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Contriving to selectively separate drugs with a hydrophilic ionic liquid

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ABSTRACT

The potential of a commercially available imidazolium-based ionic liquid ($C_2C_1imC_1SO_4$) to selectively separate two model emerging contaminants, ethynylestradiol and clenbuterol, from aqueous solutions containing non-ionic surfactants (Triton X-100 and Triton X-102) was proved. After a first stage where the binodal curves and tie-lines of the systems were obtained, all the experimental data were suitably correlated with different empirical equations. Then, a 2-step sequential extraction of ethynylestradiol and clenbuterol was investigated by means of a factorial design. In this way, while ethynylestradiol completely partitions to the light layer no matter the operating conditions, clenbuterol extraction can be tuned by a cautious selection of the ionic liquid concentration. Then, while ionic liquid concentrations higher than 70% led to about 4% of clenbuterol extraction in the upper phase, the operation at concentration levels lower than 18% entailed up to 96% of removal. The confirmation of this behavior with synthetic urine proved the relevance of the present data for the implementation of a separation process allowing the selective removal of clenbuterol and ethynylestradiol from aqueous streams, which poses undoubted significant environmental and analytical interest.

1. Introduction

The design of wastewater treatment plants is being affected by numerous factors such as the presence of emerging contaminants like pharmaceuticals and personal care products (PPCPs). Current environmental engineering trends bet in the segregation of effluents in order to achieve maximum treatment efficiencies [1,2]. In this sense, the complexity of wastewater streams like those coming from hospitals, usually containing PPCPs, X-ray contrast media or antibiotics-resistant microorganisms, threatens the environment and public health. Thus, these streams should be detached from public sewage plants in order to avoid that they end up in aquatic biotopes and can negatively affect the live beings [3]. Among the plethora of possible contaminants, clenbuterol and ethynylestradiol were selected as model drugs with different degree of hydrophobicity (log P = 2.33 and 3.90, respectively [4]), being the first a β-adrenergic receptor agonist with a bronchodilator effect for the treatment of asthma and the second an endocrine disrupting compound (EDCs) used in contraception and treatment of some cancers [5,6].

Inasmuch as the concern caused by these contaminants is growing, the investigation of new strategies for their concentration and detection are welcome. The analysis of literature reveals that most options to remove them are destructive and involve the degradation of the emerging contaminants like advanced oxidation or biodegradation [7,8]. In relation to their detection, one of the alternatives that have been successfully proposed by our group for aromatic hydrocarbons or industrial dyes from aqueous streams are based on the addition of a segregation agent [9,10]. Traditionally, polymers and salts were reported to play this role in aqueous solutions of hydrophilic organic compounds, leading to two immiscible aqueous layers [11]. This phenomenon has been described as an entropically-driven competition between the molecules present in aqueous solution to be hydrated, thus salting-out the compound with less ability to establish hydrogen bonds with water [12].

In the last years, aqueous biphasic systems experienced a renaissance with the emergence of ionic liquids. These salts bear advantageous properties that have made them to be interesting for application in an array of sectors such as electrochemistry, biotechnology or catalysis [13,14]. The availability of a myriad of anions and cations makes it possible the design of thousands of combinations, which opens up countless possibilities for their application in this kind of liquid-liquid equilibria [14]. Thus, since 2003, when Rogers and coworkers reported the ability of these salts to act as salting out agents [15], the application of these systems for the extraction of different kind of molecules has bloomed, be it for enzymes [16,17], polymers [18] or contaminants [19].

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In our foregoing research works, the ability of imidazolium-based ionic liquids to trigger phase splitting in aqueous solutions of non-ionic surfactants was demonstrated, concluding that the mingling of non-ionic surfactants with short alkyl chain imidazolium-based ionic liquid maximizes the immiscibility area [20]. Therefore, in the present work we have bet in 1-ethyl-3-methyl imidazolium methylsulfate ($C_2C_1imC_1SO_4$), as it is the shorter ionic liquid commercialized in bulk quantities, to promote phase disengagement in aqueous solutions of Triton X-100 and Triton X-102 as examples of detergents with low hydrophilic lipophilic balance values (13.5 and 14.4, respectively [20]), that can often be present in hospital or domestic wastewater effluents.

The characterization of the aqueous biphasic systems was carried out by mapping both the solubility curves and the tie-line data at different temperatures in order to ensure the thermal stability of the immiscibility region at common room conditions (20, 30 and 40 °C). Different theoretical equations were applied in order to appropriately model the experimental data both for the immiscibility region and the extraction capacity. The most workable combination in terms of phase splitting was applied to the separation of clenbuterol and ethynylestradiol, individually and mixed. Response surface methodology was applied to optimize crucial extraction conditions (temperature, pH and feed concentration) allowing a maximum efficiency of contaminants separation, and the optimum was validated with a sample of artificial urine. These data will allow proposing a viable strategy to selectively separate both contaminants in real waste-water samples, which bears undoubted interest both as a concentration and removal tool at room conditions.

2. Experimental approach

2.1. Reagents

The non-ionic surfactants Triton X-100 and Triton X-102 were purchased from Panreac and Sigma-Aldrich, respectively. $C_2C_1imC_1SO_4$ (>98%) was supplied by IoLiTec and it was kept under reduced pressure for three days at 50 °C to ensure moisture removal prior to its use. Clenbuterol (>95%) and 17α-ethynylestradiol (>98%) were provided by Sigma-Aldrich. The structures of these compounds are shown in Fig. 1.

2.2. Characterization of binodal curves

The solubility data were obtained by means of the cloud point method [20], operating in a thermostated glass cell to maintain the temperature at 20, 30 and 40 °C (F200 ASL digital thermometer with an uncertainty of ±0.01 K). The experimental procedure consisted in mixing known amounts of the surfactant and ionic liquid in a dry chamber (Sartorius Cubis MSA balance 125P-100-DA, $\pm 10^{-5}$ g), covering the entire mass fraction range. Water was added dropwise to each mixture up to turbidity/transparency is detected, thus delimiting the immiscibility region. An Anton Paar DSA-48 digital vibrating tube densimeter ($\pm 2 \cdot 10^{-4}$ g cm^{-3}), and a Dr. Kernchen ABBEMAT WR refractometer ($\pm 4 \cdot 10^{-5}$), previously calibrated following the manufacture guidelines, were used to measure densities and refractive indices in order to define the experimental points.

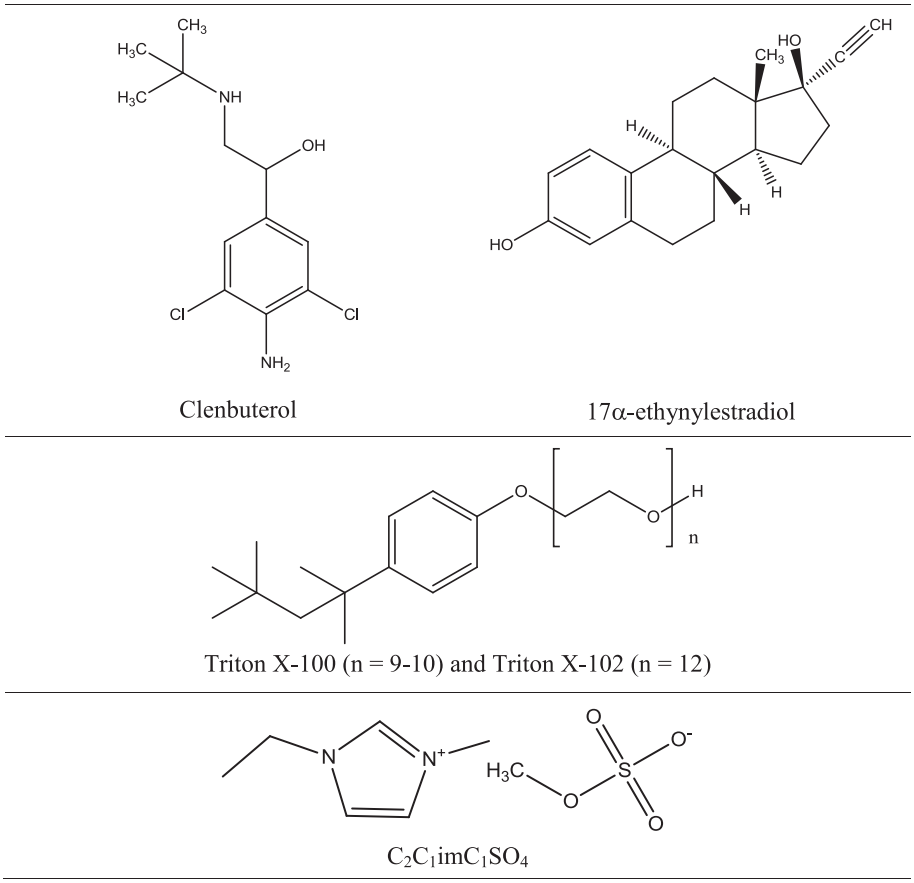

Fig. 1. Structures of the chemicals.