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Adsorption of Alkylimidazolium and Alkylpyridinium Ionic Liquids onto Natural Soils

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The mechanism of ionic liquid sorption onto selected natural soils differing in their organic content, cation exchange capacity, and particle size distribution was investigated in detail. Isotherms were employed to describe sorption. In most cases, the maximum achievable surface concentrations were well above CEC values. This observation may indicate that initially sorbed solutes modify the sorbent, a process favoring further sorption. The experimental data suggest that if a multilayer process occurs, such a mechanism will be applicable to all ionic liquids; but saturation of the second layer occurred only with the longest alkyl chain compound. The shorter alkyl chain cations did not reach saturation in the concentration range investigated here. The influence of the varying pH and ionic strength of an aquifer on sorption strength was also determined.

Introduction

Room-temperature ionic liquids (RTILs), i.e., salts with melting points below 100 °C, have been investigated in the context of a wide variety of applications (*1−3*). RTILs already in widespread use typically combine nitrogen- or phosphorus-containing organic cations with organic or inorganic anions such as bis(trifluoromethanesulfonyl)imide, hexafluorophosphide, or tetrafluorophosphate. The physicochemical properties of RTILs depend on the nature and size of both ionic constituents. Although estimates vary, there are an almost indefinite number of possible liquid combinations of these entities (*4*). Different RTILs have already proved useful as alternative solvents in organic synthesis, as potential electrolytes in batteries and solar cells, and in the separation sciences (*5−7*).

The negligible vapor pressure of RTILs, which makes them a good alternative to conventional molecular organic solvents with their emissions of noxious vapors, is often uncritically regarded as an inherently "green" property of these compounds (*8*). Traditionally, the design and choice of ionic liquids have commonly focused only on properties such as conductivity, solubility, miscibility, and viscosity; the design of modern chemical products, however, also takes their environmental toxicity and persistency into account (*9*). Several studies have reported on the biological effects of ionic liquids, evaluated on the basis of toxicological test systems at different levels of biological complexity (*10−13*). Biological studies of these new chemical entities are important; but equally important, their interactions with the abiotic envi-

ronment need to be understood before they actually enter any of its compartments (*14*).

Sorption has a critical effect on the transport, reactivity, and bioavailability of organic compounds in the environment. In particular, the sorption of a substance onto the soil is an essential parameter in any evaluation of its environmental fate. Gorman-Lewis and Fein (*15*) have measured the adsorption of one ionic liquid (1-butyl-3-methylimidazolium chloride) onto a range of surfaces representing those commonly found in the near-surface environment. In this study, the sorption strength of ionic liquids onto some soils and sediments was also determined preliminarily (*16*). All the compounds were found to be strongly sorbed onto these substrates, sorption capacities being the highest for the longest alkyl chain compounds. Moreover, extremely strong and practically irreversible sorption onto fine-textured marine sediments was also observed, which highlights the importance of the mineral component of the soil (sediment) in the sorption mechanism.

The present work investigated ionic liquid sorption onto selected natural soils differing with regard to their organic content, cation exchange capacity and particle size fraction. Sorption was described with the aid of isotherms, thus enabling the saturation concentration of ionic liquids at the water:soil interface to be defined. The influence of varying pH and ionic strength of an aquifer on sorption strength was also determined.

Experimental Section

Reagents. 1-butyl-3-methylimidazolium (BMIM), 1-hexyl-3-methylimidazolium (HMIM), and *N*-butyl-4-methylpyridinium (MBPyr) chlorides were obtained from Merck KGaA (Darmstadt, Germany), monopotassium phosphate and 85% *ortho*-phosphoric acid from POCh (Gliwice, Poland), HPLC-gradient grade acetonitrile from Lab-Scan (Dublin, Ireland), and trifluoroacetic acid from Sigma-Aldrich (USA).

Soils. Surface soils were sampled from the Pomerania region of northern Poland: fluvial agricultural soil (Eutric Fluvisols) at 54°13′44″N 18°55′46″E, clay agricultural soil (Dystric Cambisols) at 54°25′59″N 18°26′41″E, and forest soil (Orthic Podzols) at 54°30′50″N 18°28′50″E. Additionally, samples of fluvial meadow soil (Eutric Fluvisols) were taken from the industrialized and highly polluted area around the Gdańsk oil refinery (54°20′12″N 18°44′48″E). Table 1 lists selected properties of these soils. The soils were air-dried, ground in a mortar, and passed through a 2-mm sieve, then ground again in a mortar with a small rubber pestle. Their organic carbon content was determined by loss-on-ignition. The cation exchange capacity (CEC) was determined by $BaCl_2$ compulsive exchange, as described in ref *17*.

Sorption Test. The sorption capacities of the ionic liquids were determined by a batch-equilibrium technique according to OECD guidelines (*18*). Ionic liquid solutions (5 mL) prepared in 0.01M $CaCl_2$ were added to the soil (1 g). Ten concentrations (0.1−3 mM) were used for all the soils. The mixtures were agitated for 24 h, then centrifuged at 5000 rpm for 10 min. The aqueous phase was recovered as completely as possible, and the amount of ionic liquid sorbed was determined by direct analysis of the supernatant by HPLC according to the method described below. All experiments were performed in triplicate. Desorption experiments (agricultural soils only) were performed under similar conditions, but pH (phosphate buffer) and ionic strength (calcium chloride concentration) were varied as required. The sorption coefficient K_D was calculated for the saturated concentrations as the ratio of the amount of ionic liquid sorbed by the soil

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TABLE 1. Physicochemical Characteristics of the Soils

type of soil	OC (%)	pH	CEC (μeq/g)	clay (%) >0.25 mM
clayey agricultural soil	4.59	5.22	3.67	57.91
fluvial meadow soil	4.88	7.10	3.04	28.82
forest soil	3.90	4.34	1.43	35.86
fluvial agricultural soil	5.49	6.60	7.69	60.50

to the amount of the analyte in the water at equilibrium. 24 h sorption data were used in the data analysis.

HPLC Analysis of Ionic Liquids. Details of the analytical procedures for ionic liquids can be found in several papers published by our team (*19−21*). In this study, a high-performance liquid chromatograph (Perkin-Elmer Series 200) was used in conjunction with a Synergi Polar-RP 150 × 4.6 mm column (Phenomenex) (mobile phase: acetonitrile : 5 mM phosphate buffer (KH_2PO_4/H_3PO_4); pH 3; isocratic flow = 0.75 mL min^{-1}; elution profiles monitored at $\lambda = 218$ nm).

Results and Discussion

Sorption of Ionic Liquids onto Soils. Figures 1, 2, and 3 show the experimental sorption isotherms for both alkyl-imidazolium and one of the alkylpyridinium ionic liquids in the four soil types. At low concentrations, sorption of 1-hexyl-3-methylimidazolium is very fast, that of 1-butyl-3-methylimidazolium and *N*-butyl-4-methylpyridinium is some-what slower. At these concentrations (0−1 mM), it was found that the longer the alkyl chain in the alkylimidazolium cation, the stronger the sorption, regardless of soil type; this tallies with the findings of our preliminary research (*16*). But with ionic liquid concentrations >1 mM, the alkyl chain length does not seem to be the main factor responsible for sorption strength, even though the sorption behavior of differently sized ionic liquids differs. Sorption is essentially complete with the longest alkyl chain entity in the higher concentration range; this is represented by a typically convex isotherm. But saturation is not reached with the two shorter alkyl chain

ionic liquids. The sorption isotherms obtained were also described quantitatively. The experimental data were fitted to the Langmuir model:

$$S = \frac{C_{\max} \times K_L \times C}{1 + K_L \times C} \tag{1}$$

where S is the amount of ionic liquid adsorbed per unit mass of soil, K_L is the equilibrium or Langmuir constant, C is the equilibrium concentration of ionic liquid in the aquifer, and $C_{\max}$ is the maximum achievable surface concentration of the ionic liquid. Table 2 lists isotherm parameters for all the compounds. Except for the fluvial meadow soil, the fit to the Langmuir model in the remaining soils was excellent: correlation coefficients (R^2) lay in the range from 0.96 to 1.00. The R^2 values obtained for fluvial meadow soil are less significant, ranging from 0.89 to 0.92. This discrepancy could be due to the origin of the soil (a heavily polluted industrial site), and thus be responsible for this unusual ionic liquid sorption profile. At this stage of research, however, this is a rather speculative explanation and should be confirmed by future experiments.

In most cases, the fit to the Langmuir model was satisfactory: correlation coefficients (R^2) ranged from 0.89 to 1.00. The $C_{\max}$ values obtained should be compared to the cationic exchange capacities of the four soils. This level of sorption is significant: above this level, sorption can be multilayered, especially in the case of ionic species, since all accessible cation exchange sites will most probably be filled with ionic liquid cations. Excess CEC, however, may also be due not only to electrostatic but also dispersive interactions of ionic liquids with soil organic matter. Nevertheless, the results show that in most cases the maximum achievable surface concentrations are well above CEC values. This is usually because the initially sorbed solutes modify the sorbent, a situation favoring further sorption (*22*). Figure 4c shows a hypothetical diagram of this process.

Apart from the empirical models used in this study, the chemical equilibrium model could also be used to provide a detailed description of the molecular mechanism of the observed sorption process. The surface complexation model
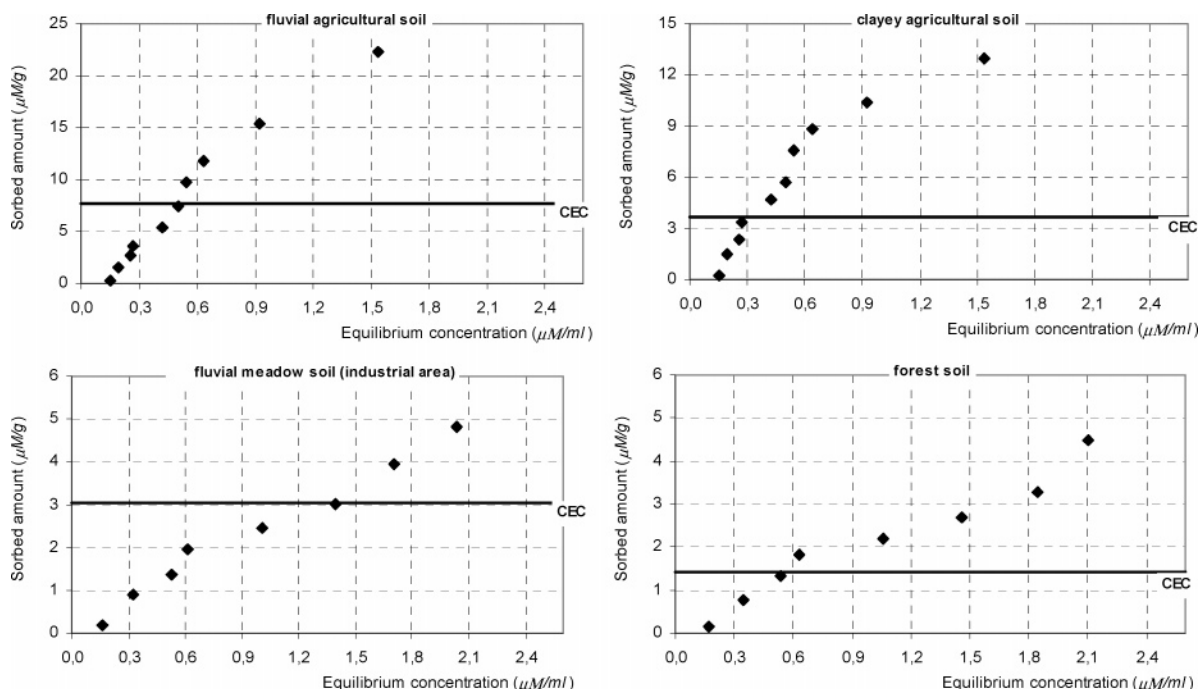

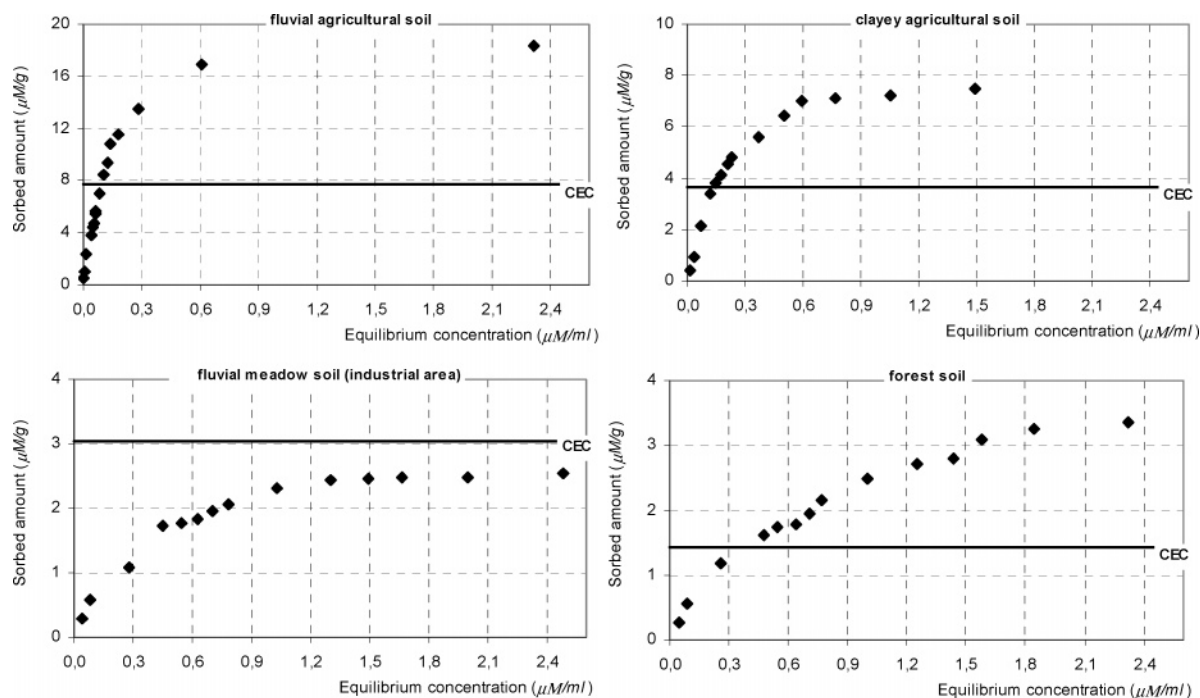**FIGURE 1. Sorption isotherms of 1-butyl-3-methylimidazolium chloride on selected soils.**

FIGURE 2. Sorption isotherms of 1-hexyl-3-methylimidazolium chloride on selected soils.
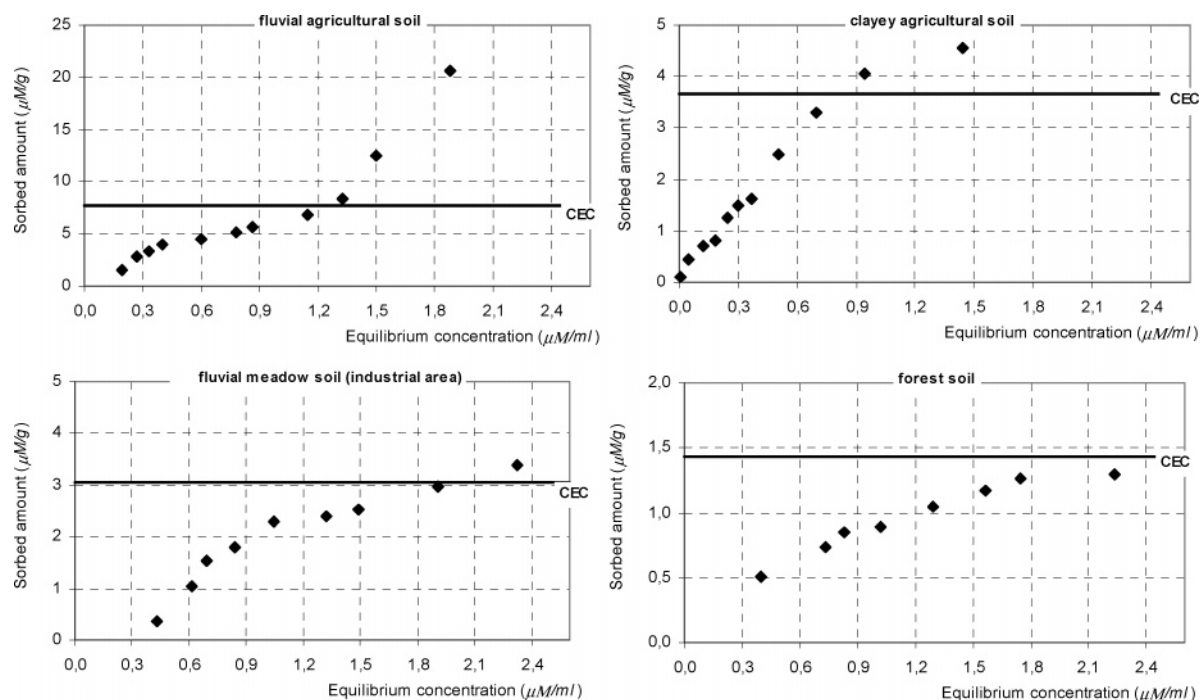

FIGURE 3. Sorption isotherms of _N_-butyl-4-methylpyridinium chloride on selected soils.

TABLE 2. Langmuir Isotherm Parameters of Ionic Liquid Sorption on to Four Soil Types

	HMIM			BMIM			MBPy		
type of soil	C_{max}	K_L	R^2	C_{max}	K_L	R^2	C_{max}	K_L	R^2
clayey agricultural soil	18.5	1.5	0.99	90.9	0.1	0.96	10.2	0.6	0.96
fluvial meadow soil	3.0	2.6	1.00	9.9	0.8	0.92	16.4	0.1	0.89
forest soil	4.2	1.5	0.99	19.0	0.1	0.97	2.1	0.7	0.98
fluvial agricultural soil	19.2	7.2	0.98	6.3	0.1	1.00	11.8	1.2	0.97

would be particularly useful since it considers the charge of both the adsorbate and the adsorbent surface; a situation that occurred in the system under study (23). The method is not without its limitations, however, since the accuracy of predictions may be substantially affected by the heterogeneity of surface sites, as is the case with soils (24). Application of these models lies beyond the scope of this paper; nevertheless, it must be stressed that final confirmation of our multilayer
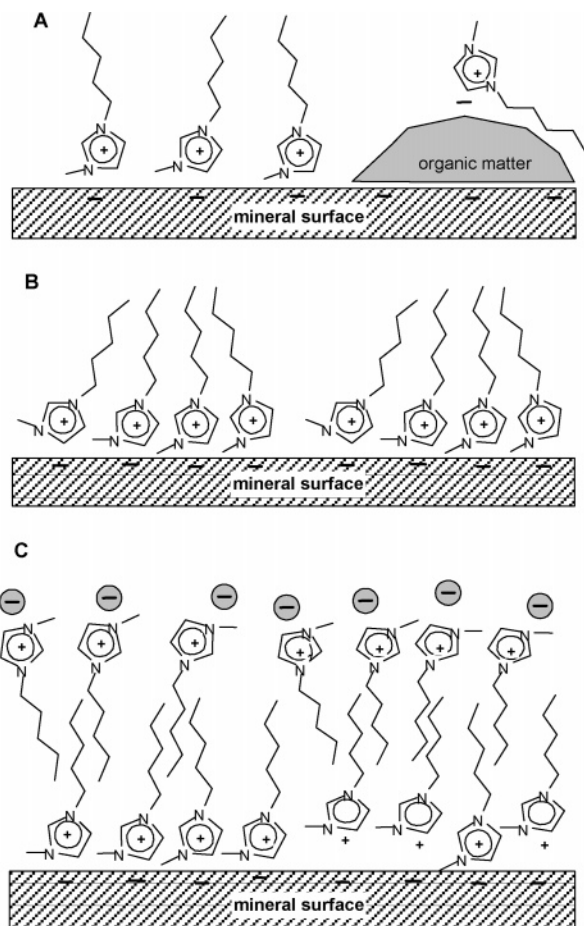
FIGURE 4. Hypothetical types of sorption of ionic liquid cations in natural soils: (A) Monolayer on a mineral surface and interaction with organic matter, (B) hemimicelle on a mineral surface, (C) admicelle on a mineral surface.

formation hypothesis would be possible only with the aid of such mathematical calculations of the thermodynamic properties of sorption.

The experimental data obtained in this study indicate that the suggested mechanism will be applicable to all ionic liquids, but saturation of the hypothetical second layer occurs only with the longest alkyl chain compound: 1-hexyl-3-methylimidazolium. As far as the shorter alkyl chain cations are concerned, particularly in fluvial agricultural soils, the suggested initial formation of a monolayer is followed by the gradual formation of a second layer, although in the concentration range under investigation this did not reach saturation. This is usually characteristic of long-chain surfactant-like chemicals and may imply that admicelles are formed on the surface above the sorption threshold (25). Enhanced sorption with increasing alkyl chain length was also observed for smaller organic molecules such as carboxylic acids and phenols, an effect attributable mainly to their dispersive interactions (26). Since N-butyl-4-methylpyridinium and 1-butyl-3-methylimidazolium cations possess only four carbons in the alkyl side chain, it is more likely that systems involving shorter alkyl chain ionic liquids lack equilibration, and/or other intermolecular forces participate in bilayer formation. After initial sorption, ionic liquids may still offer an active aromatic $\pi ... \pi$ moiety with the potential to interact with the adjacent layer of pyridinium or imidazolium cations. Should this occur, it also means that sorbed long-chain alkylimidazolium cations are incapable of such interactions, since they exhibit the typical convex type of isotherm. This would most likely be due to effective shielding

TABLE 3. Sorption Coefficients K_D of Ionic Liquids Sorbed on to Four Soil Types

type of soil	HMIM	BMIM	MBPy
clayey agricultural soil	11.9	3.8	4.4
fluvial meadow soil	1.7	1.7	1.7
forest soil	2.2	1.3	0.7
fluvial agricultural soil	77.1	14.5	6.5

of the π-system in the longer alkyl chains of the ionic liquid cation. Nevertheless, the unsaturated type of isotherms obtained for the N-butyl-4-methylpyridinium and 1-butyl-3-methylimidazolium salts is reflected by the much weaker correlation coefficients of the Langmuir model in comparison to the imidazolium entities (Table 2).

These results are consistent with our preliminary results of ionic liquid sorption, which showed that the slopes of the Freundlich isotherms of selected ionic liquid cations were greater than 1 (15). Typical of upwardly sloping isotherms, this suggests that the soil surface is substantially modified by a previously bound solute and is now susceptible to further sorption. In such a case, the extent of interaction with the soil surface will probably depend on the ionic liquid load. This observation is endorsed by recent findings regarding the behavior of imidazolium ionic liquids in a salt-free reversed phase chromatography system (27). With increasing amounts of alkylimidazolium entities, clear peak fronting was observed, which indicates a change from the convex to the concave type of isotherm. It is also known from basic studies of the sorption of surfactants onto a soil matrix that the predominant sorption mechanism is ion exchange if the compound loading is less than 70% of the soil's cation exchange capacity. With greater loadings, the cationic surfactants are adsorbed by both ion exchange and hydrophobic bonding (28).

Values of K_D, the sorption coefficient of ionic liquids, (calculated for an initial concentration of 2 mM) were the highest for fluvial- and clayey agricultural soils, and the lowest for forest and fluvial meadow soils (Table 3). The sorption strengths of ionic liquids are likely to be related primarily to the cationic exchange capacity, which is related directly to the fine clay particle fraction of the soil (<0.25 mm). Table 1 shows that the soils with the highest sorption strength (both agricultural soils) contain more than 50% of fine clays. Moreover, the organic matter content appears to be of secondary importance, even though the soil with the highest sorption strength contains the largest proportion of OC (5.49%). Also, the pH of one of the weakly sorbing soils (forest soil) is relatively low, which probably limits the availability of negatively charged active sites responsible for electrostatic interactions with ionic liquid cations. This is clearly reflected by the sorption data, which show that both imidazolium and pyridinium ionic liquids are bound only weakly to this type of soil (sorption coefficients from 0.7 to 2.2; see Table 3). The limited sorption of fluvial meadow soil could also be due to its previous contamination, but at this stage of the research, this is a rather speculative explanation.

Desorption of ionic liquids from both agricultural soils decreased with increasing alkyl chain length. In practice, therefore, HMIM became irreversibly bound to the soil component. Only about 2% of the initially sorbed 1-hexyl-3-methylimidazolium was desorbed, whereas more than 10% of the 1-butyl-3-methylimidazolium could be remobilized from the soils under investigation.

The effect of the different size of the cationic head group on ionic liquid sorption can be assessed by comparing the larger N-butyl-4-methylpyridinium with the smaller 1-butyl-3-methylimidazolium. For clayey agricultural soil their sorption coefficients do not differ very much, and for fluvial
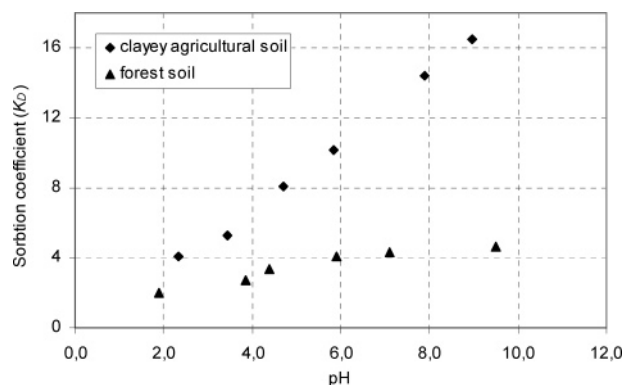
FIGURE 5. Effect of pH on the sorption coefficients of 1-butyl-3-methylimidazolium chloride.

meadow soils they are even identical. But for forest- and fluvial agricultural soils, alkylimidazolium sorption is twice as high as that of alkylpyridinium. This may, therefore, indicate that for these two soils the additional steric availability of the active sorption site may play an important role in the sorption process before molecular interactions occur.

Effect of pH and Ionic Strength on Sorption. The effects of varying the pH and ionic strength of an aquifer on sorption strength were also determined, as environmental values of these two parameters can differ widely. 1-butyl-3-methylimidazolium, one of the most widely used ionic liquids, was chosen for this experiment. These effects were examined on two types of soils: moderately strongly sorbing clayey agricultural soil and weakly sorbing, naturally acidic forest soil. Figure 5 illustrates the effect of pH on sorption coefficients at an initial ionic liquid concentration of 2 mM. The sorption coefficients of both soils increased with increasing pH, the effect being much more intensive for clayey soils. Increasing pH leads primarily to the deprotonation of negatively charged soil surfaces, thus enhancing their cationic exchange capacity. This effect was not as evident in the forest soil, very probably because its natural CEC is half that of the clayey soil. In any case, it can be assumed that lowering the pH of the water:soil system will probably remobilize sorbed ionic liquids, thus enabling, for example, their further penetration into groundwaters.

The fate of ionic liquid anions was not studied in this paper, so certain assumptions can be made only on the basis of the literature data on small organic anion sorption. Unlike the situation with cations, sorption of anions by anion exchange is usually enhanced at lower pH values owing to the formation of neutral and positively charged surface sites. This was the case especially for the more acidic organic species (26). Thus, for a given soil pH, the lower the pK_a of a compound, the greater the certainty that it will exist as an anion, thus enhancing sorption to a positively charged soil surface (29). Another factor affecting the sorption of organic compounds in soils is competition from exchangeable basic cations or anions common in the environment. For example, a study of the geochemical modulation of pesticide sorption onto soil minerals in the presence of mono- and divalent cations has been done, demonstrating the very complicated mechanisms involved in interactions with ion-saturated clay fractions (30). Competitive sorption of simple organic acids and sulfate has also been studied and satisfactorily modeled with surface complexation equations (31). It was, therefore, deemed very useful to acquire some understanding of the potential competition from common ionic species on the sorption coefficients of the ionic liquids under investigation. Adsorption onto both types of soils (as used in the pH experiment) was found to be the smaller, the higher was the ionic strength of the aquifer. It is possible that competitive

adsorption can occur at high ionic strengths; Ca^{2+} thus competes effectively for sorption sites with ionic liquid cations. This mechanism has also been suggested for the sorption behavior of other organic cations (paraquat and diquat), which were found to be exchangeable in soils extracted with solutions containing a relatively large concentration of inorganic ions (32). The mechanism (desorption curve shape) appears to be common to both soils; as in the case of the pH effect, however, the magnitude of the various sorption coefficients depends primarily on soil CEC.

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