



Counteranion-dependent sorption of imidazolium- and benzimidazolium-based ionic liquids by soot

Yue Li ^{a, b}, Li Wei ^{a, b}, Wen Zhang ^{a, b}, Zhiqiang Dong ^{a, b}, Yuping Qiu ^{a, b, *}

^a State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China

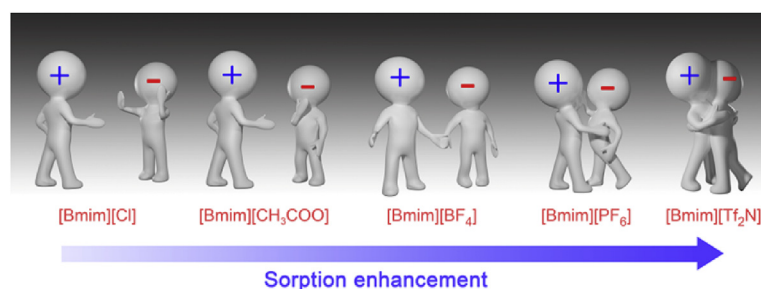
^b Shanghai Institute of Pollution Control and Ecological Security, Shanghai, 200092, China



HIGHLIGHTS

- The contribution of counteranions on IL sorption depends on the K_{IP} and K_{OW} of ILs.
- Good linear relationships between $\log K_{OW}$ and K_d and between $\log K_{IP}$ and K_d .
- $[Tf_2N]^-$ and $[PF_6]^-$ exhibit tighter association with IL cations in aqueous solution.
- The stronger IL ion-pair formed in water, the higher sorption of ILs by soot.
- The addition of weakly coordinating anions contributes to the enhanced ILs uptake.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 December 2017

Received in revised form

7 March 2018

Accepted 13 March 2018

Available online 14 March 2018

Handling Editor: Keith Maruya

Keywords:

Ionic liquids

Counteranion

Sorption

Ion-pair formation constant

ABSTRACT

Sorption of ionic liquids (ILs) to soil and porous materials as affected by anions was observed, but scarce effort has been focused on addressing the role of counteranions in sorption and the associated underlying mechanisms. In this work, two series of 1-butyl-3-methylimidazolium- (Bmim-) and *N*-butyl, methyl-benzimidazolium-based (Bmbim-based) ILs coupled with different counteranions were prepared to investigate the effect of anions on IL sorption by soot. The octanol–water partition coefficient (K_{OW}) and the ion-pair formation constant at infinite dilution in water (K_{IP}) of ILs were independently measured to explore the contribution of counteranion-dependent hydrophobicity and ion-pair. A wide range of sorption coefficients (K_d) of ILs were achieved with values varying from 59.8 to 344.3 L·kg⁻¹ for Bmbim-based ILs and from 253.4 to 489.7 L·kg⁻¹ for Bmim-based ILs. Compared with other anions, bis(trifluoromethanesulphonyl)imide ($[Tf_2N]^-$) and hexafluorophosphate ($[PF_6]^-$) exhibit tighter association with IL cations in aqueous solution due to their larger K_{OW} and higher K_{IP} . Positive linear relationships between $\log K_{IP}$ and K_d and between $\log K_{OW}$ and K_d evidenced that the counteranion-dependent sorption of ILs relies on the association strengths of IL cations and counteranions, which further influence the hydrophobicity/hydrophilicity of ion pairs. Compared with that of strongly coordinating anions (such as $[CH_3SO_3]^-$, $[CF_3COO]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, and $[Cl]^-$), the addition of weakly coordinating anions (such as $[Tf_2N]^-$ and $[PF_6]^-$) in solution contributes to markedly large sorption

* Corresponding author. State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China.

E-mail address: ypqiu@tongji.edu.cn (Y. Qiu).

enhancement of ILs. Consequently, the contribution of different counteranions on IL sorption is essentially based on the formation of ion pair with different K_{IP} and K_{ow} in aqueous solution.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Ionic liquids (ILs) are a novel class of low-melting salts composed exclusively of a bulky asymmetric cations and a variety of anions (Ranke et al., 2004; Wojstowski et al., 2018). Given their unique physicochemical properties, such as negligible volatility and thermochemical stability (Earle and Seddon, 2009; Sun and Armstrong, 2010; Chen et al., 2018), ILs have been widely used as green alternatives to conventional organic solvents for organic synthesis, extraction, and separation (Wasserscheid and Keim, 2000; Earle and Seddon, 2009). Although no IL-derived pollution incidents have been reported, their ecological impact on the aquatic and terrestrial environments remains an increasing concern (Bubalo et al., 2014; Amde et al., 2015).

The sorption of ILs by soils has been widely investigated to explore their potential fates in the environment. The cationic moieties of ILs, such as imidazolium and pyridinium cations, perform a key role in the IL adsorption process (Stepnowski et al., 2007; Pham et al., 2010). Electrostatic interaction is assumed to contribute dominantly to the total adsorption due to the presence of a positive charge in the headgroup of ILs (Stepnowski, 2005). In addition, the hydrophobic interactions between IL cations and soil organic matter are proposed as important mechanisms because the sorption is apparently enhanced with the increase in alkyl chain length in IL cations (Studzińska et al., 2008; Matzke et al., 2009; Mroziak et al., 2009).

By contrast, the structural effect of IL counteranions in the sorption process has not been fully understood. Studzińska et al. (2008) found that the chloride anion does not contribute to the sorption of [C₂mim]Cl, [C₄mim]Cl, and [C₆mim]Cl by soils as evidenced by the unchanged concentration of [Cl][−] in both initial and equilibrium solutions. However, significant difference affected by counteranions was observed between the sorption of [C₄mim][BF₄] and [C₄mim][Tf₂N] on a German standard soil (Matzke et al., 2009). The effect of anionic moieties may be related to their hydrophilic/hydrophobic nature (Huddleston et al., 2001). For example, hydrophilic anions (such as [Cl][−]) are miscible in any proportion with water, whereas ILs containing hydrophobic anions (such as [Tf₂N][−]) are virtually immiscible. Accordingly, the sorption of ILs on activated carbon follows the approximate sequence of hydrophobicity of the IL anions (Tf₂N[−] > PF₆[−] > Otf[−] > BF₄[−] > TFA[−] > Cl[−]) (Palomar et al., 2009). Furthermore, Shi et al. (2016) revealed that the sorption coefficient (K_d) of ILs on straw-based biochar is in the order of [C₂mim][Tf₂N] > [C₂mim][PF₆] > [C₂mim][BF₄], which is in accordance with the sequence of the logarithms of the *n*-octanol–water partition coefficient (K_{ow}) (Sang and Sun, 2005). However, further investigation should be conducted to explore the quantitative relationship between IL sorption and IL K_{ow} as affected by counteranions.

The ultimate causes behind the observed hydrophobicity of ILs may be related with the association/dissociation properties of ILs. In aqueous solution, ILs generally consist of hydrated cations, hydrated anions, and IL ion pairs (associated IL molecules) (Johnson, 2007). Given an IL cation type, ion-pair formation can be considered as a competition with anion solvation and is dependent on anion types. For example, weakly coordinating anions, such as [Tf₂N][−] and [PF₆][−] exhibited stronger water-mediated ion-pair

associations than strongly coordinating anions ([Cl][−] or [Br][−]) (Katsuta et al., 2007). To estimate the cation–anion binding capability of ILs, Katsuta et al. (2007) developed a method to quantitatively determine the ion-pair formation constants (K_{IP}°) of several imidazolium-based ILs at infinite dilution in water by capillary electrophoresis. K_{IP}° shows a clear trend with the order [C₄mim][Tf₂N] > [C₄mim][PF₆] > [C₄mim][BF₄], is in accordance with the sequence of their log K_{ow} .

In this work, the effect of anionic moieties on the sorption of two series of ILs based on imidazolium and benzimidazolium was systematically investigated. Soot was used in this study because of its larger sorption of ILs compared with that of other natural adsorbents. The K_{IP}° and K_{ow} values of 14 ILs were determined to compare their ion-pair association and hydrophobicity as influenced by IL counteranions. The relationships between K_{IP}° and K_d and between K_{ow} and K_d were quantitatively evaluated. Furthermore, anionic additive experiment was conducted to explore the anion-induced sorption enhancement of ILs. This work aims to fully understand the counteranion-dependent sorption change of ILs on environmental media.

2. Materials and methods

2.1. Materials

Soot was obtained from the Haber process for manufacturing ammonia from nitrogen and hydrogen in Jinlin Chemical Fertilizer Plant (Jinlin, China). After drying at 80 °C for 24 h, soot was fully ground and sieved by using a sifter (100-mesh). Eight kinds of 1-butyl-3-methylimidazolium-based (Bmim-based) ILs and six kinds of *N*-butyl, methyl-benzimidazolium-based (Bmbim-based) ILs with different anions (purities ≥ 98%) were purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China) (Table 1). All chemicals were used without additional purification. 1-Octanol (purity ≥ 99%), anhydrous sodium acetate (CH₃COONa, purity ≥ 99%), and sodium fluoborate (NaBF₄, purity ≥ 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetonitrile (purity ≥ 99.9%), lithium bis(trifluoromethanesulfonyl)imide (LiTf₂N, purity ≥ 98%), sodium methylsulfonate (CH₃SO₃Na, purity ≥ 95%), and sodium trifluoromethanesulfonate (CF₃SO₃Na, purity ≥ 98%) were purchased from Ailei Chemical Reagent Co., Ltd. (Shanghai, China).

Sodium trifluoroacetate (CF₃COONa, purity ≥ 97%) and potassium hexafluorophosphate (KPF₆, purity ≥ 99.98%) were purchased from Aladdin Industrial, Inc. (Shanghai, China).

2.2. Soot properties

The surface areas (S_{BET}) of soot were obtained from the N₂ adsorption (77 K) isotherms by applying the Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP-2020 M (Norcross, GA, USA). The structure and morphology of soot were examined through scanning electron microscopy (SEM) (FEI Nova Nano SEM 450, USA).

Download English Version:

<https://daneshyari.com/en/article/8851344>

Download Persian Version:

<https://daneshyari.com/article/8851344>

[Daneshyari.com](https://daneshyari.com)