



Interfacial behavior of polar, weakly polar, and nonpolar compounds bound to activated carbons

V.M. Gun'ko^{a,*}, V.V. Turov^a, V.I. Zarko^a, O.V. Goncharuk^a, Yu.M. Nychiporuk^a, O.P. Kozynchenko^b, J. Skubiszewska-Zięba^c, R. Leboda^c, B. Charmas^c, D.Yu. Balakin^d, Yu.G. Ptushinskii^d

^a Chuiko Institute of Surface Chemistry, 17 General Naumov Street, Kyiv 03164, Ukraine

^b MAST Carbon International Ltd., Jays Close, Viables, Basingstoke, Hants RG22 4BA, United Kingdom

^c Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, Lublin 20-031, Poland

^d Institute of Physics, 46 Prospect Nauki, Kyiv 03028, Ukraine

ARTICLE INFO

Article history:

Received 7 March 2013

Accepted 26 April 2013

Available online 9 May 2013

Keywords:

Textural characteristics

Low-temperature ¹H NMR

DSC

TPDMS

Co-adsorption

ABSTRACT

Detailed analysis of the interfacial behavior of water and weakly polar or nonpolar organics adsorbed alone or co-adsorbed onto activated carbons (AC) at different temperatures is a complex problem important for practical applications of adsorbents. Interaction of water, 1-decanol, and *n*-decane with AC possessing highly developed porosity (pore volume $V_p \approx 1.4\text{--}2.3\text{ cm}^3/\text{g}$, specific surface area $S_{\text{BET}} \approx 1500\text{--}3500\text{ m}^2/\text{g}$) was studied over a broad temperature range using differential scanning calorimetry (DSC), thermoporometry, ¹H NMR spectroscopy, cryoporometry, and temperature-programmed desorption with mass-spectrometry control methods. Comparison of the pore size distributions (PSD) calculated using the DSC thermoporometry, NMR cryoporometry, and nitrogen adsorption isotherms allows us to determine localization of adsorbates in different pores, as well as changes in the PSD of AC due to freezing of adsorbates in pores. Theoretical calculations (using *ab initio* HF/6-31G(d,p), DFT B3LYP/6-31G(d,p), and PM7 methods) explain certain aspects of the interfacial behavior of water, decane, and decanol adsorbed onto AC that appear in the experimental data. Obtained results show strong temperature dependence (above and below the freezing point, T_f , of bulk liquids) of the interfacial behavior of adsorbates on the textural characteristics and hydrophilic/hydrophobic properties of AC and the adsorbate amounts that affect the distributions of adsorbates unfrozen at $T < T_f$ in pores of different sizes.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Activated carbons (ACs) as effective adsorbents for various adsorbates are used in different dispersion media to remove organic toxicants from wastewater, to condition drinking water, to adsorb organics from wet air, and to treat aqueous solutions of organic or inorganic compounds and emulsions [1–10]. Therefore, features of individual and competitive adsorption of water and organics onto AC are of importance from practical point of view. Detailed analysis of adsorption of complex compounds from liquid media onto complex surfaces of AC possessing pores of a non-simple shape and a broad size distribution, as well as hydrophobic and hydrophilic surface sites, needs maximum comprehensive data obtained by different methods including equilibrium and kinetic adsorption of probe compounds alone and from mixtures, differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, temperature-programmed desorption with mass-spectrometry (TPDMS) control,

thermogravimetry (TG), X-ray diffraction (XRD), dielectric relaxation spectroscopy, thermally stimulated depolarization current, etc. [1–19]. Comparative studies of the interfacial behavior of adsorbates different in size, shape, and polarity at an AC surface using several methods allow deeper insight into driving forces of the interfacial phenomena dependent on textural characteristics and surface polarity of adsorbents, temperature, concentration (liquid phase), or pressure (gaseous phase) affecting the behavior of bound adsorbates remaining mobile in pores at $T < T_f$ [8–12]. Some of the mentioned methods allow one to trace these changes depending on the pore sizes since phase transition temperature (e.g., freezing, T_f , melting, T_m , glass transition, T_g , etc.), and other properties of adsorbates depend strongly on confined space effects and the surface chemistry of adsorbents [12–15]. Interesting and useful information on the interfacial behavior of adsorbed water and organics can be obtained from analysis of the temperature dependences of phase state of adsorbates over a broad temperature range using the DSC [20–24] and NMR [12,15,19] methods, since both methods can be used as phase transition – cryoporometry – thermodynamic tools. The aim of this paper is to study the behavior of water and organics (*n*-decane and 1-decanol as

* Corresponding author. Fax: +380 44 4243567.

E-mail address: vlad_gunko@ukr.net (V.M. Gun'ko).

representative organics nonpolar and weakly polar, respectively) adsorbed in different amounts onto AC with different burn-off degree (40–86%) and, therefore, having various textural characteristics (specific surface area $S_{\text{BET}} = 1451\text{--}3463 \text{ m}^2/\text{g}$, pore volume $V_p = 1.26\text{--}2.32 \text{ cm}^3/\text{g}$, pore size distributions with different contributions of nano-, meso-, and macropores), as well as a certain difference in the surface polarity and the number of surface active sites.

2. Materials and methods

2.1. Materials

Porous phenol formaldehyde resin beads [13,25] were carbonized by heating in a CO_2 flow to 1073 K at a ramp rate of 3 K/min. After sieving, samples of 250–500 μm in size have been additionally activated in CO_2 flow at 1183 K with different residence times producing ACs with different burn-off degree: 40% (C-40), 44% (C-44), 47% (C-47), and 86% (C-86) (MAST Carbon International Ltd., UK). The morphological, textural, and structural characteristics of similar carbons activated by CO_2 , as well as carbons activated by water vapor in fixed bed or fluidized bed reactors, were described in detail elsewhere [26–30].

Raman spectrum of C-47 used as a representative AC sample was recorded using a Raman microscopy (inVia Reflex Renishaw, UK).

2.2. Textural characterization

To analyze the textural characteristics of AC, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2405 N adsorption analyzer or a Quantachrome Autosorb adsorption analyzer. The specific surface area (S_{BET}) was calculated according to the standard BET method (notice that the constant of BET equation $c_{\text{BET}} < 450$ for all AC studied, e.g. $c_{\text{BET}} = 50.3$ for AC-86 with the maximal burn-off degree) [3]. The total pore volume V_p was evaluated from the nitrogen adsorption at $p/p_0 = 0.98\text{--}0.99$ (p and p_0 denote the equilibrium pressure and the saturation pressure of nitrogen at 77.4 K, respectively). The nitrogen desorption data were used to compute pore size distributions (PSDs) (differential $f_V(x) \sim dV_p/dx$ and $f_S(-x) \sim dS/dx$) using a regularization procedure [31] under non-negativity conditions ($f_V(x) \geq 0$ at any pore half-width x), at a fixed regularization parameter $\alpha = 0.01$, using the models of slit-shaped pores (modified Nguyen-Do (MND) method [32,33]) or a mixture of slit-shaped and cylindrical pores and voids between spherical nanoparticles (with the particle size distribution in the 10–50 nm range according to high-resolution microscopic images [27–29,34]) packed in random aggregates (SCV model) using a self-consistent regularization (SCR) procedure [35,36]. The SCV/SCR method (due to the self-consistent regularization) allows us to estimate the contributions of different types of pores into the total porosity (weight coefficients c_{slit} , c_{cyl} , and c_{void} shown in Table 1). The differential distribution functions $f_V(x)$ (PSD_V, $f_V(x) \sim dV/dx$, $\int f_V(-x)dx \sim V_p$) were converted into incremental PSD (IPSD) at the sum $\sum f_{V,i}(x) \sim V_p$. The differential PSD functions with respect to the pore volume $f_V(x)$ and the specific surface area (PSD_S, $f_S(-x) \sim dS/dx$, $\int f_S(x)dx \sim S$) were used to estimate the contributions of nano- ($x \leq 1 \text{ nm}$), meso- ($1 \text{ nm} < x \leq 25 \text{ nm}$), and macropores ($25 \text{ nm} < x < 100 \text{ nm}$), as well as the deviation (Δw) of the pore shape from the SCV-models of pores assuming that the S_{BET} value correspond to real specific surface area [37] (Table 1). Additionally, nonlocal density functional theory (NLDFT) and quenched solid DFT (QSDF) methods (Quantachrome software) using an equilibrium model with slit-shaped and cylindrical pores for carbons were used to calculate the differential PSD (dV/dx) functions.

Table 1

Textural characteristics of AC calculated with SCV/SCR method.

AC	Burn-off degree (%)	S_{BET} (m^2/g)	S_{nano} (m^2/g)	S_{meso} (m^2/g)	S_{macro} (m^2/g)	V_p (cm^3/g)	V_{nano} (cm^3/g)	
C-40	40	1520	1178	337	5	1.26	0.55	
C-44	44	1516	1161	329	26	1.62	0.50	
C-47	47	1451	1150	276	24	1.38	0.40	
C-86	86	3463	1478	1981	4	2.32	0.60	
		V_{meso} (cm^3/g)	V_{macro} (cm^3/g)	c_{slit}	c_{cyl}	c_{void}	Δw	χ (%)
C-40		0.62	0.08	0.591	0.279	0.130	0.243	19.6
C-44		0.46	0.66	0.352	0.381	0.267	0.222	18.2
C-47		0.51	0.47	0.520	0.136	0.344	0.761	43.2
C-86		1.58	0.15	0.517	0.395	0.087	0.589	37.1

2.3. ^1H NMR spectroscopy

^1H NMR spectra of static samples were recorded at 190–290 K using a Varian 400 Mercury spectrometer (magnetic field of 9.4 T) of high resolution with the probing 90° pulses at duration of 3 μs with eight scans and 2–3 s delay between them. The absence of significant changes in signal intensity of liquids at $T > T_f$ (i.e., without phase transition) allows one to assume that the spin system can completely relax between the pulses.

Relative mean errors were smaller than $\pm 10\%$ for ^1H NMR signal intensity for overlapped signals and $\pm 5\%$ for single signals and $\pm 1 \text{ K}$ for temperature. The accuracy was improved using digital treatment of signals with compensation of phase distortion and zero line nonlinearity with the same intensity scale at different temperatures. Repeated measurements of samples gave practically the same spectral picture at the same temperatures. The spectra were recorded during heating of samples (cooled to 190–200 K) to 280–290 K at a step $\Delta T = 10 \text{ K}$ and a heating rate of 5 K/min (for 2 min) and maintained at a fixed temperature for 8 min.

The ^1H NMR signal intensity (20 kHz bandwidth) of static samples was determined only for mobile n -decane and water molecules bound to AC. This is due to short transverse relaxation time of solids (OH groups at an AC surface) and frozen adsorbates, such as water (ice) or solid decane at $T < T_{f,d} \approx 243.5 \text{ K}$. This technique applied to a variety of adsorbates and adsorbents was described in details elsewhere [12,19].

Water and other liquids can be frozen in narrower pores at low-temperatures that can be described by the Gibbs–Thomson (GT) relation for the freezing point depression [12,15]

$$\Delta T_m = T_{m,\infty} - T_m(R) = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R} = \frac{k}{R}, \quad (1)$$

where $T_m(R)$ is the melting temperature of a frozen liquid in cylindrical pores of radius R , $T_{m,\infty}$ is the bulk melting temperature, ρ the density of the solid, σ_{sl} is the energy of solid–liquid interaction, ΔH_f is the bulk enthalpy of fusion, and k is a constant (for water adsorbed on AC $k_{\text{CT}} = 75 \text{ K nm}$ was calibrated using N_2 DFT PSD). On the basis of this equation and the methods sensitive to transition of phase, different versions of cryoporometry, relaxometry, and thermoporometry were developed to study the structural characteristics of a variety of solid and soft materials and bioobjects [12,15,19].

2.4. Calorimetry

Microcalorimetry investigations of interaction of AC with water, 1-decanol, and n -decane were carried out using a PYRIS Diamond (Perkin Elmer Instruments, USA) differential scanning calorimeter or a DAC 1.1A (EPSE, Chernogolovka, Russia) differential automatic

Download English Version:

<https://daneshyari.com/en/article/6999541>

Download Persian Version:

<https://daneshyari.com/article/6999541>

[Daneshyari.com](https://daneshyari.com)