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Adsorption of ionic liquids onto activated carbons: Effect of pH and temperature

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ABSTRACT

Adsorption isotherms and kinetics of three ionic liquids (1-methyl-3-octylimidazolium chloride, 1-butyl-3-methylimidazolium chloride and *N*-octylpyridinium bromide) were studied on several types of activated carbon (AC) – a microporous granular AC (from China), a microporous–mesoporous AC fabric (Zorflex from Calgon) and an AC prepared from Artichoke leaves using phosphoric acid activation. ACs were characterized by N_2 adsorption measurement at 77 K (DFT pore size distribution), acido-basic titrations (Boehm method) and point of zero charge measurement. Isotherms were studied, using UV–visible spectrometry, in buffer solutions at pH = 2, 7 and 9, in the temperature range 20–50 °C. Kinetics models were found to be dependent on adsorbent type. Adsorption uptakes were correlated to the AC porous structures. The kind of interactions between organic cations and the carbon surface were found to be related to the amount of oxygenated groups and to the ionic liquid type. Presence of oxygen groups promoted electrostatic interactions which were stronger for the more hydrophilic cation (1-butyl-3-methylimidazolium). The calculated thermodynamic parameters showed that as compared to methylimidazolium, the adsorption of longer chain cations and pyridinium like cations was more favorable.

1. Introduction

Ionic liquids (ILs) being ionic in composition comprise discreet, dissociated ions. Very low vapor pressure, nonflammability and tunable variations in properties add flexibility to this class of solvents [1–3].

ILs are consistently categorized as green solvents in comparison to the conventional organic solvents [4–6]. But at the same time, the high solubility of some of them in water may pose a serious threat to the environment since they can be toxic for living organisms [7–9]. Their synthesis and industrial applications may produce waste streams containing ILs. Owing to their extraordinarily stable chemical and thermal properties; it would become necessary to introduce a treatment process to avoid any potential damage to the environment. Some methods to purify the water containing ILs have been reported: biodegradation [10], chemical degradation [11], photocatalysis [7], and adsorption [12–17]. The adsorption was studied onto: natural soils [12], aquatic sediments [13], montmorillonite [14], bacterial and mineral surfaces [15] and activated carbon [16,17]. Since long, activated carbon (AC) has been the most common and successful adsorbent for the treatment of waste streams [18–20]. A recent investigation for adsorption of imidazolium based ILs onto AC has reported effects of cations, anions and surface chemistry on adsorption efficiency [16]. It was also found that increasing the length of alkyl chain and hydrophobicity of the anion/cation improves its adsorption capacity. Hydrophilic ILs can also adsorb on an AC surface having hydrogen bond donor groups and generally longer ILs have greater adsorption capacity on AC. However, the adsorption kinetics and the effect of pH on adsorption were not studied [16].

The present work aims at investigating the adsorption profile on various activated carbons (ACs) coming from different origins, of three water soluble ILs of first generation selected among the most known and studied organic cations (imidazolium and pyridinium based ILs). The adsorption mechanism of ILs was studied as a function of concentration, pH and the adsorbent characteristics.

2. Experimental

2.1. Ionic liquids

Three types of ionic liquids used were 1-methyl-3-octylimidazolium chloride (OMImCl: $C_{12}H_{23}N_2Cl$), 1-butyl-3-methylimidazolium chloride (BMImCl: $C_8H_{15}N_2Cl$) and octylpyridinium bromide (OPyBr: $C_{13}H_{22}NBr$). OMImCl and OPyBr were synthesized in our laboratory using microwave irradiation [21] and conventional synthesis, respectively. BMImCl (98% purity) was supplied

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by Solvionic and used without further purification. The ILs were synthesized from bromo/choloro-alcane and nitrogenated heterocycle (imidazole or pyridine). The conventional synthesis reactions were conducted under magnetic stirring, by reflux in solvent (acetonitrile or ethyl acetate). The products were purified by successive washing in ether, cyclohexane and diethyl acetate. In order to remove the traces of solvent, the final IL product was vacuum dried for 5 days.

Sizes of the three cations of used ionic liquids (1-methyl-3-octylimidazolium: $OMIm^+$, 1-butyl-3-methylimidazolium: $BMIm^+$, and octylpyridinium: OPy^+) were estimated from simple molecular models made using "Chemsketch 3D Viewer", assuming a parallelepiped shape. The estimated sizes of $OMIm^+$ ($1.42 \times 0.53 \times 0.18\ nm^3$) and OPy^+ ($1.43 \times 0.51 \times 0.18\ nm^3$) are quite similar while for $BMIm^+$ ($0.92 \times 0.54 \times 0.19\ nm^3$) length is slightly smaller.

2.2. Activated carbons

The three activated carbons (AC) were, a microporous coal based granular AC (from China), a mesoporous AC fabric (Zorflex FM10 from Calgon) and an AC prepared from Artichoke leaves using phosphoric acid activation. The Chinese AC was dried in oven at 110 °C prior to use and stored in an air tight container. The AC fabric was washed with 5 M HCl (Chimie Plus) for 2 days and then with UHQ water in a soxhlet extractor for 2 weeks till the pH of the replaced water was equal to the pH of the UHQ water. The AC fabric was then dried in an oven at 110 °C and stored for later use. The method used for the preparation of AC from Artichokes using phosphoric acid activation (H_3PO_4, 75%, Prolabo) was similar to the one used previously in this laboratory [22].

The Chinese carbon was in the form of cylindrical pellets (radius = 1 mm, length = 3–4 mm) and the particle size of Artichoke AC was in the range of 10–1000 μm. The Zorflex fabric was formed of woven elemental fibers of ~10 μm diameter.

2.3. N_2 adsorption–desorption at 77 K

N_2 adsorption–desorption isotherms of the activated carbons were measured using an automatic adsorption instrument (ASAP 2000, Micromeritics) at 77 K. Prior to measurements, carbon samples were degassed at 300 °C for 12 h under vacuum. The specific surface areas of the activated carbons were calculated using the BET or Langmuir equations (area of one N_2 molecule: 0.162 nm^2).

The pore size distribution (PSD) was determined by using the NLDFT (Non-Local Density Functional Theory Model) method applied on the adsorption isotherm assuming a model of finite slit pores having a diameter-to-width aspect ratio of 6 (pores diameter from 3.5 to 250 Å) [23]. Data at $P/P_0 < 0.01$ were obtained using incremental fixed doses of ~10 $cm^3\ g^{-1}$ (STP). The equilibration interval was set up at 300 s. The microporous and mesoporous surface areas and volumes were determined by the NLDFT method. The DFT pore size distribution of the fabric and Chinese ACs loaded at pH 9 with $OMIm^+$ were studied in the same condition as the raw ACs, but after degassing at 50 °C for 12 h under vacuum.

2.4. Boehm titrations and point of zero charge measurement

The pH_{PZC} (pH at point of zero charge) of ACs was determined by the so-called pH drift method [24] by adding 0.15 g of AC in aqueous NaCl solutions (50 mL at 0.01 mol L^{-1}). The pH of the deoxygenated solutions (achieved by N_2 bubbling for 1 h) were adjusted to successive initial values between 2 and 12. The suspensions were stirred for 48 h under N_2 and the final pH was measured and plotted versus the initial pH. The pH_{PZC} is the value at which $pH_{final} = pH_{initial}$. The pH_{PZC} value of a porous carbon is also known to be related with the oxygen surface group content which controls the acido-basic properties. Moreover, it was reported to be decreasing together with the oxygen content [24].

Boehm titrations quantify the basic and oxygenated acidic surface groups on activated carbons [25]. Surface functional groups such as carboxylic (R–COOH) and the P-containing acidic groups, lactone (R–OCO), phenol (Ar–OH), carbonyl or quinone (RR′C═O) and basic groups were determined. Surface functional groups were quantified by assuming that $NaOC_2H_5$ reacted with all groups; NaOH did not react with the RR′C═O groups; Na_2CO_3 did not react with RR′C═O and R–OH groups; and that $NaHCO_3$ only reacted with R–COOH groups and the P-containing acidic groups.

Experimentally, about 0.05 g of each sample of prepared activated carbon was mixed in a closed polyethylene flask with 150 mL of a 0.1 mol L^{-1} aqueous reactant solution (NaOH, or Na_2CO_3, or $NaHCO_3$). The mixtures were stirred for 48 h at a constant speed of 150 rpm at room temperature. Then, the suspensions were filtered through 0.45 μm membrane filters (Durapore®-Millipore). To determine the oxygenated groups content, back-titrations of the filtrate (20 mL) were performed with standardized HCl (0.1 mol L^{-1}).

2.5. Adsorption experiments: kinetics and isotherms

The mother solutions of ILs (50 mM/L) were prepared from a weighted amount of purified and dried IL products dissolved in UHQ (Ultra High Quality) water obtained by osmosis (18.2 MΩ purity). The adsorption experiments were at first all performed at room temperature by stirring (300 rpm) stoppered 100 mL flasks containing the adsorbent and the adsorbate. The ionic liquids concentrations in the solution and on the ACs, for adsorption kinetics and isotherms, were determined by using UV–visible spectrometry (Varian, Cary50) after filtration on glass fiber filters (PALL, Type A/E, P/N 61631, pore size: 1 μm). The maximum absorbance was obtained at 211 nm for OMImCl and BMImCl, and at 260 nm for OPyBr.

The kinetics were studied at pH 9 only for 24 h. All the isotherms were studied at room temperature under controlled pH conditions in buffer solutions at pH 2, 7 and 9. The buffer solutions were made by mixing KCl and HCl for pH = 2, tris(hydroxymethyl)-aminomethane and HCl for pH = 7 and disodium tetraborate decahydrate (borax) and HCl for pH = 9 [26]. A 50 mL volume of the adsorbate solution made in the buffer (both made using UHQ water) was stirred with varying amounts of AC in each case. The contact time was 24 h in case of Chinese AC and 12 h both for the fabric and Artichokes ACs. The AC weights used were 0.1 g for the Chinese AC and 0.05 g each for the fabric AC and the Artichokes AC.

The isotherms of adsorption of various ILs on the Chinese AC were at least studied at three constant temperatures between 20 and 55 °C (T = 20, 30, 32.5, 40, and 55 °C). The temperature variation studies of the isotherms at pH = 7, were conducted in water without any buffer solution.

3. Results and discussion

3.1. Characterization of activated carbons

3.1.1. Surface chemistry

Chinese AC has the least amount of acidic functional groups, whereas Artichokes AC has the most (Table 1). Chinese AC contains only very small amount of phenolic groups and possesses a pronounced basic character (pH_{PZC} = 9.5). The absence of any phosphorus in the composition of the Chinese AC probed by X-ray microanalysis might indicate a production of this carbon through physical activation. The Zorflex fabric contains very weak amount