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Measurement and correlation of aqueous biphasic systems composed of alcohol (1-propanol/2-propanol/*tert*-butanol) + $(NH_4)_2SO_4$ + H_2O at 298 K and a textile dye partition

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A B S T R A C T

Aqueous biphasic systems (ABS) are a promising method for separation and purification of several biomolecules. The use of organic compounds as phase former in ABS have been studied with the main finality to obtain systems with lower viscosity compared to conventional systems (composed of a polymer and a salt or two different salts). In this work, the effect of three different alcohols (1-propanol, 2-propanol, and tert-butanol) in ABS composed of alcohol + ammonium sulfate + water was evaluated. The phases diagrams were obtained, and the alcohol nature presented direct influence at the biphasic region. The experimental data were also correlated using an NRTL and UNIQUAC model, and the NRTL model presented a low mean deviation (RMSD < 0.33%). The partition of a textile dye, Remazol Brilliant Blue R, was evaluated and presented partition coefficients (K) higher than 26.4 and extraction efficiency up to 97.2%, indicating a potential application of these systems.

1. Introduction

The Aqueous Biphasic Systems (ABS) are a kind of liquid-liquid extraction. The phases of these systems are usually formed by aqueous solutions of two different polymers, two salts or a polymer and a salt [1,2]. The phases of the ABS coexisting in equilibrium and are nontoxic, nonflammable, and thus, is an environmentally accurate extraction medium [1,3], and in general, are successful applied at separation and purification of different biomolecules, such as proteins [4,5], phenolic compounds [6,7], as well as toxic metal ions [8,9] and other organic molecules [10]. Molecules like ionic liquids (ILs) [10,11], deep eutectic solvents (DES) [12–17] and organic compounds, e. g. alcohols and acetone [18–21], has been recently applied as phase formers to substitute the conventional systems.

The search for alternative processes for the extraction and purification that are economically viable and effective has been intensified in the last years [22], and in this context, these alternatives ABS emerged as a promising technique. Aqueous biphasic systems formed by saline solution and hydrophilic organic solvents, such as alcohols, have been investigated because of their advantages as easy recovery, which implies in low environmental impact, higher selectivity, lower viscosity, fast segregation of phases, and low cost when compared to a polymer-salt ABS, for example [19,21,23,24].

Dyes are organic molecules widely used in the textile, food, pharmaceutical and cosmetic industries [25]. The disposal of effluents with these dyes, even in low concentrations, has been a problem for the environment since they can be toxic and cause contamination besides damaging the aquatic flora and fauna. Moreover, the dyes disposal on nature inhibits the penetration of the sunlight into the receiving water bodies and impair the oxygenation processes in water (photosynthesis). Thus, the removal of these compounds is needful to maintain the normal regulation of the aquatic life [11,26–28].

Several methods like adsorption [27,29], advanced oxidation process [30] and liquid-liquid extraction [31] between others chemical e physical treatments [32] are being used to reduces the dye concentration in the wastewater. However, the most of these techniques present high operating costs and low efficiency. In this way, different methods of removal these compounds need to be

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studied, and the ABS can be an attractive alternative considering its low cost, and high separation efficiency [32,33].

Thus, this study aims to evaluate the influence of the alcohol nature at the liquid-liquid equilibrium (LLE) and a textile dye extraction in ABS composed of alcohol, ammonium sulfate, and water. For this, the alcohol 1-propanol, 2-propanol, and *tert*-butanol were evaluated. NRTL and UNIQUAC models were used to correlate the phase equilibrium data. The textile dye, Remazol Brilliant Blue R, was used to evaluate the ability of these alcohol-based systems to be applied to molecules extraction.

2. Materials and methods

2.1. Materials

The liquid-liquid equilibrium data were obtained using aqueous solutions of ammonium sulfate ($(NH_4)_2SO_4$ – 99.4 wt % pure) from Neon (São Paulo, Brazil) and the alcohols: 1-propanol (99.98 wt % pure) from Neon (São Paulo, Brazil), 2-propanol (99.5 wt % pure) from Carlo Erba Reagents (São Paulo, Brazil) and *tert*-butanol (99.0 wt % pure) from Dinâmica (São Paulo, Brazil). The ammonium sulfate was previously dried at 398 K, for at least 2 h and maintained at a desiccator with silica gel until the use. Osmolized water was used in all experiments. The textile dye Remazol Brilliant Blue R used to partition assays was provide by Acros Organics (New Jersey, USA). The characteristics of each alcohol used in this work are in Table 1.

2.2. Methods

2.2.1. Determination of phase diagrams

The binodal curves were obtained by cloud point method [35–37]. For this, an aqueous solution of $(NH_4)_2SO_4$ at 40.0 wt %, and other aqueous solution of each alcohol at 70.0 wt % were prepared. The $(NH_4)_2SO_4$ or alcohol solution was added dropwise to each other, under agitation, for the detection of the cloud point (biphasic region). In the following, water was dropwise added until the detection of a clear and limpid solution (monophasic region). This procedure was repeated until enough points were obtained in the binodal curve. The ternary system composition was determined by weight quantification (AUX320, Shimadzu) with an uncertainty of ±0.0001 g. All procedure was made at 298.15 K with an uncertainty of ±0.1 K, using a jacketed glass cell and water flow from a thermostatic water bath (Lab Companion RW – 1025G), and atmospheric pressure (around 91 kPa) [37].

2.2.2. Determination of the tie-lines

For each system under study, six points of overall composition in the biphasic regions were chosen. The components of the system were gravimetrically weight (±0.0001 g) in centrifuge tubes, vigorously stirred using a vortex mixer (Gomixer, MX-S) and allowed to reach equilibrium at 298.15 ± 0.1 K for approximately 24 h [38]. The top and bottom phases were carefully separated, using glass Pasteur pipettes, and the phases compositions were quantified by the gravimetric method proposed by Merchuk et al. [39]. Eq. (1) was fitted to the experimental binodal curves.

$$w_1 = a\exp\left(-bw_2^{0,5} - cw_2^{3}\right) \tag{1}$$

where w_1 and w_2 are the mass fraction of ammonium sulfate and alcohol respectively, and *a*, *b* and, *c* are constants obtained by the regression of the experimental binodal data.

To obtain the phase composition of each tie-line, the following mass balance (Eqs. (2)–(5)) were solved:

$$Y_T = \left(\frac{Y_M}{\alpha}\right) - \left(\frac{(1-\alpha)}{\alpha}\right).Y_B \tag{2}$$

$$Y_T = A.exp\left(B.X_T^{0,5} - C.X_T^{3}\right) \tag{3}$$

$$Y_B = A.\mathrm{exp}\left(B.X_B^{0,5} - C.X_B^{3}\right) \tag{4}$$

$$X_T = \left(\frac{X_M}{\alpha}\right) - \left(\frac{(1-\alpha)}{\alpha}\right).X_B \tag{5}$$

where, X and Y correspond to the salt and alcohol concentration and the superscripts *T* and *B* are the mass fraction of the top and bottom phases, respectively. *M* represents the global composition (overall mixture) of each tie-line. The parameter α is the ratio between the top and the overall composition mass.

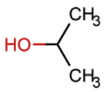
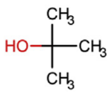
The slope of tie-line (STL) represents the ratio between the difference of alcohol mass fraction in the top and bottom phases and the difference of salt mass fraction in both phases (Eq. (6)). The tie-line length (TLL) was obtained by Eq. (7).

$$STL = \frac{Y_T - Y_B}{X_T - X_B} \tag{6}$$

$$TLL = \sqrt{(X_T - X_B)^2 + (Y_T - Y_B)^2} \tag{7}$$

The critical point of each ABS was determined by the extrapolating of the STL (Supporting Information) which were fitted using Eq. (8).

Table 1
Alcohol chemical structure, molecular weight (Mw) Logarithm of Octanol-Water Partition (log K_{OW}), boiling point (Bp) [34].

Alcohol	Chemical Structure	CAS number	M_w (g mol^{-1})	log K_{OW}	Bp (K)
1-propanol		71-23-8	60.1	0.36	370
2-propanol		67-63-0	60.1	0.25	356
tert-butanol		75-65-0	74.1	0.54	355