



Transport of imidazolium-based ionic liquids with different anion/cation species in sand/soil columns



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ABSTRACT

Ionic liquids (ILs) have been widely used as environmentally friendly solvents to replace volatile organic solvents in the chemistry industries. They have a high water solubility and potential risk to organisms in the soil–water environment. At present, most studies focused on the batch sorption of ILs in soil and neglected the investigation of IL transports in soil, which results in a lack of understanding of the structure-dependent mobility of ILs in the environment. Laboratory-scale sand/soil column experiments were performed to study the transport of imidazolium-based ILs, such as [C₄mim][OTF], [C₄mim][TOS], [C₄mim][MeSO₃], [C₄mim][BF₄], [C₂mim][BF₄], and [C₆mim][BF₄] including different counteranions and alkyl chain lengths of IL cations. Batch experiments were also carried out to compare the difference of sorption distribution coefficient (K_d) between the batch and column experiments. A one-dimensional convective–dispersive model using CXTFIT code was created based on the measured breakthrough curves (BTCs) to estimate the column transport parameters. For the anion, [BF₄⁻], the K_d of ILs in both batch and column experiments increased with increasing alkyl chain lengths of the IL cation. In batch tests, counteranions showed no influence on the K_d of [C₄mim][OTF], [C₄mim][TOS], [C₄mim][MeSO₃], [C₄mim][BF₄], [C₂mim][BF₄], and [C₆mim][BF₄]. However, in column tests, the BTCs of 1-butyl-3-methylimidazolium-based ILs were anion dependent as evidenced by the change of retardation factor (R) for different counteranions. Furthermore, the effects of transport distance (11 cm, 15 cm, 19 cm, and 24 cm) on the mobility of ILs were estimated. The longer distances signified an increase in the contact time and more binding sites for ILs and therefore, the smoother shapes of BTCs in column experiments.

1. Introduction

Ionic liquids (ILs) are low-melting or room-temperature molten salts composed exclusively of cations and anions. Due to their important physicochemical properties, such as low vapor pressure, high thermal capacity, non-flammability and high solubility (Hajipoura and Rafiee, 2009; Hizaddin et al., 2015), ILs were regarded as “green” alternatives to traditional volatile organic solvents (Won et al., 2013; Pham et al., 2010). Specially, the imidazolium-based ILs, consisted of 1-alkyl-3-methylimidazolium-substituted cations and the respective anions, have widely applied ILs in the field of organic synthesis (Yuan et al., 2015), biocatalysis (Vitz et al., 2009) and extraction (Ferreira et al., 2015). Most of them show weak biodegradability and highly water-soluble, which would result in quick dispersion into the environment through liquid effluents and then into soils and sediments (Coleman and Gathergood, 2010; Amde et al., 2015). In recent years, an increasing number of studies show potential environmental fates of imidazolium-based ILs to human cells and aquatic organisms (Gouveia et al., 2014;

Biczak et al., 2014). Their toxicities to various levels of biological organization strongly depend on the structure and properties of the anion/cation species of imidazolium-based ILs (Zhao et al., 2014).

To explore the fate and behavior of imidazolium-based ILs in the environment, batch sorption experiments were conducted in various soil-IL systems (Jungnickel et al., 2011; Reinert et al., 2012). It demonstrated that the cation species of ILs play a primary role in IL sorption in soils (Piotr et al., 2007; Wu et al., 2014). Generally, imidazolium-based cation has a positive charge delocalized aromatic structure with different alkyl chains. Hence, the sorption mechanism between imidazolium-based ILs and soil, which is a combination of electrostatic interaction and hydrophobic interaction (Pham et al., 2010), is complicated (Jungnickel et al., 2011; Mrozik et al., 2012). In contrast, the anion species of ILs showed negligible influence in IL sorption in soils (Asadabadi and Saïen, 2016). However, in other batch sorption systems (e.g., biochar or activated carbon), different counteranions of ILs displayed their sorption differences (Shi et al., 2016; Wang et al., 2015). In soil sorption systems, the contribution of counteranions

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of ILs is overshadowed by the cation species of ILs. To understand the impact of IL anion species, the transport of ILs with different cations and anions in the soil column should be further investigated, thereby accurately reflecting the mobility of ILs in the environment and the dynamic affinity between ILs and soils.

Both batch and column methods are conventionally applied to determine some critical parameters for evaluating the sorption of contaminants in soils (Ahmad et al., 2013). Batch experiment is the simplest experimental setup, that has been widely applied to study equilibrium sorption isotherms and to describe the static sorption capability of soil (Bermudez-Couso et al., 2012). However, this type of experiment failed to imitate the natural hydrodynamic condition between soil and solute solution due to the high liquid-solid ratio and irregular oscillations (Florido et al., 2010; Zakari et al., 2016). Column experiment describes the fundamental transport parameters, which can predict the contaminant plume in natural porous media. This method has been successfully used in studying the transport of various contaminants (e.g., pesticides, heavy metals, and antibiotics) in the soil systems (Dusek et al., 2015; Martínez-Lladó et al., 2011; Wehrhan et al., 2007). Compared with these chemicals, ILs show a weak affinity to soil particles and a negligible degradability in the environment (Jungnickel et al., 2011; Mrozk et al., 2012; Oliveira et al., 2016), thereby resulting in the high mobility of ILs in natural soil-groundwater systems. Studzinska et al. (2009) have preliminarily studied the ILs transport process in soil utilizing the column leaching experiments. However, the influence of IL anions was not concerned and the column transport parameters were not documented.

To estimate the transport parameters of ILs in the soil column, the classical one-dimensional convective-dispersive solute transport model was investigated in this work. The mathematical transport parameters are inverted using chemical non-equilibrium model with CXTFIT, which was widely used to estimate the parameter of solute transport in soils (Genuchten, 1995; Qi et al., 2012). This study aims to systematically evaluate the effects of anion/cation species on ILs sorption in soils via batch and column experiments and to quantitatively describe the transport of ILs in the soil column using a one-dimensional model.

2. Materials and methods

2.1. Soils and ILs

Surface soil samples (0–15 cm depth) were collected from agricultural sites in Tsitsihar, a city in the north of China. After air-dried and sieved through a 1-mm mesh screen, the textured soil was prepared by mixing sand (soil:sand = 1:8) to obtain the desirable infiltration rates in the soil column experiments. The measurement of the total organic carbon (TOC) of samples was carried out by using a TC/TN analyzer (TOC-VCPN, Shimadzu, Japan). The cation exchange capacity (CEC) was determined using the compulsive exchange method (Gillman and Sumpter, 1986). The selected properties of textured soil used in this experiment are shown in Table S1.

Six kinds of ILs with different alkyl-chain cations and anions (purity > 98%) including [C₄mim][OTF] (1-butyl-3-methylimidazolium trifluoromethanesulfonate), [C₄mim][TOS] (1-butyl-3-methylimidazolium tosylate), [C₄mim][MeSO₃] (1-butyl-3-methylimidazolium methylsulfonate), [C₄mim][BF₄] (1-butyl-3-methylimidazolium tetrafluoroborate), [C₂mim][BF₄] (1-ethyl-3-methylimidazolium tetrafluoroborate), and [C₆mim][BF₄] (1-hexyl-3-methylimidazolium tetrafluoroborate) were purchased from Shanghai Chengjie Chemical Co. Ltd (Shanghai, China). The structures of ILs drawn by ChemDraw are listed in Table 1.

2.2. Batch sorption experiments

The sorption values of ILs in the sand/soil were determined by batch experiments. A mixture of 0.01 mol/L NaCl and 100 mg/L NaN₃ was

Table 1

The structure of imidazolium-based ILs used in this study.

| Chemicals | Structure |
|--|-----------|
| [C ₂ mim][BF ₄] | |
| [C ₄ mim][BF ₄] | |
| [C ₆ mim][BF ₄] | |
| [C ₄ mim][TOS] | |
| [C ₄ mim][MeSO ₃] | |
| [C ₄ mim][OTF] | |

used as a background solution to keep stable solution ionic strength and inhibit the biological activity. The 0.80 ± 0.010 g mixture samples (soil:sand = 1:8) and 20 mL aqueous ILs (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 mmol/L, respectively) solution in 25-mL glass tubes with Teflon-lined caps were rotated end over end at 40 rpm at 25 ± 0.2 °C for 24 h. Results of the preliminary tests showed that the sorption reached apparent equilibrium within 12 h. No volatilization or degradation of ILs occurred during the sorption process, as verified by HPLC analysis (Shi et al., 2016). Then, the solution was centrifuged at 4000 rpm for 5 min and filtered using 0.22 mm-pore-size membrane syringe filters to analyze the IL concentration levels using HPLC. The amount of adsorption was determined based on the differences in the IL concentration before and after adsorption. The experiments were performed in duplicate, and the data were present as the mean value.

Freundlich isotherm model was used to fit the experimental data in the IL batch sorption processes (Wang et al., 2015). The Freundlich model equation is expressed as follows:

$$q_e = KC_e^{1/n} \quad (1)$$

where C_e is the equilibrium concentration of ionic liquid in solution (mmol/L), q_e is the equilibrium adsorption amount (mmol/g), and n is an indication of linearity. K is a constant representing the strength of binding to the soil surface [(mmol/g)/(mmol/L) ^{n}], which is numerically equal to the apparent distribution coefficient (K_d , L/g) at an equilibrium concentration of 1.0 mmol/L.

2.3. Column experiments

Column experiments were conducted at laboratory conditions (25 ± 0.2 °C) to study the IL transport as affected by cation/anion species. The glass column (internal diameter of 2.2 cm and a length of 24 cm) was equipped with a top ball (200 mL) used for adding the solution and a bottom layer of quartz (2 mm) to avoid loss of mixture samples. To explore the effects of column depth on IL transport, the column was designed to have three side outlets at the depth of 11, 15, and 19 cm (Fig. S1). The fixed bed column, except for the top ball, was filled with mixture samples. Flow rate (Q) runs constantly at 8 mL/min and controlled by the peristaltic pump, and the initial IL concentration (C_0) was 2 mmol/L. Pentafluorobenzoic acid (PFBA, 50 mg/L), as the nonreactive tracer, was applied to determine the hydrodynamic

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