



A biocompatible stepping stone for the removal of emerging contaminants



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ABSTRACT

The presence of emerging contaminants like pharmaceuticals in the environment is prompting the search of new methods to concentrate and remove them from soils, sediments and effluents. A completely biocompatible aqueous biphasic system composed of Tween 20 or Tween 80 and the ionic liquid choline chloride has been designed for extracting non-steroidal anti-inflammatory drugs from aqueous streams. After an initial evaluation of the salting out potential of the selected ionic liquid at different temperatures, the extraction capacity of these systems to be applied for ibuprofen and diclofenac removal from aqueous streams was assessed. Very high levels of contaminant removal (higher than 90%) were reached for all the temperature and feed concentrations used. The suitability of the proposed biocompatible aqueous biphasic systems for the treatment of drugs-polluted effluents from surfactant-based soil washing operations is envisaged.

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1. Introduction

Emerging contaminants are currently gaining social awareness due to their potential deleterious effects in the environment. Nonetheless, there is still an absence of legislation ruling the presence of these pollutants [1], and only the Water Framework Directive (2000/60/EC) [2] presents vague guidelines related to the water policies in the EU. More specifically, research funds are being invested in different international joint initiatives in order to merge research efforts tackling efficient wastewater treatment processes to remove these compounds [3]. Among the emerging pollutants, non-steroidal anti-inflammatory drugs (NSAIDs) are the most utilized group of analgesic and anti-inflammatory drugs worldwide, due to their suitability to treat the pain triggered by common illnesses [4]. Thus, the last report by the Spanish Ministry of Health stresses that arylpropionic derivatives are by far the largest used pharmaceuticals (about 65.1% of the total drug consumption), being ibuprofen the one with higher intake rate (43.9%) and diclofenac, an arylacetic acid derivative, the second one [5].

This scenario has compelled to analyze the possible presence of these compounds in the environment, as they can be excreted without having been metabolized. In this sense, different authors have shed light on their presence in waste water treatment plants

(WWTPs), and have concluded that these compounds are not effectively removed after the treatment [6]. More specifically, ibuprofen and diclofenac concentration has been detected in the inlet streams of different WWTPs at concentration levels of 516 and 250 ng/L, recording less than 50% and 15% of removal in the outlet effluents, respectively [7]. In this sense, NSAIDs have also been detected in ground waters (in the order of ppb and ppt) and sediments (in the order of ppm and ppb) due to the great development of new analytical techniques [8,9]. It is clear that the continuous introduction of these pollutants may seriously affect drinking water supplies, ecosystems and human health, as reviewed by Sirés and Brillas [10].

Given the observed limitations of WWTPs, new treatment strategies have been investigated such as advanced oxidation processes or membrane technologies [11,12]. However, little information can be found related to the application of liquid–liquid extraction to the removal of these contaminants. Aqueous biphasic systems, a phase splitting typically caused by a salt in the presence of aqueous solutions of polymers, have emerged as a valuable separation strategy. Coutinho and coworkers have demonstrated the suitability of this method for the removal of NSAIDs and strogens [13,14] by using ionic liquids.

In the last years, the outbreak of these neoteric solvents, with appealing properties such as their negligible volatility and tunability [15], has boosted the implementation of ‘all-purpose’ aqueous biphasic systems in combination with salts and polymers [16,17].

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Recently, we have demonstrated the capacity of imidazolium-based ionic liquids to trigger phase segregation in aqueous solutions of non-ionic surfactants with a number of advantages like their low interfacial tension, rapid phase disengagement, low cost and bulk availability of the surfactants [18]. In this work, we concluded that more hydrophilic ionic liquids were more prone to trigger liquid–liquid demixing, so the search of more hydrophilic families could open up new opportunities to be applied in polluted effluents obtained after surfactant-based soil washing processes, where this kind of surface active compounds are usually employed as contaminant solubilizers.

On the basis of the abovementioned, more hydrophilic and generally recognized biocompatible ionic liquids like choline chloride ($N_{11120H}Cl$) [19,20] have been proposed to trigger phase segregation in aqueous solutions of non-ionic surfactants. In this case, Tween 20 and Tween 80 have been chosen since they are considered as GRAS by the US FDA and they are classified as safe food additives in many countries (E432 and E433, respectively) [21]. The immiscibility windows of the systems were firstly investigated at different temperatures, by characterizing the binodal curves and tie line data. The results were discussed on the basis of the surfactant and ionic liquid hydrophobicity and operation temperature. The extractive performance for two model NSAIDs, ibuprofen and diclofenac, was determined in order to suggest a viable strategy for removing them from aqueous polluted effluents.

2. Experimental

2.1. Chemicals

The non-ionic surfactants polyethoxylated sorbitan monolaurate (Tween 20) (>97%) and monooleate (Tween 80) (>99%), the NSAIDs ibuprofen (>98%) and diclofenac (>98.5%) were acquired from Sigma–Aldrich and employed as received without further purification. Choline chloride (>99%) was also purchased from Sigma–Aldrich and submitted to vacuum for several days at 70 °C to ensure moisture removal prior to its use. The chemical structures of all these compounds are shown in Fig. 1.

3. Experimental procedure

3.1. Binodal curves determination

The binodal curves were ascertained in a magnetically stirred jacketed glass cell (Fig. S1) at temperatures ranging from 298.15 to 333.15 K. The temperature was controlled with a F200 ASL digital thermometer with an uncertainty of ± 0.01 K. The cloud point method was the experimental technique for binodal data determination [18]. Briefly, binary mixtures with known compositions of ionic liquid and surfactant were prepared in a dry chamber, and drop-wise additions of water were carried out until the disappearance of solids, thus characterizing the S + 2L region. Afterwards, water was added up to turbidity vanishing in order to fully map the binodal curves. The concentration of these points was determined by weighting in an analytical Sartorius Cubis MSA balance (125P-100-DA, $\pm 10^{-5}$ g). The binodal curve was also characterized by measuring densities and refractive indices at different temperatures, using an Anton Paar DSA-48 digital vibrating tube densimeter ($\pm 2 \cdot 10^{-4}$ g cm $^{-3}$), and a Dr. Kernchen ABBEMAT WR refractometer ($\pm 4 \cdot 10^{-5}$), both calibrated in accordance with the manufacture instructions.

Experimental tie-lines were calculated by preparing a ternary mixture from the biphasic region, left under stirring for 1 h, and afterwards, an idle period of 48 h was left in order to reach the equilibrium. The two segregated layers were split and their

composition was quantified by measuring densities and refractive indices (estimated uncertainty of concentration $\pm 0.02\%$).

3.2. Ibuprofen and diclofenac extraction and quantification

For the study of NSAIDs partition, different aqueous solutions of Tween 80 containing ibuprofen and diclofenac at concentrations of 35 mg/L were introduced in glass ampoules, since it falls in the range usually detected in environmental samples [8,9]. Choline chloride was added until the desired composition within the biphasic region was reached. The mixture was vigorously stirred and left to settle for at least 48 h at 298.15 K and 333.15 K. The layers were carefully separated in order to quantify ibuprofen and diclofenac by HPLC measurements. HPLC-DAD (Agilent 1260 infinity) is equipped with a Kinetex Biphenyl column (4.6 \times 150 mm; internal diameter 5 μ m). 10 μ L of sample were eluted in gradient mode for 15 min at a flow rate of 1 mL/min, using a mixture water/ethanol at the following ratios: 65:30 for 10 min and 15:80 for the separation. Retention times for ibuprofen and diclofenac were 10.149 and 10.713 min, respectively. The calibrations were carried out with stock solutions prepared in methanol at a concentration of 3.5 mg/mL, and were appropriately diluted in Milli-Q water (0.1–10 mg/L).

4. Results and discussion

4.1. Choline chloride as segregation agent

First of all, the segregation potential of the ionic liquid $N_{11120H}Cl$ in aqueous solutions of the non-ionic surfactants Tween 20 and Tween 80 was explored at several temperatures (298.15, 313.15, 323.15 and 333.15 K). The experimental data are compiled in Tables S1 and S2 in the SI, and they can be visualized in Figs. 2 and 3. The analysis of the influence of temperature on the binodal curves allows concluding that liquid–liquid demixing is eased at higher temperatures for both surfactants. This is attributed to the lower ability of the non-ionic surfactant to establish hydrogen bonds with water at higher temperatures, which furthers the salting out effect provided by the $N_{11120H}Cl$ ionic liquid. This behavior is coincident with previous results for other systems containing non-ionic surfactants like Triton X-100 and Triton X-102 with the ionic liquid $C_2C_1imC_2SO_4$ [18].

An exhaustive literature analysis on the effect of temperature on the immiscibility window has been carried out, and the main results are summarized in Table S5. In order to better classify the information, the table has been divided into the four main types of aqueous biphasic systems found, namely, those based in polymers, ionic liquids, surfactants and organic solvents. As can be noticed, two main behaviors can be inferred, depending on the nature of the compounds competing for the water molecules: a proportional relationship between the area of the immiscibility window and temperature is observed when organic solvents, polymers or surfactants are salted out by inorganic or organic salts, [22,23]. Contrarily to this, the systems composed of ionic liquids and inorganic or organic salts display smaller biphasic regions at higher temperatures [24,25]. The reason for these trends lies in the weakening of the hydrogen bonds between the water molecules and the hydrophilic moiety of polymers, non-ionic surfactants and organic solvents at elevated temperatures, which leads to an increased hydrophobicity of these compounds. On the contrary, the completely different properties of ionic liquids involve greater interplays with water at higher temperatures. Therefore, when non-ionic surfactant and ionic liquids are put together, a synergic effect is observed at elevated temperatures, since a greater ability for water solvation of the ionic liquid is summed

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