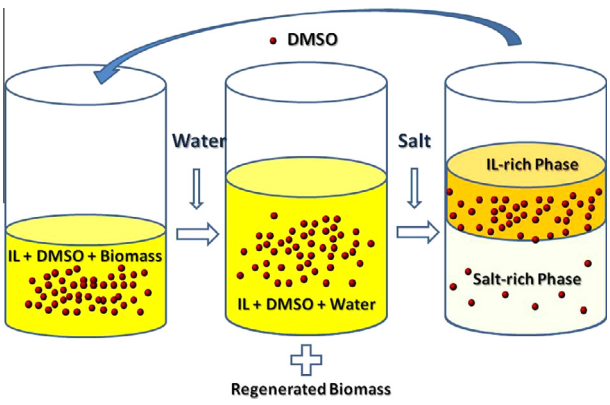

Fig. 1. Recycling of IL together with DMSO by using ABS method in biomass processing.

various temperatures and atmospheric pressure. The experimental procedure adopted was previously used by us and is described in detail elsewhere [12,52]. The experimental binodal curves were correlated according to the following equation proposed by Merchuk et al. [53]:

$$Y = a\exp(bX^{0.5} - cX^{0.3}) \quad (1)$$

where X and Y are the mass fractions of ionic liquid and salt. The constants a, b and c were obtained by least-squares regression.

2.3. DMSO partitioning

The amount of DMSO in each aqueous phase was quantified through material balance method [52]. After the careful separation of both phases, the concentrations of IL and salt in the upper and lower phases were determined by an ion chromatography (Basic IC 792, Methohm, Switzerland). A Karl–Fisher moisture titrator (MKS210, Kyoto Electronics, Kyoto) was used to measure the water content in all samples. The partition coefficients of DMSO (K_{DMSO}), were determined as the ratio of the concentration of DMSO in the ionic liquid and in the inorganic salt aqueous-rich phases, accordingly to:

$$K_{DMSO} = C_T/C_B \quad (2)$$

where C_T and C_B are the concentration of DMSO in the top and bottom aqueous-rich phases, respectively. For all the mixtures evaluated, the top layer is the IL-rich phase while the bottom phase is the inorganic salt-rich phase.

2.4. Density and pH measurements

The solutions from monophasic region to biphasic region with an increasing mass ratio of K_3PO_4 to [$C_n$mim]Cl in the presence of DMSO were prepared. The density (g mL^{-1}) of each phase was measured using an automated DES PHOTIME. The pH value was tested by a PHS-25 pH meter equipment.

3. Results and discussion

3.1. Effect of IL structure

A broad range of ILs was studied to identify the IL structural features responsible for the formation of ABSs and the extraction of DMSO. The ILs investigated here were [C_2mim]Cl, [C_4mim]Cl, [C_6mim]Cl, [C_8mim]Cl, [Amim]Cl, [BDmim]Cl, [C_2mim]Br, [C_4mim]Br, [C_6mim]Br and [C_8mim]Br, and all the above ILs were able to promote ABSs with K_3PO_4 in the presence of DMSO. The structures of the ILs studied are displayed in Fig. 2.

The experimental weight fraction data for each phase diagram are reported in Supporting Information. The binodal curves of IL + K_3PO_4 + water + 20% DMSO are plotted in Fig. 3. The binodal curves of all systems were correlated with Eq. (1), and the respective parameters a, b, c, along with their corresponding standard deviations were obtained by the nonlinear regression. The results are listed in Table 1. From the correlation coefficients (R^2) obtained, it is safe to admit that Eq. (1) provides a good description of the experimental data. The phase diagram in Fig. 3 provides information about the concentration of phase-forming components required to form two phases, and the concentration of phase components in the top and bottom phases. Moreover, the closer to the axis origin a binodal curve is, the higher the IL hydrophobicity, and the higher their ability to phase split [25].

Taking into the account the alkyl chain length in [$C_n$mim]Cl, the size of the ILs with alkyl chains shorter than the hexyl is the dominant effect on the formation of ABSs, while self-aggregate in