Adsorption 9: 303–309, 2003

Assessment of Hydrophobic-Hydrophilic Properties of Microporous Materials from Water Adsorption Isotherms

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Received August 15, 2002; Revised May 29, 2003; Accepted June 3, 2003

Abstract. The characterization of the hydrophobic-hydrophilic properties of different types of microporous materials, namely activated carbons, pillared clays and zeolites, was made by the determination of water adsorption isotherms. The data were analysed by the Dubinin and Astakhov (D-A) equation. The use of the E parameter of the D-A equation as a measure of the hydrophobic-hydrophilic character is proposed. When the information obtained from the E parameter is compared with the information that can be obtained from other parameters used in the literature to characterize the hydrophobicity of materials, it is found that the former is more sensitive and is more directly related with the shape of the adsorption isotherms which, ultimately, is the more direct manifestation of the hydrophobic-hydrophilic properties of a given material.

Keywords: hydrophobicity, water-adsorption, zeolites, pillared clays, activated-carbons

Introduction

The adsorption of water vapour in porous materials is an important subject due to a number of aspects that, ultimately, are related with the hydrophobic-hydrophylic properties of solid surfaces. Examples of situations where the water adsorption is relevant, besides the obvious desiccation processes (Colier et al., 1986) are those related with the abatement of volatile organic compounds (VOCs) which are, in many situations, toxic and carcinogenic substances (Stenzel, 1993; Hamad et al., 1997; Pires et al., 2001). In fact, water vapour is, in most cases, also present in the atmospheres that are to be purified, or that are to be sampled for the control analysis of VOCs (Schumaker et al., 1992; Gawlowski et al., 1999; Brancaleoni et al., 1999; Giaya et al., 2000). It is important to emphasize that, although water adsorption is involved in important practical processes, the mechanism of the adsorption of water is not fully understood and is still object of discussion (Gregg and Sing, 1982; Stoeckli and Huguenin, 1992; Do and Do, 2000).

The different types of microporous materials that are relevant, or have potential interest in adsorption, can be grouped mainly in three families: active carbons, zeolites and, more recently, materials obtained from intercalation processes, as pillared clays (PILCs). It is usually accepted that the surfaces of activated activated carbons are mostly hydrophobic, although the adsorption of water can occur in the oxygen-containing sites that exist in a small fraction of the total area (Kraehenbuehl et al., 1986). On the other hand, a large number of zeolitic structures have a great affinity to water but the degree of hydrophilicity is, for a given structure, related into a certain extent with the chemical composition of the framework (Chen, 1976; Flanigen et al., 1978; Li et al., 1991). The pillared clays are obtained from the intercalation of swelling clays by large oxygen-containing cations and subsequent calcinations. The preparation methods and the textural and surface chemistry properties of PILCs were reviewed

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by different authors (Pinnavaia, 1983; Vaughan, 1996; Clearfield, 1996; Gil et al., 2000). Compared with other adsorbents, pillared clays are, relatively new materials and, therefore, are less studied. In what concerns the water adsorption properties, PILCs can be considered as intermediate materials between active carbons and zeolites (Malla and Komarneni, 1990; Yamanaka et al., 1990; Zhu et al., 1995; Pires and Carvalho, 1997).

An important question in the studies dealing with the adsorption of water is the attempt to quantify the concept of hydrophobicity–hydrophilicity of a given solid. For this, there are different proposals in the literature, some of which are based on the measure of the water loss at different temperatures by thermogravimetry (Anderson and Klinowski, 1986) or by using data from thermogravimetry and nitrogen adsorption (Giaya et al., 2000). Kawai and Tsutsumi (1992) proposed the evaluation of hydrophilic-hydrophobic character by the measurement of immersion heats. The analysis of water adsorption isotherms has also been used to obtain information on the hydrophobic-hydrophylic nature of solid surfaces (Kraehenbuehl et al., 1986; Stoeckli and Huguenin, 1992; Stoeckli et al., 1994; Llewellyn et al., 1995; Salame and Bandosz; 1999; Olson et al., 2000; Matsumoto et al., 2001). Unlike what happens with the determination of textural parameters, as surface area or microporous volume, for which specific methods exist, the evaluation of the hydrophobic character has not, therefore, a well established methodology. This is even more relevant when rather different types of solid materials have to be compared as, for instance, when composite adsorbents need to be developed and one of these materials was supported in a polymeric matrix.

With this work the authors intended to contribute to the evaluation of the hydrophobic-hydrophylic properties of different families of microporous materials, namely active carbons, pillared clays and zeolites, based on the analysis of water adsorption isotherms. Typically, the determination of a water adsorption isotherm involves a great amount of time (several days), which can be considered a drawback for a characterization method. Nevertheless, in recent years, the development of high-precision automated apparatus allowed to partially overcome some inconveniences of this situation. The analysis of the water adsorption isotherms was made by the equation of Dubinin and Astakhov (D-A) (Dubinin, 1988, 1989; Bansal et al., 1988). The D-A equation had an empirical nature when was proposed, however, more recently, some authors (Chen and Yang, 1994) consider that the D-A equation can have a theoretical justification. This equation has the form:

$$w = w_0 \exp[-(A/E)^n] \tag{1}$$

where w is the amount adsorbed, at temperature T and relative pressure p/p^0, w_0 is the limiting adsorption in the micropores, A is the adsorption potential ($A = RT\ln(p^0/p)$) and n and E are temperature invariant parameters. It was shown that the D-A equation can describe the adsorption of water in activated carbons (Stoeckli et al., 1994) and zeolites (Simonot-Grange et al., 1991, 1992) but, to our best knowledge, the D-A equation has not been applied to the adsorption of water in a series of different families of microporous materials namely with the objective of using the energetic E parameter as an attempt to quantify their hydrophobic-hydrophylic properties.

Experimental

Materials

Three commercial activated carbons, labelled as RB1, RB3 and CarbTech were used. The surface chemistry of these samples was characterized by the method of Boehm titration, as described elsewhere (Boehm, 1994). Briefly, this method consists in equilibrating a given amount of solid (1 g was equilibrated during 24 hours) with different basic or acid solutions of NaOH, $NaCO_3$, $NaHCO_3$ and HCl, the excess of acid or base being titrated with NaOH or HCl, respectively. The results, expressed as type of site, total acidity and total basicity are given in Table 1. The pillared clay (labelled as PTS-PILC) was prepared according to a previously optimised method (Pires et al., 1997) and had a basal spacing of 1.8 nm. The NaY zeolite was from Aldrich and the dealuminated samples, labelled as SS(813,1093) and SS(813,1033,1093), were obtained from the intermediate NH_4Y form, by a well-studied

Table 1. Results of the Bohem titration of the activated carbon samples (sites in mmol g^{-1}).

Sample	Carboxylic	Lactonic	Phenolic	Total acidity	Total basicity
RB1	–	–	0.238	0.238	0.445
RB3	–	–	0.150	0.150	0.510
RB4	–	–	0.135	0.135	0.475
CarbTech	0.005	0.038	0.143	0.185	0.220

self-steaming (SS) method with different plateaus of temperature, for periods of 3 hours, namely 813 and 1093 K or 813, 1033 and 1093 K (Carvalho et al., 1990). The dealumination was confirmed by X-ray diffraction, infrared spectroscopy and low temperature nitrogen adsorption. The Si/Al ratios of the samples were previously determined (Pires et al., 2002) and add the values of 2.3 for the initial NaY zeolite and 4.4 and 17.7 for the SS(813,1093) and the SS(813, 1033,1093) samples, respectively. A well-characterised silica-alumina, currently used as reference material for nitrogen adsorption (Micromeritics P/N 004/146821/00), was also studied.

Methods

Thermogravimetry

To compare the information obtained in the present work with that obtained with other methodologies proposed in the literature, the samples were hydrated during three days, in a desiccator saturated with moisture at 298 K, after which a given amount (typically 25 mg) was submitted to a thermogravimetric analysis. This was made in a TG-DSC model 111 (Setaram, France), which had sensitivity of 10 μg. The experiments were made under a flux of dry nitrogen with a ramp of 2.5 K/min between 298 and 673 K.

Adsorption Isotherms of Nitrogen at 77 K

Before the experiments the samples (about 50 mg) were outgassed at 573 K, for 2 h after a ramp of 10 K/min, under a dynamic vaccum better than 10^{-2} Pa. In previous studies (Pires et al., 1991; Carvalho et al., 1996; Pereira et al., 1998) it was verified that no significant changes in the isotherms were noticed when longer outgassing times were used. Nitrogen was 99.995% pure and the data were collected, either in a manual Pyrex-made volumetric apparatus where the pressure readings were made with a model 600a (Datametrics, USA) pressure transducer, or in an automated instrument model ASAP 2010 (Micromeritics, USA).

Adsorption Isotherms of Water

The adorption isotherms of water were determined at 303 ± 0.1 K in an automated apparatus, model Omnisorp 100cx (Coulter, USA), using a fixed vapour dosing method. The outgassing conditions for all samples were similar to those used in the case of the nitrogen adsorption. The amounts adsorbed on an empty cell were used to correct the data of the adsorption isotherms. The adsorption of water in the above mentioned reference sample of silica-alumina, was also studied in a pyrex made manual volumetric apparatus, equipped with a pressure transducer model CMR 262 (Balzers, Germany). In the region of low relative pressures, the manual apparatus had an accuracy in the pressure readings that was lower than what is possible to achieve with the automated apparatus but, at higher pressure where the accuracy of both installations was comparable, the agreement between the data obtained by the two methods was better than 5%.

Results and Discussion

In Fig. 1, the adsorption isotherms on N_2 at 77 K are shown. The isotherms for the NaY and the activated carbon samples are of type I according to the IUPAC classification (Sing et al., 1985). In the case of the dealuminated zeolites and the pillared clay, a slight hysteresis (not shown) was noticed. This most probably results from the adsorption in the inter crystalline space, due to the aggregation of the small particles of the pillared clay and as a result of the dealumination process in the case of the dealuminated zeolites. For these latter solids the decrease in the adsorption capacity, in relation to the sodium form of Y zeolite, is noticeable. The nitrogen adsorption isotherm in the silica-alumina sample was characteristic of a mesoporous material, that is, type IV with a hysteresis loop (not shown) of type H1 according of to the IUPAC classification (Sing

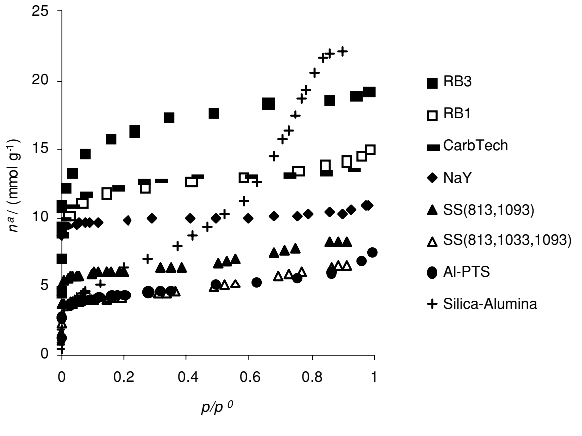

Figure 1. Nitrogen adsorption isotherms at 77 K for the different solids.

Table 2. Equivalent surface areas (A_{BET}), microporous volumes (w_{micro}) and total pore volumes ($w_{\mathrm{micro+meso}}$) obtained from the nitrogen adsorption at 77 K. The w_{micro} values computed by the Dubinin-Radushkevich method (Gregg and Sing, 1982; Yang, 1987) and the $w_{\mathrm{micro+meso}}$ were obtained from the amounts adsorbed at $p/p^0 = 0.95$.

Sample	A_{BET} ($\mathrm{m^2\,g^{-1}}$)	w_{micro} ($\mathrm{cm^3\,g^{-1}}$)	$w_{\mathrm{micro+meso}}$ ($\mathrm{cm^3\,g^{-1}}$)
NaY	830	0.34	0.36
SS(813,1093)	505	0.21	0.29
SS(813,1033,1093)	348	0.16	0.24
Silica-Alumina	210	0.085	0.77
PTS-PILC	355	0.16	0.24
CarbTech	977	0.41	0.49
RB1	985	0.44	0.51
RB3	1305	0.53	0.66

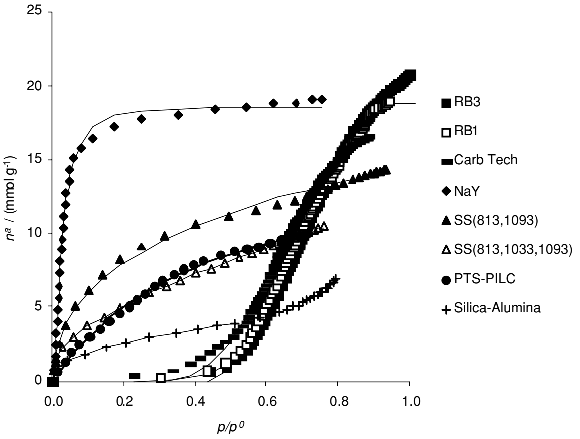

Figure 2. Water adsorption isotherms at 303 K in the studied materials.

et al., 1985). The textural parameters in Table 2 were obtained from the analysis of the curves in Fig. 1.

In Fig. 2, the water adsorption isotherms are shown. Contrarily to what happened to the nitrogen adsorption, the shape of the curves is now much more dependent on the type of material, ranging from the high rectangular character of the water isotherm in NaY zeolite, to the S-shaped curves in the case of activated carbons as reported by other authors (Stoeckli, 1994; Salame and Bandosz, 1999, 2000). Qualitatively, and as expected, the pattern of the water isotherms in Fig. 2 exemplifies the degree of hydrophobicity of the different materials studied, ranging from the more hydrophilic NaY zeolite, where the water molecule is expected to interact strongly, namely with the charge compensating sodium ions, to the more hydrophobic nature of the surface of active carbons.

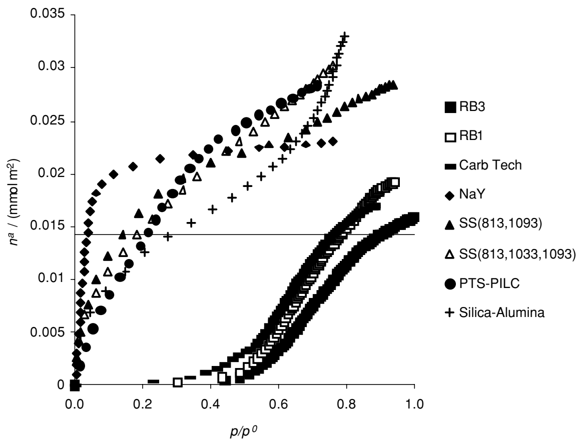

Figure 3. Water adsorption at 303 K in the studied materials, expressed by unit of surface area (A_{BET} measured with nitrogen at 77 K). The solid line represents the amount that corresponds to a monolayer of liquid water at 303 K in a section of one square meter.

The effect of the nature of the surface on the adsorption of water can be evidenciated if the adsorbed amounts are expressed by unit of surface area, that is, dividing by the respective A_{BET} values (measured with the nitrogen adsorption) although, due to the fact that we are dealing with microporous solids, theA_{BET} values have to be interpreted with caution. The results are expressed in Fig. 3 that shows that the more hydrophobic materials, always adsorb less water per unit of area in all range of relative pressures. In the case of the dealuminated samples, the absolute values are always inferior to those obtained in the NaY zeolite (Fig. 2). However, in Fig. 3 the curves for the dealuminated samples cross the isotherm for NaY zeolite, what may result from the formation of mesopores, due to the dealumination process.

As mentioned before, the D-A equation was fitted to the experimental data using the non liner least squares method to the adsorbed amounts as a function of the adsorption potential (A), obtaining directly the values of E, w_0 and n. The correlation coefficients were between 0.998 and 0.9995, and the chi-square of the fit were between 0.14 and 0.003, confirming that the D-A equation can be successfully used to describe the water adsorption isotherms in the studied materials, illustrated by the solid lines in Fig. 2. In the case of the silica-alumina the range of the applicability of the equation was until relative pressures of 0.4. For all the other samples, the D-A equation could be applied until

Table 3. Parameters obtained from the fitting of the D-A equation (see text) to the isotherms of adsorption of water at 303 K.

Sample	E (kJ mol^{-1})	w_0 (cm^3 g^{-1})	n
NaY	9.98	0.33	4.35
SS(540,820)	6.59	0.26	1.11
SS(540,760,820)	4.46	0.23	0.83
Silica-Alumina	5.42	0.10	0.89
PTS-PILC	4.87	0.19	1.46
CarbTech	1.34	0.31	2.28
RB1	1.14	0.35	1.97
RB3	1.04	0.36	1.92

relative pressures near 0.9. The parameters of the D-A equation (E, w_0 and n) are given in Table 3. The relative standard deviations associated to the estimation of the E parameters were of 7% for the silica-alumina sample and less than 3% for the other solids. In the case of the water adsorption in activated carbons the values of the E parameter that can be found in the literature are in the range 0.8–2.5 kJ mol^{-1} (Stoeckli et al., 1994) and, therefore, the values obtained in the present work are within this range. For the NaY zeolite our E values are lower than those reported by Simonot-Grange et al. (1992) but this can be due to the fact that the D-A equation, apparently, was not fitted to the entire range of data in that study. The case of the silica-alumina sample is quite peculiar in this context because, unlike the other materials, this sample is mainly a mesoporous solid and the shape of the water adsorption isotherm prevents a precise definition of the w_0 parameter. It must be emphasize that, the results of the application of the D-A equation to this solid must be interpreted with caution since this is not a microporous material. Therefore, the parameters in Table 3, for the silica-alumina sample, were obtained with the data for the first part of the isotherm, that is, for relative pressure below 0.5. As is it displayed in Table 3, no apparent relation with the degree of hydrophobicity of the surface seems to be associated with the n parameter. In what concerns the w_0 values, these are always similar or higher than the microprous volume, estimated from the low temperature nitrogen adsorption (Table 2), in the case of the more hydrophilic materials, and are lower in the case of the activated carbons. The fact that in the more hydrophilic substances the adsorbed amounts exceed the equivalent amount of a monolayer of liquid water (solid line in Fig. 3) at low relative pressures (below $p/p^0 = 0.2$), contrarily to what happens with the activated carbons, it is most probably a clear indication that different mechanisms of water adsorption are present, in the inorganic materials and in the activated carbons. In fact, in these latter materials, the amount of a monolayer of liquid water is only exceeded at high relative pressures (above 0.7) where other phenomena, which are not so directly related with the nature of the surface, as cooperative adsorption (Gregg and Sing, 1982), are also relevant.

In the case of the E parameter, the values are in line with the hydrophobic-hydrophilic character of the surfaces (Fig. 3) suggesting that a quantification can be made on this basis. The higher value is registered for the NaY zeolite (about 10 kJ mol^{-1}) and the lower values were given in the case of the activated carbons (<2 kJ mol^{-1}). The pillared clay has an E value about half of the NaY zeolite, comparable to the more dealuminated sample. It must be emphasized that the difference in the values of E found between the Carb Tech sample by one side and the RB1 and RB3 samples by other side, although in the range of 0.2–0.3 kJ mol^{-1}, is also in line with the results of the characterization of these solids by Bohem titration, as given in Table 1. In fact, evidences for the existence of a higher number of stronger acid sites (carboxylic and lactonic) for Carb Tech were given by the Bohem titration, which could promote stronger interactions with the water molecules than in the case of the RB1 and RB3 samples.

From what was exposed, the E parameter, which can be related with the heat of adsorption (Stoeckli et al., 1994, 1994a), seems to express adequately the degree of hydrophobicity of a given surface. However, to compare the information on the hydrophobicity of the surfaces obtained from the E values with the information obtained from other parameters used in literature, a normalization was made and Fig. 4 was constructed. The h_1 values were obtained from thermogravimetric measurements, by dividing the amount of the water loss up to 423 K by the value of the water loss until 673 K (Anderson and Klinowski, 1986). h_2 was computed by subtracting from the total pore volume, estimated from nitrogen adsorption, the volume that corresponds to the water loss above 423 K and dividing the result by the total pore volume (Giaya et al., 2000). To compare with h_1 and h_2, which vary between 0 and 1, the h_E parameter was defined as the ratio between the lower value of E and the value of E for a given material, thus attributing the value of 1 to the more hydrophobic material. Figure 4 show that any of the three parameters can obviously differentiate the NaY zeolite from

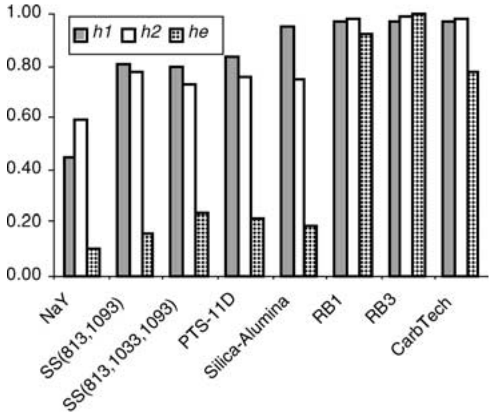

Figure 4. Hidrophobicity indices obtained from different methodologies: h_1 from thermogravimetric measurements; h_2 from thermogravimetric and nitrogen adsorption data; h_E from the values of E obtained by the D-A equation fitted to water adsorption data.

the activated carbons or from the dealuminated samples. However, for instance, the dealuminated samples and the pillared clay, according to h_1 or h_2, are almost indistinguishable which, inclusively, is not in agreement with the differences found in the water adsorption isotherms for these samples, but can be differentiated with h_E. In this case, the values of h_E have the expected trend and, for instance, the material SS(813,1033,1093) has a higher h_E than the sample SS(813,1093). Moreover, in the case of the activated carbons, where the values of water loss above 423 K are very small, the values of h_1 or h_2 are practically the same, unlike what happens with h_E, and the differences can be correlated with the results of the characterisation of acidity of the samples (Table 1), showing that the total acidity and, mainly the presence of the more strong acid centres, make the activated carbons less hydrophobic.

In conclusion, the values of E, obtained from the fitting of the D-A equation to the water adsorption data can be used to evaluate the hydrophobic-hydrophylic properties of materials that, actually, can be rather different in their nature. Moreover, the E values can be the basis of a definition of a scale of hydrophobicity of solids, comparable to other more empirical scales, but with the advantage of being more sensitive, i.e., more directly related with the shape of the water adsorption isotherms.

Acknowledgment

M.L. Pinto thanks Fundação para a Ciência e Tecnologia (FCT) for a PhD grant. This work was partially funded by FCT thought Centro de Ciências Moleculares e Materiais.

Nomenclature

A	Adsorption potential (D-A equation)
A_{BET}	Specific surface area, or "apparent" specific surface area in the case of the microporous solids, obtained from the nitrogen adsorption data at 77 K, by the BET model
E	Energetic parameter (D-A equation)
h_1	Hidrophobicity indice, from thermogravimetric measurements
h_2	Hidrophobicity indice, from thermogravimetric measurements
h_E	Hidrophobicity indice, from the E parameter of the D-A equation
n	Exponent in the D-A equation
n^a	Adsorbed amounts (mmol g^{-1})
p	Pressure
p^0	Saturation pressure
w	Adsorbed amount (cm^3 g^{-1})
w_0	Limiting adsorption (cm^3 g^{-1})
w_{micro}	Microporous volume, obtained from the nitrogen adsorption data at 77 K, by the Dubinin-Radushkevich method.
$(w_{\mathrm{micro+meso}})$	Total pore volume (microporores + mesopores) obtained from the nitrogen adsorption at 77 K.

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