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Chapter 20

THE CAPABILITY OF BINARY SYSTEM CONTAINING WATER-SOLUBLE IONIC LIQUIDS FOR TYPICAL ENDOCRINE DISRUPTOR CHEMICALS EXTRACTION FROM SEDIMENTS

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ABSTRACT

A binary system containing water and different water-soluble ionic liquids (WSILs) were considered for extraction of three typical endocrine disruptor chemicals (EDCs), 17β-estradiol (17β-E2), bisphenol A (BPA), and nonylphenol (NP), from three model sediments. Imidazolium and pyridinium based ionic liquids with different anions (tetrafluoroborate or chloride) were selected as representative WSILs to assess the extraction of EDCs from different sediments by the binary system containing water and WSILs at different molecular ratio. Comparing with extration of EDCs by water, the presence of 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]PF_4) or N-butyl-3-methyl pyridinium tetrafluoroborate ([bmpy]PF_4) in the binary system at low molecular ratio could decrease the extraction of EDCs. However, at high molecular ratios, WSILs in binary system significantly increase the extraction of EDCs, especially for those from sediments with high organic matter content. At a molecular ratio of 5: 5 (WSIL: water), extraction by the binary system containing [bmim]PF_4 was more efficient than that by [bmpy]PF_4. However, at a molecular ratio of 1: 9, contrary results were gained. Cation-π, π-π, and hydrogen bond interaction of phenolic hydroxyl and "-N=C(H)-N-" were proposed to be the major interactions between WSILs and EDC molecules, while these interactions were greatly inhibited when water molecule presented in the binary system at high ratio. And also the adsorption of WSILs on sediments could affect the extraction efficiency when they presented at low ratio. At the same molecular ratio, the presence of [bmim]PF_4 and 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) resulted in

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similar extraction efficiencies, which might suggest that anions of WSILs play minor role for extraction of EDCs in this study.

Keywords: water-soluble ionic liquid, sediments, extraction, 17β-estradiol, bisphenol A, nonylphenol

1. INTRODUCTION

Endocrine disruptor chemicals (EDCs), also called environmental hormone, have already become a threat to the global eco-system. As the typical EDCs, 17β-estradiol (17β-E2), bisphenol A (BPA), and nonylphenol (NP), are widely exist in environment, including soils and sediments.

Organic solvents have been used to extract organic contaminants from soil or sediment. Most of these organic solvents are volatile organic compounds (VOCs), which often exhibit high toxicity. Some techniques including soxhlet extraction, shaking extraction, microwave or ultrasound-assisted extraction, supercritical fluid extraction, and so on, use organic solvents to extract different organic contaminants from soils or sediments. Ionic liquids (ILs) are composed of organic cations and organic or inorganic anions, which remain liquid at the temperature below 100 ^{o}C (Fan et al., 2008). Recently, ILs were used as the alternatives of the traditional volatile organic solvents, to extract chemicals from water or solid phase (Pino et al., 2008). For example, 1-butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF_6) and 1-butyl-3-methyl imidazoliumchloride ([bmim]Cl) were used as the extractants, to assess the extraction of several organic contaminants, including DDT, dieldrin, hexachlorobenzene, and pentachlorophenol, from two different soils (Khodadoust et al., 2006).

In this study, two water-soluble ILs, 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim]PF_4) or N-butyl-3-methyl pyridinium tetrafluoroborate ([bmpy]PF_4), were selected as the representative imidazolium-based and pyridinium-based IL respectively, to compare the extraction of three typical EDCs from three different sediments by different binary systems containing water-soluble ILs and water. After that, the difference of extraction by the binary systems containing ILs with different anions at certain ratio (i.e. [bmim]PF_4 and [bmim]Cl) were also studied.

2. MATERIALS AND METHODS

2.1 Materials

[bmim]PF_4 was synthesized as described elsewhere (Zhao et al., 2006). Briefly, [bmim]Cl was prepared by adding equal amount (0.3 mol) of 1-methylimidazole and 1-chlorobutane to a round-bottomed flask fitted with a reflux condenser and reacting for 48 h at 70 ^oC until a yellow viscous liquid is formatted. The viscous liquid was then cooled and washed with ethyl acetate and dried under vacuum at 80 ^oC to remove the solvent. [bmim][PF_4] was prepared by slowly adding sodium tetrafluoroborate (0.1 mol) into [bmim]Cl (0.1 mol) in acetone. After stirring for 12 h, and dried under vacuum at 80 ^oC. [bmpy]PF_4 were provided by the Center for Green Chemistry and Catalysis, LICP, CAS.

Nonylphenol (NP, technical grade) was purchased from Tokyo Chemical Synthesis Ind. Co. Ltd, Japan. Standards of BPA and 17β-E2 were purchased from J&K Scientific Ltd. HPLC-grade methanol, acetone, dichloromethane, and acetonitrile were purchased from Biaoshiqi Company of Tianjin, China.

Three sediments, namely Liaohe River sediment, Yuqiao reservoir sediment, and Yellow River sediment, were used as the simulated sediments used in this study, with their properties shown in Table 1.

Table 1. Properties of sediments

Sediments	OC-%	Sand-%	Silt-%	Clay-%	pH
Liaohe River sediment	5.89	36.7	55.9	7.4	6.75
Yuqiao reservoir sediment	2.56	38.3	50.4	11.3	7.13
Yellow River sediment	0.27	82.62	9.80	7.58	7.03

2.2 Extraction experiments

Before extraction experiments, batch sorption experiments (48 h) were conducted to gain the polluted sediments by three EDCs, respectively. By accommodating the amount of analytes added to the water-sediments system, a pre-sorbed concentration of about 1 mg/kg was gained for all the three EDCs in three sediments. After the sorption experiments, the system was centrifuged at 3000 r/min for 30 min and the supernatant was replaced with the extracts containing [bmim]PF_4 or [bmpy]PF_4 and water at different molecular ratio from 1:9 to 5:5. [bmim]PF_4 was also compared with [bmim]Cl in the IL/water binary system at a ratio of 5:5, and the extraction percent of EDCs from the Liaohe River sediment and the Yellow River sediment were examined.

2.3 Analysis

Waters 1525 high-performance liquid chromatograph, with Waters 2475 fluorescence detector and 2487 UV detector (Waters Company, USA) was utilized for chemical analysis. Acetonitrile and water was used as mobile phase. Isocratic elution was carried out with a flow rate of 0.8 mL/min. For analysis of BPA and NP, excitation and emission wavelengths of the fluorescence detector were 233 and 302 nm, respectively. For analysis of 17β-E2, 205 nm was used by the UV detector.

3. RESULTS AND DISCUSSION

3.1 Effect of IL/water ratio

The extraction percent of BPA by pure water was 37.7 % (from the Yellow River sediment), 49.8 % (from the Yuqiao reservoir sediment), and 73.0 % (from the Liaohe River sediment), respectively. While the extraction percent of 17β-E2 was 9.3 % (from the Yellow River sediment), 26.2 % (from the Yuqiao reservoir sediment), and 55.0 % (from the Liaohe River sediment), respectively. For NP, the concentration in the pure water extractant was lower than its limit of detection. The exist of IL at a molecular ratio of 1:9 (IL:water) can further inhibit the extraction of BPA and 17β-E2 from all three sediments (Figure 1). However, the extraction percent increased with the increase of the IL ratio in the binary solution, when the ratio was larger than 2:8. At the ratio of 5:5, an extraction percent of ~80 % could occur for all three EDCs from three sediments by the binary system (Figure 1).

3.2 Effect of sediments property

As a whole, for sediments with high OC content, EDCs were difficult to be extracted, especially for NP (with highest K_{ow}). This suggests that presence of organic carbon components are adverse to the extraction of these EDCs by the IL-water binary system However, for chemicals in the Yellow River sediments, whose OC content was very low, the extraction percent of 17β-E2 and NP was lower than that in the other two sediments. This might be due to the possible stronger bond interaction between the analytes and the mineral surface of the Yellow River sediments.

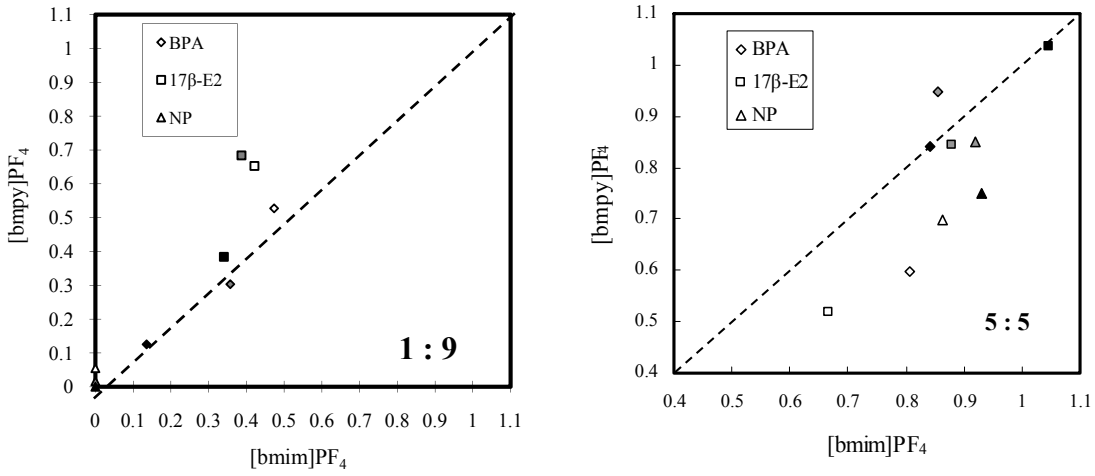

Figure 1. Comparison of extration percent with binary system containing $[bmim]PF_4$ or $[bmpy]PF_4$ and water at the ratio of 1:9 and 5:5 from three different sediments. Black points: Liaohe River sediements; Gray points: Yuqiao reservoir sediment; White points: Yellow River sediment.

3.3 Comparison of imidazolium-based and pyridinium-based IL

At the molecular ratio (IL:water) of 5:5 and 1:9, different extraction capability exhibited for binary system containing $[bmim]PF_4$ or $[bmpy]PF_4$ and water. At the ratio of 5:5, existence of imidazolium-based IL seems to be more propitious to the extraction of three EDCs, especially from the Yellow River sediment. This might because that, (i) the two "N" in the imidazolium structure enhance the probability of the happening of "cation-π" interaction; (ii) the "H" in the "-N=C(H)-N-" structure induces more stronger H bond interaction with the analytes; (iii) the five-membered ring of the imidazolium ring holds larger electron cloud density compared with that of six-membered pyridinium ring. However, for the binary system at the ratio of 1:9, contrary phenomenon was observed. It seems that the existence of [bmpy] based IL was more propitious to the extraction of the EDCs. This was attributed to the difference of sorption of two different IL. At the low ratio in solution, sorbed IL could enhance the sorption of EDCs. The sorption of $[bmim]PF_4$ was greater than that of $[bmpy]PF_4$. Therefore, the extraction was somewhat inhibited.

3.4 Comparison of ILs with different anions

At the same molecular ratio of 5:5, the presence of [bmim]PF_4 and 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) resulted in similar extraction efficiencies from the sediments with low or high OC content (Figure 2), which might suggest that anions of WSILs play minor role for extraction of EDCs in this study.

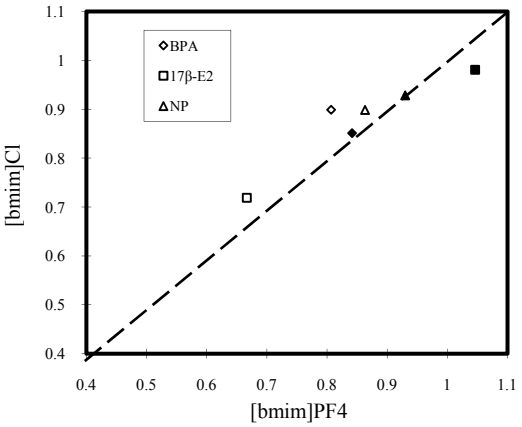

Figure 2. Comparison of extration percent with binary system containing [bmim]PF_4 or [bmim]Cl and water at the ratio of 1:9 and 5:5 from two different sediments. Black points: Liaohe River sediments; White points: Yellow River sediment.

4. ACKNOWLEDGMENTS

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