Fluid Phase Equilibria 414 (2016) 156–163

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Steric and energetic interpretations of the equilibrium adsorption of two new pyridinium ionic liquids and ibuprofen on a microporous activated carbon cloth: Statistical and COSMO-RS models

Lotfi Sellaoui [a, b], Hanen Guedidi [a], Sylvain Masson [a], Laurence Reinert [a], Jean-Marc Levêque [a, c], Salah Knani [b], Abedelmottaleb Ben Lamine [b], Mohamed Khalfaoui [b], Laurent Duclaux [a, *]

[a] Univ. Savoie Mont-Blanc, LCME, F-73000 Chambéry, France
[b] Unité de Recherche de Physique Quantique, UR 11 ES 54, Faculté des Sciences de Monastir, Tunisia
[c] Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Malaysia

A R T I C L E I N F O

Article history:
Received 13 October 2015
Received in revised form
3 January 2016
Accepted 4 January 2016
Available online 6 January 2016

Keywords:
Ionic liquids
Ibuprofen
Adsorption
Activated carbon cloth
Statistical model
COSMO-RS

A B S T R A C T

The adsorption isotherms of two new ionic liquids (4-tert-butyl-1-propylpyridinium bromide: IL1 and (4-ter-butyl-1-(2 carboxyethyl) pyridinium bromide: IL2) and ibuprofen (2-[4-(2-methylpropyl) phenyl] propanoic acid: IBP) on an activated carbon cloth were studied at 286, 298 and 313 K. Experimental adsorption isotherms were simulated by a single energy monolayer model using statistical physics, allowing to determine the number of molecules per site (n), the density of receptor sites (N_M) and the concentration at half saturation ($c_{1/2}$). Simulation results suggested that two adsorbates were docked per receptor sites of the activated carbon cloth surface. As a function of temperature, the study of the monolayer adsorbed quantity has indicated that the adsorption process is exothermic. The magnitudes of the estimated adsorption energies have indicated that IBP and ILs have been physisorbed on the adsorbent. The conductor-like screening model for real solvents (COSMO-RS) was applied to calculate three specific interaction energies of ILs and IBP with a graphene layer, i.e., the electrostatic misfit energy (E_{MF}), the hydrogen-bonding energy (E_{HB}) and the Van der Waals energy (E_{vdW}). The COSMO-RS model has proved that the interaction of all the three studied adsorbates with a graphene layer mainly depends on the Van der Waals contribution. The highest interaction energies of IL2 and IBP with the carbon surface have been explained by the additional contribution of hydrogen bond attributed to the presence of a carboxyl group on these molecules.

1. Introduction

Ionic liquids (ILs) are organic salts of low melting points (below 373 K) and negligible vapor pressure which are considered as green solvents as well as viable substitutes for volatile organic compounds [1,2]. Since many of them are water soluble, their toxicities and ecotoxicities may have an impact on the environment [3,4]. Industrial use of ILs in the future may thus be a source of pollution as they could be released in the environment by industrial liquid effluents. Thus, removal or recovery procedures should be developed in the case of any accidental release. Advanced oxidation [5], biodegradation [6] and adsorption on activated carbons [7,8] are treatment techniques that can be used for the removal of water soluble ILs. This latter method offers several advantages as it is non-destructive and cost-efficient. Ibuprofen (IBP) is an emergent pollutant, used as an anti-inflammatory and antipyretic drug. This compound has been frequently detected in the treated sewage from the wastewater treatment plants among several other pharmaceutical molecules [2]. Several studies have been carried out on the removal of ibuprofen from aqueous solutions by adsorption on activated carbons of different origins and physical-chemical properties [9–12]. The interactions of the IBP carboxylic group with the oxygenated surface groups (carbonyl and carboxyl groups) of the activated carbons were already pointed out for their role in the promotion of the ibuprofen adsorption [12]. Both the negative charge of the adsorbate at pH 7 and its hydrophobicity control the

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* Corresponding author.
E-mail address: laurent.duclaux@univ-smb.fr (L. Duclaux).

http://dx.doi.org/10.1016/j.fluid.2016.01.007
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adsorption properties. On the other hand, the adsorption of the positively charged IL cations, was found to be promoted by some electrostatic attractions with the negatively charged oxygen surface groups of the carbons [8]. Palomar et al. showed that the adsorption properties of an IL at pH 7 were related both to the hydrophobicity of its anion and cation. They highlighted an important role played by the length of the alkyl chain grafted to the cationic moiety [13,14]. These authors mentioned that the adsorption efficiency of the methylimidazolium based ILs on an activated carbon was affected by the engaged structure of the ILs (anion and cation moieties) and the surface of the adsorbent [13]. It was also observed by Lemus et al. that the ultramicropores of an activated carbon adsorbent were accessible to small ILs [13]. Similarly, several studies showed that ibuprofen could be preferentially adsorbed in the smaller micropores (i.e. ultramicropores) of the microporous activated carbons [15].

The aim of this work is to compare the adsorption properties of ibuprofen and two pyridinium ILs on a microporous activated carbon, in order to understand the effect of their different chemical natures on the adsorption phenomena. Two pyridinium ILs have been selected and synthesized due to some similarities in terms of molecular size and chemical functionalities with ibuprofen. The adsorption isotherms of these three molecules were studied separately at 286, 298 and 313 K. Predictive models and/or computational simulations were used to enable a better understanding of the adsorption phenomena. The adsorption isotherms have been firstly simulated and interpreted by a steric model by using a statistical physics treatment. In second approach, the interaction energies of the ILs and ibuprofen molecule with the solvent and a graphene plane were calculated using the COnductor-like Screening MOdel for Real Solvents (COSMO-RS) and correlated with the adsorption properties.

2. Experimental

2.1. Materials

The activated carbon cloth (900–20) was provided by Kuraray Chemical (Japan). Its porosity has been characterized by N_2 adsorption–desorption at 77 K as well as CO_2 adsorption at 273 K using an automatic sorptometer (ASAP 2020, Micromeritics). Prior to measurements, samples were degassed for 12 h at 523 K under vacuum. N_2 adsorption data at $P/P_0 < 0.01$ were obtained by using incremental fixed doses of 10 $cm^3\ g^{-1}$ (STP), setting the equilibration interval at 30 s. CO_2 adsorption data were obtained at P/P_0 ranging from 4×10^{-4} to 3.5×10^{-2}, using a 45 s equilibration time. The BET specific surface area, not significant for microporous materials in the 0.1–0.3 relative pressure range [16] has been then computed in the 0.01–0.05 relative pressure range giving a value of 1910 $m^2\ g^{-1}$. Pore size distribution (PSD) of the activated carbon for pore diameters higher than 0.7 nm has been determined by using NLDFT (Non Local Density Functional Theory) models applied on the N_2 adsorption isotherms at 77 K [17]. Additionally, the pore size distribution for diameters smaller than 0.7 nm (narrow micropores or ultramicropores) has been evaluated using CO_2 adsorption isotherms at 273 K. An infinite slit pore model has been assumed for CO_2 adsorption [18], while a finite slit pore model has been used for N_2 adsorption simulations [17]. The whole PSD of the adsorbent in the microporous and mesoporous pore size domain (Fig. 1) indicates the absence of mesoporosity and the presence of both ultramicropores (volume of 0.34 $cm^3\ g^{-1}$ and surface of 1148 $m^2\ g^{-1}$) and supermicropores (volume of 0.34 $cm^3\ g^{-1}$ and surface of 528 $m^2\ g^{-1}$). The activated carbon cloth is mainly acidic [15] with only few surface groups and the amount of oxygenated groups (0.84 meq g^{-1}) that is about twice the one of basic groups (0.43 meq g^{-1}). As the surface group content is very low, the adsorbent could assumed to be chemically an arrangement of pure graphene layers with only hydrogen atoms bonded at the edge of the planes.

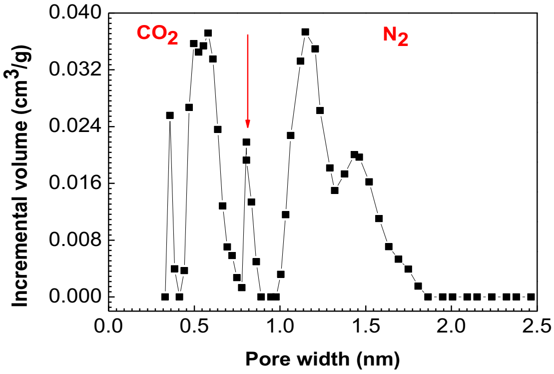

Fig. 1. PSD of the adsorbent in the microporous and mesoporous pore size domain. The arrow indicates the limit between ultra and super micropores.

2-[4-(2-Methylpropyl) phenyl] propanoic acid, also named ibuprofen (IBP), was purchased from Sigma–Aldrich (>98% purity). Two new ionic liquids: 4-tert-butyl-1-propylpyridinium bromide named IL1, and 4-ter-butyl-1-(2 carboxyethyl) pyridinium bromide referred to IL2 have been synthesized in our laboratory by mixing at room temperature in a flask stoichiometric proportions of 4-tert-butylpyridine (96%, Aldrich) and 1-bromopropane (99%, Aldrich) or 3-bromopropionic acid (>99%, Aldrich) respectively, in order to obtain 25 g of each IL. The details for the synthesis of these ILs have already been reported [19]. The pKa value of IL2 was determined by volumetric titration. The atomic positions of IL1, IL2 and IBP are determined by using ChemDraw. The dimensions of the smallest parallelepiped in which each molecule is included is obtained by using ChemDraw and taking into account the Van der Waals radius value (0.1 nm) of the hydrogen atoms present at the extreme positions. Some properties of both ILs and IBP are given in Table 1.

2.2. Adsorption isotherms

Isotherms have been determined at pH 7.4 in a buffer solution prepared by dissolving 5.871 g of potassium dihydrogen phosphate (KH_2PO_4) and 21.512 g of disodium phosphate (Na_2HPO_4) in 5L of UHQ water (Ultra High Quality, 18,2MΩ purity). The mother IL1, IL2 and IBP solutions (0.5 mmol/L) were prepared from the buffer solution. Further solutions of given concentrations (from 0.05 to 0.5 mmol/L) were derived from the mother solutions by dilution with the buffer. Disks of activated carbon cloth (10 mg) were cut off and stirred in closed flasks containing 30 mL of the adsorbate solution at a given concentration. The flasks were agitated for 5 days in an orbital shaker (New Brunswick Scientific, Innova 40) which was set at 250 rpm to reach equilibrium. Solutions were then filtered using a fitted syringe with a 0.45 μm filter (Durapore®-Millipore). The ILs and IBP concentrations were further quantified by high performance liquid chromatography (HPLC) equipped with a high pressure pump (Waters 515), a photodiode array detector (Waters 996) and a Sunfire C_{18} column (5 μm, 4.6 × 250 mm). For IBP analysis, an isocratic mode (flow rate of 1 mL min^{-1}) was used with a 80v/20v methanol/acidified UHQ water solution (0.1 vol. % of 95 wt. % phosphoric acid) as mobile phase. IL1 (or IL2) was analyzed in the same mode using a mobile phase composed of 88 vol. % (85 vol. % for IL2) of acidified UHQ water (1 vol. % of 95 wt. % H_3PO_4 added to the total volume) and 12 vol. % (15 vol. % for IL2) of methanol. Detection was operated at 222 nm and 220 nm for the ILs