Journal of Environmental Chemical Engineering 2 (2014) 137–142

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Partitioning of reactive red-120, 4-(2-pyridylazo)-resorcinol, and methyl orange in ionic liquid-based aqueous biphasic systems

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ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form 30 November 2013
Accepted 4 December 2013

Keywords:
Azo dyes
Aqueous biphasic system
Partition coefficient
Ionic liquid

ABSTRACT

In this paper partitioning behaviors of reactive red-120, 4-(2-pyridylazo)-resorcinol, and methyl orange as model azo dyes in ionic liquid-based aqueous biphasic systems were studied. For designing aqueous biphasic systems and investigating the partitioning of the model dyes, phase diagrams and binodal curves were obtained at 25 °C for [C_4mim][Br]/salt systems at different pH values. It was found that the partition coefficients of the studied dyes depended on their chemical structures, pH of the aqueous phase, temperature and composition of the aqueous biphasic system. Ionic liquid-based aqueous biphasic extraction was an efficient and suitable method for partitioning of dyes into ionic liquid-rich top phase. Efficient extraction of dyes into IL phase was done within 1 min. The hydrophilic ionic liquid 1-butyl-3-methylimidazolium bromide, [C_4mim][Br], in top phase was efficiently recovered by using the hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [C_4mim][PF_6]. In the recycling process, almost no dye was extracted into [C_4mim][PF_6] phase.

Introduction

Azo dyes are characterized by the presence of one or more azo (–N=N–) functional group and aromatic rings as common groups in their chemical structures, they may also have other groups such as sulfonic acid groups as reported [1]. Many studies [2] indicate that these dyes or their metabolites (e.g. aromatic amines) may be highly toxic and potentially carcinogenic, allergenic and mutagenic (on exposed) to living organisms. Azo dyes are used primarily in the textile dyeing processes due to their superior fastness to the applied fabric, high photolytic stability, and resistance to microbial degradation. Colored waste waters containing azo dyes may result in major environmental problems. Therefore, these dyes should be removed from the large volume of aqueous effluent before being released into the environment [3,4].

Aqueous biphasic (ABP) system is an efficient method for extraction of various substrates [5–8]. Common ABP systems are formed by introduction of two types of hydrophilic polymers, polyethylene glycol (PEG) with dextrin, or one polymer with one salt (for example PEG and phosphate salt) into water; the result is formation of two immiscible aqueous phases. Often, a sufficiently high concentration of a kosmotropic salt (solutes that contribute to the stability and structure of water–water interactions) in a polymer–water system can induce phase separation to yield a salt-rich (polymer-poor) phase at the bottom and a salt-poor (polymer-rich) phase at the top [9]. Both phases are certainly in equilibrium. Based on these principles, some ABP systems containing diverse hydrophilic polymers and different salts have been introduced [10–12]. Different ABP systems and their corresponding phase diagrams based on different types of ionic liquids and inorganic salts have been also reported which are known as ionic liquid-based aqueous biphasic (IL-based ABP) systems [13,14]. Some of these systems have been used for separation and determination of selected biological compounds [15–18]. In recent years, ionic liquids (ILs) have been increasingly used for separations [19] because of their unique specifications such as negligible volatility and non-flammability under ambient conditions, wide liquid temperature range, high thermal and chemical stability, high solvating capacity for organic, inorganic and organometallic compounds and their finely tunable physicochemical properties when different cations or anions are used [20,21].

In this work partitioning behaviors of three model azo dye: reactive red-120 (RR-120), 4-(2-pyridylazo)-resorcinol (PAR), and methyl orange (Table 1) in IL-based ABP systems have been studied.

Experimental

Instruments

The UV absorption spectra of the samples were recorded against the solvent blank using Ultrospec-4000 spectrophotometer

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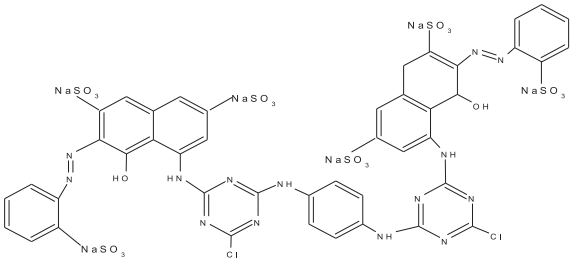
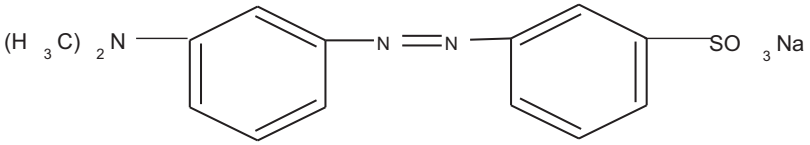
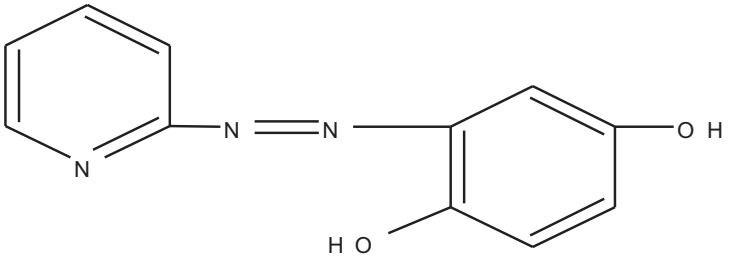
http://dx.doi.org/10.1016/j.jece.2013.12.005

Table 1
The chemical structures of the azo dyes used in this study.

Dye	Chemical structure
RR-120	
Methyl orange	
PAR	

(Pharmacia Biotech) operated in double-beam mode. The pH measurements were made with a Metrohm 780 pH meter using a combination glass electrode. The NMR spectra were recorded on a Brucker-Advanced DPX/250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer.

Reagents

Ammonium hexafluorophosphate was purchased from Fluka; 1-bromobutane, 1-methylimidazolium, potassium phosphate salts, methyl orange, and 4-(2-pyridylazo)-resorcinol (PAR) were purchased from Merck; reactive red-120 (RR-120) was from Sigma–Aldrich with the highest purity available and was used without further purification. Ionic liquids: 1-butyl-3-methylimidazolium bromide, [C_4mim][Br], and 1-butyl-3-methylimidazolium hexafluorophosphate, [C_4mim][PF_6], were synthesized as described in literature [22] and their chemical structures were verified by using NMR spectroscopy. Pure water which was distilled and deionized (0.5 μS cm^{-1}) was used throughout the work.

Preparation of phase diagram for IL/salt aqueous biphasic system

First of all, it should be noted that different phosphate species which has been used as different salt for adjusting pH are referred as "salt" in the text. The phase diagram was prepared using the cloud-point method [9]. Briefly explaining, a known amount of IL was weighed into a test tube and an appropriate volume of the salt (40.0 w/w% for both pH 9.70 and 11.60, and 35.4 w/w% for pH 7.02) was added drop-wise into the test tube while shaking. By appearance of turbidity, the total mass of the added salt was calculated. By knowing the weights of both IL and the salt, the weight percentages of both IL and salt were calculated. For instance, to obtain the first point on the binodal curve for IL/phosphate buffer (pH 9.7), 0.6 g of 68.1 w/w% IL solution was weighed into a test tube and 10 μL of 40.0 w/w% potassium phosphate solution was added drop-wise into the test tube while shaking. By appearance of turbidity, the total mass of the added potassium phosphate was 0.0124 g. Knowing the weights of both IL and the added potassium phosphate, the weight percentages of IL and salt in the resulted solution were calculated and were found to be 58.02 w/w% and 0.95 w/w%, respectively. This was the first point on the binodal curve (Fig. 1b). To specify the second point of the binodal curve, minimum amount of water, required to have a clear solution again, was obtained by drop-wise addition of water to the above mixture. This amount of water was considered later for calculating the weight percents of the IL and salt corresponding to the second point on the binodal curve. In the next step, potassium phosphate solution was added drop-wise to the clear solution mentioned above until it was turbid. The weight percentages of IL and salt in the resulted solution were calculated afterward to obtain the second point of the binodal curve, i.e. where the turbidity appeared again. The sequential addition of water and salt was repeated until sufficient data points for constructing the phase diagram were obtained. It should be mentioned that the points shown on a binodal curve refer to those weight percent by weights of IL and salt with which their corresponding solutions have turbid appearances. And, complete phase separation is observed for those percent by weights of IL and salt that are located in the region above the binodal curve. Ionic liquid and salt with percent by weights corresponding to the points below the binodal curve produce one-phase solutions.

Tie line lengths (TLLs) for different salt and IL compositions were calculated according to:

$$\mathrm{TLL} = \sqrt{(Y_T - Y_B)^2 + (X_T - X_B)^2}$$