

Interaction of Novel Ionic Liquids with Soils

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Abstract With the constant development of new ionic liquids, the understanding of the chemical fate of these compounds also needs to be updated. To this effect, the interaction of a number of novel ionic liquids with soils was determined. Therefore, three novel headgroups (ammonium, phosphonium, or pyrrolidinium) with single or quaternary substitution were tested on a variety of soils with high-to-low organic matter content and high-to-low cation exchange capacity, thereby trying to capture the full range of possible soil interactions. It was found that the ionic liquids with single butyl alkyl chain interacted more strongly with the soils (especially with a higher cation exchange capacity), at lower concentrations, than the quad-substituted ionic liquids. However, the quad-substituted ionic liquids interacted more strongly at higher concentrations, due to the double-layer formation,

and induced stronger dipole interaction with previously sorbed molecules.

Keywords Sorption · Ionic liquids · Ammonium · Phosphonium · Pyrrolidinium · Imidazolium · Natural soils

1 Introduction

With the continuing research on ionic liquids, industries are developing new and novel compounds. As part of the chemical fate of these compounds in the environment, the interaction with the soil matrix should be studied. However, the study of sorption phenomena of ionic liquids is still limited and is mainly restricted to a small number of chemicals (mostly imidazolium and pyridinium salts) and a small number of soil matrices. It has been well established that the strength of sorption depends on both ionic liquid structure and physicochemical properties of sorbates. Chemometric and laboratory (Mroziak et al. 2012; Stepnowski 2005) studies indicate that the most determining factors in soils are cation exchange capacity (CEC), organic matter content (OM), and clay minerals (Gorman-Lewis and Fein 2004; Matzke et al. 2009). The pore water properties like pH and ionic strength have also been shown to play an important role in the sorption process. For long-chained imidazolium and pyridinium salts, “double layer” formation phenomena were observed (Markiewicz et al. 2013; Stepnowski et al. 2007). Thermodynamic parameters indicate that interactions of ionic liquids (ILs) with the surface are a spontaneous exothermic process (Mroziak

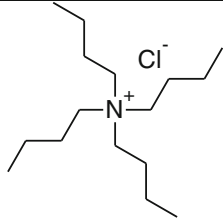
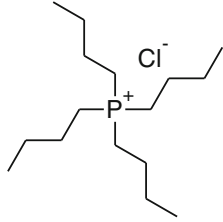
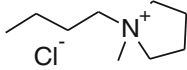
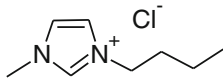
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Table 1 Ionic liquids

| Name | Abbreviation | Molecular weight | Structure |
|--|--------------|------------------|---|
| Tetrabutylammonium chloride | TBAM | 277.92 |  |
| Tetrabutylphosphonium chloride | TBPH | 294.88 |  |
| 1-Butyl-1-methylpyrrolidinium chloride | PYR | 177.71 |  |
| 1-Butyl-3-methylimidazolium chloride | BMIM | 174.67 |  |

et al. 2008a). Laboratory migration studies through soil layers are in agreement with batch tests showing that longer-alkyl-chained ILs interact more strongly with the soil surface than the short ones (Mrozik et al. 2009; Studzinska et al. 2009). The attempts to use HPLC to model environmental interactions of ILs and soils were also conducted (Mrozik et al. 2008b), and it was found that such modeling may support the choice of the appropriate test parameters for experimental studies. An up-to-date knowledge of the fate of ionic liquids in soils may be found in the review made by Jungnickel et al. (2011).

Besides imidazolium and pyridinium salts, little is known about the behavior of other ionic liquids such as ammonium, phosphonium, or pyrrolidinium salts in natural environment, even though these salts are widely used as surface modifiers of natural clay. The best studied ionic liquids are quaternary ammonium salts on natural mineral sorbents (Sekrane et al. 2011; Vidal and Volzone 2009; Wagner et al. 1994) and montmorillonites modified by pyridinium phosphonium and imidazolium derivatives (Abdallah and Yilmazer 2011; Ganigar et al. 2010; Goswami et al. 2012; Livi

Table 2 Properties of the tested soils

| Type of soil | ID | pH _{KCl} | OM (%) | CEC (meq g ⁻¹) | CC (%) |
|----------------------------|-----|-------------------|--------|----------------------------|--------|
| Clayley brown soil | R2 | 5.8 | 6.0 | 99 | 69.3 |
| Alluvial agricultural soil | R3 | 6.6 | 5.5 | 298 | 60.5 |
| Sandy-clayey silt | CA1 | 5.3 | 21.5 | 270 | 94.0 |
| Beach sand | CA3 | 7.6 | 0.14 | 30 | 0.17 |

OM organic matter, CEC cation exchange capacity, CC clay content

Table 3 Sorption coefficient K_d (milliliters per gram) and desorption D (percent) of ionic liquids

| Ionic liquid | R2 | | R3 | | CA1 | | CA3 | |
|---------------------|-----------------------------|---------|-----------------------------|---------|-----------------------------|---------|-----------------------------|---------|
| | K_d (ml g ⁻¹) | D (%) | K_d (ml g ⁻¹) | D (%) | K_d (ml g ⁻¹) | D (%) | K_d (ml g ⁻¹) | D (%) |
| BMIM | 5.7 | 29 | 7.1 | 10.5 | 7.1 | 15 | 1.1 | 54 |
| TBAM | 10.1 | 21 | 15.1 | 5 | 11.5 | 14 | 4.7 | 34 |
| TBPH | 12.5 | 16 | 16.8 | 3 | 13.3 | 9 | 5.3 | 29 |
| PYR | 3.8 | 25 | 7.8 | 12 | 7.6 | 15 | 1.3 | 52 |
| EMIM ^a | 2.6 | 38 | 2.3 | 27 | 1.3 | 24 | 0.5 | 48 |
| EMIMOH ^a | 2.1 | 70 | 2.5 | 39 | 1.0 | 58 | 0.4 | 70 |
| PMIMOH ^a | 2.3 | 67 | 2.9 | 30 | 2.1 | 50 | 1.1 | 62 |
| HMIM ^a | 4.2 | 25 | 7.5 | 8 | 9.0 | 14 | 2.0 | 37 |
| OMIM ^a | 10.6 | 20 | 12.1 | 5 | 8.6 | 12 | 3.7 | 32 |
| BPy ^a | 4.1 | 29 | 4.4 | 17 | 2.6 | 20 | 1.2 | 59 |
| MBPy ^a | 5.5 | 22 | 6.4 | 10 | 3.1 | 20 | 1.3 | 55 |
| AmBPy ^a | 8.6 | 18 | 23.7 | 6 | 4.9 | 10 | 1.6 | 30 |

EMIM 1-ethyl-3-methylimidazolium, *EMIMOH* 1-(2-hydroxyethyl)-3-methylimidazolium, *PMIMOH* 1-(3-hydroxypropyl)-3-methylimidazolium, *HMIM* 1-hexyl-3-methylimidazolium, *OMIM* 1-methyl-3-octylimidazolium, *BPy* *N*-butylpyridinium, *MBPy* *N*-butyl-4-methylpyridinium, *AmBPy* *N*-butyl-4-(dimethyl)aminopyridinium

^a Values obtained for those compounds are from Mroziak et al. (2012)

et al. 2011; Reinert et al. 2012; Tiwari et al. 2008). Obtained complexes are usually robust (due to ion exchange interactions) and stable (i.e., against thermal decomposition). It may give some overview of the possible behavior of ammonium or phosphonium salts in natural soils. The analyzed soils possess a number of interactions (ion exchange, dispersive, or pi-pi), such that we may speculate strong sorption of these classes of ionic liquids.

The aim of the current paper is to determine the sorption of three novel compounds on a variety of soils. Previously studied compounds will be used as a comparison.

2 Materials and Methods

2.1 Chemicals

The ionic liquids used in these studies were chlorides of 1-butyl-3-methylimidazolium (BMIM), tetrabutylammonium (TBAM), tetrabutylphosphonium (TBPH), and 1-butyl-1-methylpyrrolidinium (PYR) and were obtained from Sigma-Aldrich (USA). The ILs used did not undergo any pretreatment. Table 1 shows the details of studied compounds.

HPLC gradient grade acetonitrile was from Sigma-Aldrich (USA), and anhydrite calcium chloride was purchased from P.P.U. "Standard" (Poland).

2.2 Soils

The soils were collected in Poland and were previously characterized and used in our prior studies. All soils were air-dried, ground, and sieved. Table 2 lists some of the relevant properties.

2.3 Adsorption of Ionic Liquids

The batch equilibrium technique (OECD 2000) was used to determine the sorption capacities of the ionic liquids. Six concentrations of ionic liquids (0.1, 0.5, 1, 5, 10, 50, 100, and 200 mM for TBAM and TBPH or 300 mM for BMIM and PYR) prepared in 0.01 M CaCl₂ were added (5 ml) to 1 g of dried soil. Next, they were shaken for 24 h and then centrifuged at 3,059×g for 10 min. The supernatant was used to determine final sorbed concentrations. All experiments were performed in triplicate. The ratio of the amount of ionic liquid sorbed by the soil to the amount of the analyte in the solution at equilibrium state was calculated as sorption coefficient, K_d .

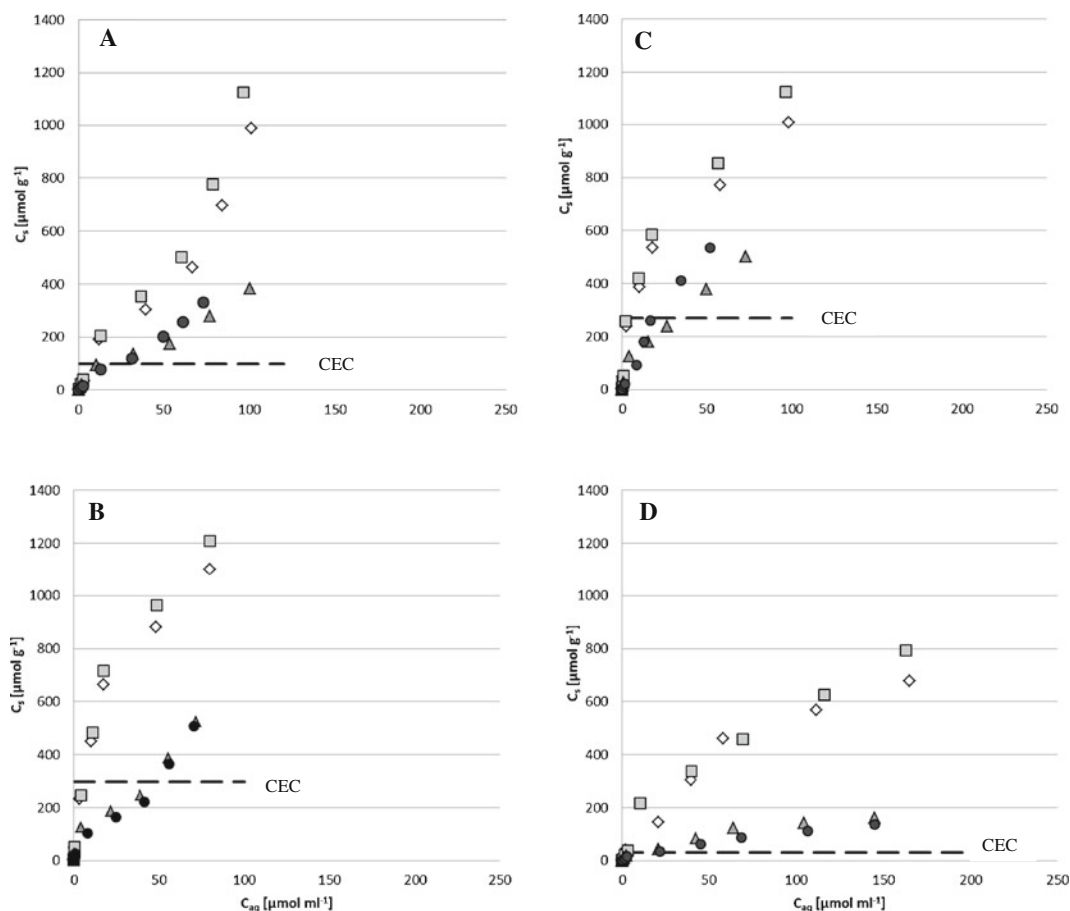


Fig. 1 The sorption isotherms of TBAM (diamond), TBPH (square), PYR (triangle), and BMIM (circle) cations on four soil types: R2 (a), R3 (b), CA1 (c), and CA3 (d). CEC cation exchange capacity

2.4 Chromatographic Analysis

The chromatographic system was composed of a Series 200 vacuum pump (PerkinElmer) with a Series 200 Autosampler and a 732 IC conductometric detector (Metrohm). High surface area with high bonded phase coverage phenyl/hexyl column (Thermo Scientific, 150×4.6 mm, particle size 5 μm) was used for all separations. Chromatographic data were recorded by IC Net 2.3 Metrohm software. The mobile phase contained a mixture of water and acetonitrile (90:10, v/v); the separation was carried out under isocratic conditions. All experiments were carried out at room temperature.

3 Results

As shown in Table 3, the highest sorption coefficients, K_d , were observed for TBPH on R3 soil (116.8 ml g⁻¹)

and the weakest for BMIM on CA3 soil (1.1 ml g⁻¹). This is in agreement with the previously determined conclusion (Beaulieu et al. 2008; Gorman-Lewis and Fein 2004; Matzke et al. 2009; Mroziak et al. 2008b, 2009, 2012; Stepnowski 2005, 2007; Stepnowski et al. 2007; Studzinska et al. 2008)—which states that the molecular volume, representing the lipophilicity of the sorbate, is the dominant determinant for sorption. The general sorption order of tested compounds is TBPH > TBAM > PYR > BMIM. Sorption strength of soils is in agreement with our previous studies which is in the order of R3 > CA1 > R2 > CA3 (Mroziak et al. 2009, 2012), correlating with the cation exchange capacity, organic matter content, and clay mineral content of the soils. At lower concentrations, salts with only one butyl side chain (BMIM and PYR) exhibit stronger affinity to the surface compared with tetrabutyl ones (TBAM and TBPH) (Fig. 1). This is a result of the size of the cations, as at first layer, there is less space for

Table 4 Freundlich parameters for test ionic liquids

| Ionic liquid | R2 | | | R3 | | | CA1 | | | CA3 | | |
|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1/n | K_F | R^2 | 1/n | K_F | R^2 | 1/n | K_F | R^2 | 1/n | K_F | R^2 |
| BMIM | 0.834 | 19.4 | 0.996 | 0.624 | 220.8 | 0.994 | 0.762 | 84.2 | 0.988 | 0.754 | 14.1 | 0.986 |
| TBAM | 0.939 | 16.8 | 0.994 | 0.778 | 204.5 | 0.986 | 0.763 | 198.6 | 0.974 | 0.850 | 28.8 | 0.983 |
| TBPH | 0.961 | 16.0 | 0.994 | 0.788 | 195.7 | 0.988 | 0.803 | 154.3 | 0.972 | 0.882 | 23.4 | 0.986 |
| PYR | 0.823 | 23.8 | 0.990 | 0.645 | 228.7 | 0.989 | 0.716 | 133.7 | 0.989 | 0.759 | 13.4 | 0.975 |
| EMIM ^a | 0.75 | 16.7 | 0.987 | 0.63 | 188.8 | 0.978 | 0.66 | 36.4 | 0.986 | 0.67 | 19.9 | 0.960 |
| EMIMOH ^a | 0.88 | 10.6 | 0.988 | 0.70 | 43.8 | 0.933 | 0.64 | 37.6 | 0.987 | 0.65 | 20.0 | 0.956 |
| PMIMOH ^a | 0.59 | 12.7 | 0.905 | 0.78 | 41.1 | 0.97 | 0.68 | 35.6 | 0.978 | 0.70 | 16.2 | 0.968 |
| HMIM ^a | 0.84 | 20.2 | 0.978 | 0.63 | 348.3 | 0.957 | 0.67 | 175.4 | 0.981 | 0.73 | 20.9 | 0.950 |
| OMIM ^a | 0.88 | 20.8 | 0.996 | 0.74 | 154.8 | 0.970 | 0.67 | 248.9 | 0.959 | 0.92 | 26.4 | 0.910 |
| BPy ^a | 0.91 | 11.4 | 0.998 | 0.73 | 80.1 | 0.995 | 0.60 | 172.9 | 0.967 | 0.57 | 57.1 | 0.936 |
| MBPy ^a | 1.02 | 5.4 | 0.988 | 0.73 | 100.0 | 0.997 | 0.61 | 157 | 0.947 | 0.60 | 46.0 | 0.931 |
| AmBPy ^a | 1.28 | 21.3 | 0.985 | 0.98 | 35.6 | 0.996 | 0.63 | 147.6 | 0.989 | 0.62 | 14.3 | 0.940 |

EMIM 1-ethyl-3-methylimidazolium, *EMIMOH* 1-(2-hydroxyethyl)-3-methylimidazolium, *PMIMOH* 1-(3-hydroxypropyl)-3-methylimidazolium, *HMIM* 1-hexyl-3-methylimidazolium, *OMIM* 1-methyl-3-octylimidazolium, *BPy* *N*-butylpyridinium, *MBPy* *N*-butyl-4-methylpyridinium, *AmBPy* *N*-butyl-4-(dimethyl)aminopyridinium

^a Values obtained for those compounds are from Mroziak et al. (2012)

larger compounds (TBAM and TBPH) and the charge of the cation experiences less steric hindrance, so it can interact better with the charged surface. However, with increasing concentrations and gradual building of the next sorption layer, tetrabutyl salts now show much higher sorption. This is due to the four butyl chains which offer more induced dipole–induced dipole interactions for the next sorbing molecules. Comparing to other imidazolium or pyridinium salts (Mroziak et al. 2012), for the same soils, the obtained sorption coefficients are equal or higher (tetrabutyl compared to 1-methyl-3-octylimidazolium and *N*-butyl-4-(dimethyl)aminopyridinium). Studies concerning interactions of ammonium and phosphonium salts with clay minerals (Abdallah and Yilmazer 2011; Calderon et al. 2008;

Mittal 2012) proved that stronger sorption occurs in the case of phosphonium salts. Desorption displays the inverse correlation to sorption strength. That is, the higher the sorption coefficient, the lower is the desorption. Pyrrolidinium and imidazolium salt show no significant difference in sorption, as do TBPH and TBAM.

To mathematically describe the results, Langmuir and Freundlich models were used. Parameters of these isotherms are listed in Tables 4 and 5. Correlation coefficients are slightly better for the Langmuir model (0.997–0.999) than for the Freundlich model (0.972–0.996). Considering the Freundlich model, it can be observed that fitting is better for TBAM and TBPH (0.972–0.996) than for longer-chained imidazolium/pyridinium (0.910–0.996) (Tables 4 and 5). Calculated

Table 5 Langmuir parameters for test ionic liquids

| ILs | R2 | | | R3 | | | CA1 | | | CA3 | | |
|------|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|
| | C_{max} | K_L | R^2 | C_{max} | K_L | R^2 | C_{max} | K_L | R^2 | C_{max} | K_L | R^2 |
| BMIM | 18 | 0.91 | 0.997 | 14 | 8.66 | 0.989 | 14 | 8.66 | 0.989 | 26 | 0.25 | 0.999 |
| TBAM | 98 | 0.12 | 0.999 | 123 | 0.99 | 0.999 | 123 | 0.99 | 0.999 | 73 | 0.18 | 0.999 |
| TBPH | 34 | 0.32 | 0.995 | 85 | 1.17 | 0.998 | 85 | 1.17 | 0.998 | 107 | 0.14 | 0.999 |
| PYR | 41 | 0.35 | 0.999 | 20 | 5.72 | 0.994 | 20 | 5.72 | 0.994 | 15 | 0.38 | 0.994 |

constants from both isotherms (K_F and K_L) indicated that the structure of ionic liquids (especially number of alkyl side chains) was the major factor determining a concentration-dependent sorption. The Freundlich adsorption coefficients (K_F) for ammonium and phosphonium salts, especially in soil R3 (195.7–228.7), are also higher than those for imidazolium and pyridinium salts (Mrozik et al. 2012), which indicates high affinity of those compounds to the soil surface. The parameter $1/n$ is related to the distribution of energy on the heterogeneous sorption sites and also expresses maturation degree and heterogeneity of the OM domain (Ran et al. 2003; Semple et al. 2007). Low $1/n$ values indicate a more heterogeneous sorption site energy distribution or a higher degree of OM maturation (Ran et al. 2007). Values below 1 indicate a gradual sorption of ionic liquids to sites with lower energies, which is reflected by the convex shape of isotherms. The average $1/n$ values in this study were in the range of 0.62–0.98, and the lowest values are obtained for R3 soil (0.62–0.78) which exhibited the highest sorption potential for all ILs tested.

The K_L values are, again, the highest for tetrabutyl salts with the same soil order R3>CA1>R2>CA3. The C_{\max} (maximum sorption capacity) parameter of the Langmuir model indicates stronger soil affinity to TBPH and TBAM than to BMIM and PYR, even though we have observed higher sorption in lower concentrations of salts having single butyl chain.

4 Conclusions

With the constant development of novel ionic liquids, it is a prerogative that the environmental parameters of these compounds also be tested. Therefore, in this paper, we determined the interaction of novel ionic liquids with the soil matrix. We compared four ionic liquids, differing in the number of substituted alkyl chains. It was found that the ionic liquids with single butyl alkyl chain interacted more strongly with the soils (especially with a higher CEC) than the quad-substituted ionic liquids. However, the quad-substituted ionic liquids interacted more strongly at higher concentrations, due to the double-layer formation, and induced stronger dipole interaction with previously sorbed molecules.

Therefore, the higher the level of substitution, the higher is the potential for chemical persistence in the environment.

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