Original Research

Prediction of the Adsorption Coefficients for Imidazolium Ionic Liquids in Soils Using Cyanopropyl Stationary Phase

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Abstract

Because of potential widespread application of ionic liquids in industrial processes, they should be evaluated before being allowed to enter the environment. The sorption of the substance on soil and sediment is an essential parameter in a new approach of chemical design. The HPLC method involving cyanopropyl-reversed phases for determining sorption coefficients may be an alternative tool in predicting the soil sorption properties of a variety of compounds in comparison to traditional laboratory methods.

We obtain significant correlation of capacity factors, *log k',* and organic carbon normalized sorption coefficients, *log K_{oc},* for the set of homologous ionic liquids (1-alkyl-3-methylimidazolium salts) for meadow soils, CL1, CL2 and agricultural soils AG2, AG3 (R^2=0.97, 0.97, 0.98 and 0.99, respectively). Results for marine sediment are also significant (R^2=0.99). The correlation with forest soil, WO and peat, PE data is also reasonably good (R^2= 0.92 and R^2=0.94). However, the set including both 1-alkyl-3-methylimidazolium and 1-alkyl-3-ethylimidazolium salts gives good results only for CL1, AG2, PE soil and marine sediment SE (R^2=0.93, 0.94, 0.95 and 0.94). These differences may be explained due to molecular structure of the ionic liquids used and properties of the soil (cation exchange capacities and organic matter content).

Keywords: ionic liquids, sorpiton, soil, sediment, cyanopropyl phase, predicition

Introduction

Room temperature ionic liquids (RTIL) are a new class of compounds usually consisting of an organic cation and a variety of organic or inorganic anions. Apart from their negligible vapour pressure (believed to be the main 'green' feature of ionic liquids) one of their most attractive characteristics is the potential to be 'designed to order.' Liquid below 100°C, these compounds make ideal non-volatile solvents for a variety of industrial chemical syntheses [1-4]. RTIL already in common use typically involve nitrogen- or phosphorus-containing organic cations such as alkylimida-

zolium, alkylpyridinium, alkylpyrrolidinium or alkylphosphonium, and anions like bis(trifluoromethanesulphonyl) imide, hexafluorophosphate or tetrafluorophosphate [5], (Figure 1). Ionic liquids are started to be use in the industry

Fig. 1. Generic structure of 1-alkyl-3-methylimidazolium (*A*) and N-methylpyridinium (*B*) ionic liquid cations. R_1: methyl – decyl; R_2: methyl – etyl.

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(*i.e.*: Basionics™ or Basil™ from BASF Group, Ludwigshafen, Germany). Because of their potential widespread application in industrial processes, ionic liquids should be evaluated before being allowed to enter the environment.

To evaluate the environmental fate of any newly produced chemical, the sorption of the substance on soil is an essential parameter. Furthermore, the interaction between the compound and the sediment is equally important if we are to understand the behavior and fate of these compounds in aquatic systems.

In a recent contribution of ours, the sorption of selected imidazolium ionic liquid cations with different alkyl side chain lengths (from C_3 to C_6) was determined and compared [6]. This enabled us to follow the changes in sorption behavior due only to the variation in lipophilicity of the cations under scrutiny. The mechanism of ionic liquid sorption onto selected natural soils differing in their organic content, cation exchange capacity and particle size distribution was also investigated [7]. In most cases the maximum achievable surface concentrations were well above cation exchange capacity (CEC) values. This observation may indicate that initially sorbed solutes modify the sorbent, a process favoring further sorption.

One of the main limitations for continuing this evaluation is a time-consuming traditional laboratory method for the determination of adsorption coefficient K_d. Moreover, there are an almost indefinite number of possible liquid combinations of these entities, thus high throughput methodologies are prerequisite for time-reasonable evaluation of these entities. The HPLC method involving polar reversed phases for determining sorption coefficients may be an alternative tool in predicting the soil sorption properties of a variety of compounds. Because of the dual nature of the stationary phase, which is a compound of apolar as well as polar parts, the interactions of the polar and apolar parts of a molecule take place in a similar way, as happens in the case of soil components [8].

Proposed first by Vowles [9] and Hodson [10], correlations of sorption coefficients (especially organic carbon normalized sorption coefficients K_{oc} but also octanol-water partition coefficients, K_{ow}) with capacity factors obtained from HPLC are a widely used method for a number of chemicals [11-17]. In those studies many different types (octadecylsylicate, physically immobilized humic acid on silica, cyanopropyl phases) of HPLC columns were tested to estimate if there are any correlations of capacity factors and sorption coefficients. The humic acid-filled column is certainly the approach which is closest to real soil conditions [13-15, 17]. However, the use of such stationary phase is limited, due to the lack of commercial availability. Therefore, it is a strong argument against their use in a legislative context such as the testing of chemicals. Kordel et al. [17] studied whether a humic acid column can be replaced by a different type of stationary phase widely available. They proposed cyanopropyl columns as most suitable for that purpose. The successful validation of this technique was proved by an intercomparison task [18], which made cy-

anopropyl phase suitable for standard testing of chemicals [8]. In some studies [9-10] it was found that log K_{oc} was more highly correlated with HPLC capacity factors measured on a cyanopropyl column than on C_{18} column and that the correlation improved with increased mobile phase water content. In the studies of Gawlik et al. [19-20], a strong correlation was observed between capacity factors and measured K_{oc} values for 48 nonionic compounds. However, authors questioned the general applicability of the K_{oc} approach because of the minor role that organic carbon content played in controlling sorption for one of the soils.

The cyanopropyl method can be applied to all substances for which K_{oc} data are available, provided that a suitable device for HPLC detection exists. Therefore, in this paper, the applicability of this test was verified for ionic liquids and compared with the K_{oc} available from our recent studies. Capacity factors were estimated from retention data of ionic liquids using a cyanopropyl stationary phase and were further correlated with K_{oc} values obtained in a batch equilibration test.

It is also possible to gain positive correlations between log K_{oc} and log K_{ow} values obtained from retention values of certain range of organic modifier content in the mobile phase.

For this study we used seven ionic liquids. Such a limited number of compounds (there are more than 20 types of ionic liquid, cations commercially available) is due to the few sorption data that exist for ionic liquids.

Materials and Methods

Chemicals

The ionic liquids selected for these studies were obtained from Merck KGaA (Darmstadt, Germany). They are presented in Table 1.

Anhydrous citric acid and tri-sodium citrate dihydrate were purchased from POCh (Gliwice, Poland). Methanol HPLC gradient grade was purchased from Labscan Limited (Dublin, Ireland) and POCh (Gliwice, Poland).

Soils

Surface soils were sampled from the Pomerania region of northern Poland: three different agricultural soils (including fluvial soil), AG1 – AG3; two meadow soils (one fluvial type), CL1 – CL2; peaty soil, PE and forest soil, WO. Base characteristics of the soils are presented in Table.2. The soils were air-dried, ground in a mortar, and passed through a 2mm sieve. Their organic carbon content was determined by loss-on-ignition method and the cation exchange capacity (CEC) was determined by $BaCl_2$ compulsive exchange [21].

Marine sediment (SE) was collected in Puck Bay (southern Baltic Sea). Sediments from this part of the bay are greenish–gray sapropel, similar to mud rich in organic matter.

Table 1. Ionic liquids used.

Name	Abbreviation	Molecular mass	Miscibility with water
1-propyl- 3-methylimidazolium tetrafluoroborate	PMIM BF$_4$	212	miscible
1-butyl- 3-methylimidazolium chloride	BMIM Cl	174	miscible
1-amyl-3- methylimidazolium tetrafluoroborate	AMIM BF$_4$	240	miscible
1-hexyl-3-methylimidazolium chloride	HMIM Cl	203	miscible
1-octyl-3-methylimidazolium chloride	OMIM Cl	230	partly miscible
1-butyl-3-ethylimidazolium tetrafluoroborate	BEIM BF$_4$	240	miscible
1-ethyl-3-ethylimidazolium bromide	EEIM Br	216	miscible

Table 2. Characteristics of the investigated soils.

SOIL	OC (%)	Clay (%) <0.25 mm	pH	CEC (µeq/g)
AG1	7.70	69.6	5.20	9.34
AG2	4.59	57.9	4.60	3.67
AG3	5.49	60.5	5.50	7.69
CL1	2.90	35.1	4.80	6.54
CL2	4.88	28.82	4.90	3.04
PE	38.5	29.2	5.90	1.11
WO	3.90	35.86	3.90	1.43
SE	10.5	80.4	6.30	14.5

Adsorption coefficients K_d and K_{oc} used in this work were obtained from our previous studies [6-7], and from data from available publication [22].

Estimation of sorption coefficients by HPLC

The experimental method for determining K_{oc} by high performance liquid chromatography was applied following OECD guidelines [8]. Separation was performed on the Perkin Elmer LC 200 Series with autosampler. In the experiment following HPLC, a cyanopropyl reversed phase Supelco Discovery Cyano column was used. The column dimension was 150 x 4.6mm ID. The analyses were performed at ambient temperature at a flow rate of 0.8 ml min^{-1}. The elution profiles were monitored at 220 nm by UV detector. The separation column was equilibrated with the mobile phase until the baseline was stabilized. Sample injections (10 µl) were made at this point. Concentrations of ionic liquids were 1 mmol l^{-1}. The mobile phase was methanol/ 0.01M citrate buffer pH 6.0 (55/45% v/v). The adsorption coefficient was deduced from the capacity factor ($k'=(t_R - t_0)/t_0$).

Results and Discussion

Cyanopropyl stationary beds are mostly reported as a reversed phase; however, in the growing percentage of organic solvent, order of elution can change from the reversed to the normal one. In the conditions recommended by OECD, Supelco Discovery Cyano exhibited normal phase elution order – more hydrophobic molecules were eluted earlier from the column. Retention parameters are presented in Table 3.

Results obtained just for the homologous series of 1-alkyl-3-methylimidazolium ionic liquids (PMIM, BMIM, AMIM and HMIM) give a significant correlation between *log k'* and *log K_{oc}* for meadow soils CL1, CL2 and agricultural soils AG2, AG3 (R^2=0.97, 0.97, 0.98 and 0.99, respectively). Results for marine sediment are also significant (R^2=0.99). The correlation with forest soil, WO and peat, PE data is also reasonably good (R^2= 0.92 and R^2=0.94). However, the chromatographic method does not appear suitable for predicting the behavior of ionic liquids in AG1 soil, owing to the very poor respective correlation coefficients of R^2 = 0.83. Moreover, estimated sorption coefficients for that soil are of greater number than those for PE or WO soil. A possible explanation of this observation may be due to the large number of finest soil fraction,

Table 3. Retention parameters of ionic liquids on Supelco Discovery Cyano HPLC.

Ionic liquid	k'	log k'
PMIM	1.07	-0.008
EEIM	0.98	-0.026
BMIM	0.80	-0.097
BEIM	0.67	-0.08
AMIM	0.70	-0.149
HMIM	0.65	-0.190
OMIM	0.66	-0.180

despite the fact the AG1 soil is characterized by high organic carbon content. As highlighted in previous studies [6-7, 22], the sorption strengths of ionic liquids is likely to be related primarily to the cationic exchange capacity, which is related directly to fine clay particle fraction (< 0.25 mm), not only to the organic matter. In that case the type and amount of clay particles determines CEC strongly. AG1 soil posses higher CEC value (9.34 μmol g^{-1}) in comparison to PE and WO soil (1.11 and 1.43 μmol g^{-1}, respectively). This result may be proof that selected interaction types play an important role in sorption processes. Ionic liquids can undergo many different reactions with the soil matix, especially in soils with high organic carbon content and high clay fraction content, than with soils of low OC. Therefore the correlation with log k' may be so low for tested cyanopropyl phase. This kind of phase will probably not react the same way with ILs, with the same strength as organic matter in soil. In the case of organic matter role in sorption it is also a very important source of exchangeable biding sites, but age and quality of humic substances play important roles.

The log K_{oc} values obtained for the set, including both 1-alkyl-3-methylimidazolium and 1-alkyl-3-ethylimidazolium salts (EEIM and BEIM), may decrease the significance of investigated correlation (R^2= 0.58 for WO soil). In those compounds (EMIM and BEIM) symmetry in the structure is better than in the rest of the ionic liquids tested, thus dipole moments are smaller. The π…π interaction, in the case of 1-alkyl-3-ethylimidazolium moieties, in the range corresponding to the relative molecular masses of methylimidazolium entities (BMIM and AMIM), will be relatively weaker, and also limited because of the sterically unfavorable access of the π-system of the solute to the π-system in the stationary phase [23]. Therefore sorption of EEIM and BEIM in relation to corresponding in mass 1-alkyl-3-methylimidazolium salts (BMIM and AMIM), is weaker. However, for the set of all six ionic liquids used, on CL1, AG2 soils and marine sediment, SE, we acquired reasonably good correlation (R^2=0.93; R^2= 0.95 and R^2= 0.94, respectively). CL1 and

AG2 soil results can be explained due to relatively high values of CEC in comparison to remaining soils. In that case, probably the quality of the organic matter makes the soils much more favorable to sorption of ILs. In those matrices, mentioned effects (π…π interactions) may not play a crucial role. PE soil (with low CEC) values or correlation was also very satisfactory (R^2 = 0.94). However, this soil contains immature organic matter, which makes this soil hardly comparable to the remaining soils if the general mechanism of sorption is discussed. Current explanation of good correlation is impossible at this stage.

Detailed results for all soils and ionic liquids are presented in Table 4.

K_{OC} is considered a useful model for the sorption of relatively nonpolar chemicals to soils with high organic carbon and low clay content with variation by a factor of three to five. Significant correlations between K_{OC} and molecular size, self polarizability were observed. However, for polar acids and amines, K_{OC} values varied up to two orders of magnitude and poor correlations were obtained for most of the parameters examined [24].The sorption of polar or ionizable organics may not follow the K_{OC} model even in soils having sufficient organic carbon content. From our study, correlation on AG1 soil is a common example of that phenomena. Despite high content of organic matter, we obtained very poor correlation of *log k'* and *log K_{oc}*. Probably, for that soil, correlation of capacity factors with clay content (which is also very high) is a realistic approach.

As reported in different studies [25-30] sorption of polar or ionic substances on soils was more correlated with CEC and sediment clay content than organic carbon content. Soils used in our experiments give mostly excellent and good correlations with organic matter. However, as found in previous studies [6-7, 22], sorption of ionic liquid cations is also more CEC and clay content dependent, due to favorable electrostatic interactions with soil surface. As in the case of soils used in our work, we may assume that organic matter is a adominant source of surface negative charges. Therefore, correlation of capacity

Table 4. Values of log KOC compared linearly to log k' derived from HPLC retention data of ionic liquids and respective regression coefficients.

	log k'	Log K_{oc}							
		AG1	AG2	AG3	CL1	CL2	WO	PE	SE
1-propyl-3-methylimidazolium	0.008	2.29	2.24	2.56	2.83	1.07	1.59	0.85	2.54
1-butyl-3-methylimidazolium	0.097	2.44	2.60	2.80	2.84	1.50	1.81	1.17	3.53
1-amyl-3-methylimidazolium	0.149	2.89	2.94	3.01	3.03	1.59	1.80	1.72	4.23
1-hexyl-3-methylimidazolium	0.190	3.47	3.00	3.07	3.45	1.83	1.96	1.79	4.39
1-ethyl-3-ethylimidazolium	0.026	2.54	2.15	2.53	2.62	1.59	1.46	0.95	2.65
1-butyl-3-ethylimidazolium	0.081	2.75	2.52	2.47	2.87	1.54	1.37	1.30	2.92
R^2		**0.75**	**0.95**	**0.75**	**0.93**	**0.60**	**0.58**	**0.94**	**0.94**

factors and partition constants are significant. In the case of AG1 soil the CEC values are mostly due to type and content of the clay particles.

We have made an attempt to correlate estimated log *k'* with existing literature values of K_{oc} and K_d [22]. Results of correlation between the data obtained for two marine and one lake sediments are poor (R^2= 0.007; 0.11 and 0.77, respectively). A possible explanation may be that the ionic liquid with the longest alkyl chain (1-octyl-3-methylimidazolium salt, OMIM) used in those studies is more weakly bounded to the surfaces of sediments than shorter chain moieties (BMIM and HMIM). Thus, OMIM does not follow trends in rising vales of log K_{oc}. Moreover, our estimated *log k'* for that compound also do not fit to the trend for homologous series of ionic liquids (BMIM= *-0.097*; HMIM= *-0.190* and OMIM= *-0.180*). Compared to our results, we may suggest that, for sets of ionic liquids with alkyl chains shorter than six carbons used on mentioned sediments, the significant correlation of log K_{oc} with log k' should be obtained.

Conclusion

Sorption occurs when the free energy of the interaction between an environmental solid and an organic sorbate is negative. Enthalpy-related forces include van der Waals and electrostatic interactions, hydrogen bonding and $\pi...\pi$ and dipole – dipole interactions and chemisorptions, whereas partitioning is considered the primary entropy-driven force [31]. The great advantage of the HPLC method for determining sorption coefficients is mainly due to representing all energetic compartments that are represented by one retention value, thus reflecting a net intensity of sorption.

Despite the sorption of ionic liquids it is rather strongly correlated with CEC and clay content of the soil or sediment, we obtained results that proved the HPLC method of determining sorption coefficients is suitable for homologous series of ionic liquids, for a wide variety of soils.

In the case of 1-alkyl-3-methylimidazolium and 1-alkyl-3-ethylimidazolium salts with longer side chains (more than six carbons) there are some limitations in applicability of the presented method. Further investigations on those compounds should be evaluated.

The estimates of K_{OC} made by HPLC method cannot fully replace batch equilibrium tests. However, it can be a powerful tool which supports the choice of appropriate test parameters for adsorption/ desorption studies, thus calculating *Kd* (distribution coefficient) or *Kf* (Freundlich adsorption coefficient).

Acknowledgement

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