HYDROPHILICITY QUANTIFICATION OF HIGHLY HYDROPHOBIC DECADODECASIL 3R*

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Sorption properties of the clathrasil Decadodecasil 3R (DD3R) have been investigated by measuring equilibrium sorption isotherms of water. The dependence of the adsorbed amount on the relative water pressure has been found almost invariant of temperature. This behaviour has been explained by a scarce population of hydrophilic sorption sites isolated sufficiently from each other and by a poly-molecular adsorption on them. Such a behaviour is consistent with a simple BET model. Both the low concentration of hydrophilic sorption sites and their weak strength confirm the generally accepted assumption on weakly hydrophilic character of DD3R.
Key words: Decadodecasil; Clathrasil, isotherm; Sorption of water; Heat of wetting; Hydrophilicity scale.

The first synthesis of clathrasil Decadodecasil 3R has been reported by Gies[1]. This has been accomplished under hydrothermal conditions using 1-aminoadamantane as a template. Another investigation of synthesis conditions for DD3R has been performed by Gunawardane *et al.*[2] who examined the dependence of phase composition and crystallisation yield of synthesis on template concentration and temperature. An optimum procedure for DD3R crystallisation which ensures the phase purity of DD3R yield has been developed by den Exter *et al.*[3,4].

The structure of clathrasil DD3R has been solved by Gies and co-workers[1,5]. It should be noted that an essential difference exists between clathrasils and zeolites, as in

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contrast to zeolite frameworks, clathrasils consist of a unique linkage of window connected cages.

DD3R crystallises in space group $R\bar{3}m$ with unit cell (UC) parameters $a = b = 1.3660(3)$ nm and $c = 4.0891(8)$ nm. The crystal structure is built by corner-shearing [SiO$_4$] tetrahedra. The UC is thus composed of 120 SiO$_2$ units which are arranged into 9 pentagonal dodecahedra [5^{12}] cages and 6 decahedra [$4^3 5^6 6^1$] cages. The mentioned building units, usually referred to as fundamental cages, are shown in Figs 1a and 1b using the representation based on Si and O atoms.

The most interesting property of DD3R structure consists in the fact that the fundamental cages form in the clathrasil framework large 19-hedron [$4^3 5^{12} 6^1 8^3$] cavities which are interconnected through 8-membered rings (pore size 0.44×0.36 nm^2). There are six 19-hedra in UC. Thus, the 19-hedron cavities form a two-dimensional pore system between dodecahedral layers. Figure 1c shows 19-hedron cavity and Fig. 2 represents a projection of the clathrasil framework parallel to [5^{12}] layer. We generated
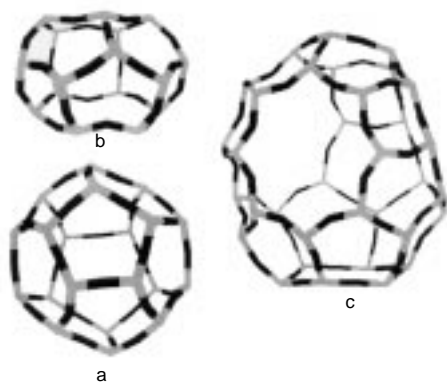

FIG. 1

Building units of the clathrasil DD3R. Black sections: oxygen atoms, gray sections: silicon atoms; a pentagonal dodecahedra, b decahedra, c 19-hedra cavity
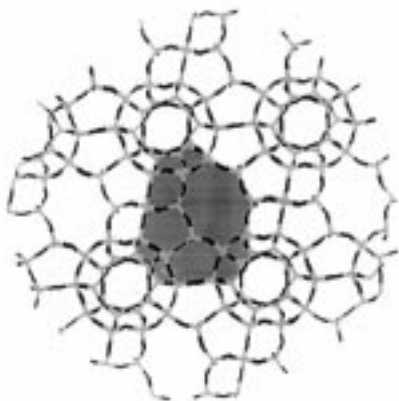

FIG. 2

Projection of clathrasil framework parallel to [5^{12}] layer

all the above details of the DD3R structure using the atomic parameters given by Gies[1]. On the basis of the above structure data, the volume of the unit cell can be estimated as

$$V_{UC} = a^2 c \sin 120° = 6.8027 \ [nm^3] \ . \tag{1}$$

This gives an estimate of apparent density ρ_c of clathrasil crystals (free of guest molecules) as

$$\rho_c = \frac{120 M_{SiO_2}}{V_{UC} N_A} = 1.714 \ [g \ cm^{-3}] \ , \tag{2}$$

where N_A denotes the Avogadro number.

As-synthesised clathrasil DD3R contains guest molecules in its framework. First of all the 1-aminoadamantane molecule ($C_{10}NH_{17}$) is located in each 19-hedron cavity of DD3R, which can only be removed upon calcination at high temperature[1] (973 K). Decahedron cages which are estimated to amount only to 0.035 nm³ of free volume are too small to accommodate guest molecules[1]. On the other hand, the pentagonal dodecahedron cages, with free volume of the cage amounting to approximately 0.070 nm³ were found to contain, upon synthesis atmospheric gases, mainly N_2 (ref.[1]).

After template removal, the large cavity may host molecules of sorbing species. The corresponding free volume of the large cavity has been reported in ref.[1] to amount to about 0.35 nm³. So far there exist only limited data on sorption of guest molecules into DD3R.

Sorption of N_2 indicates an accessible microporous void volume of 0.15 ml g⁻¹, whereas the free void volume calculated on the basis of geometric considerations has been estimated as 0.18 ml g⁻¹ (*cf.* ref.[5]). Further on, for methane, ethane, propane, butane, isobutane, oxygen, ammonia, dinitrogen oxide, hydrogen, CO_2, ethylene, propylene and butadiene sorption isotherms were measured at 296 K by some of us[3,4] using a volumetric apparatus. A preliminary sorption measurement of water vapour on DD3R (ref.[4]) confirmed an expected low hydrophilicity of the material.

In a perfect all-silica material containing exclusively Si–O–Si bonds the adsorption of water vapour should be negligible. It seems of interest to characterise all-silica materials of the clathrasil type by adsorption of different probe molecules to get information on number, strength and nature of hydrophilic sorption sites. The present paper aims to investigate the sorption energetics of water onto DD3R. The heats of adsorption will be evaluated *via* analysis of the adsorption isotherms measured at different temperatures and the system will be located on the hydrophilicity scale by comparing the water immersion heat values for other weakly hydrophilic systems.

EXPERIMENTAL

Adsorbent. Crystals of clathrasil DD3R were obtained as described in detail elsewhere[3,4]. To remove the template, the as-synthesised crystals were calcinated for 6 h at 973 K with heating rate 1 K min^{-1}.

The characterisation of both the as-synthesised DD3R and the calcinated material by XRD and FTIR is presented in refs[3,4]. These analyses have shown that the high calcination temperature does not damage the crystal structure. Elemental analysis of the crystals performed using ICP-AES has shown that clathrasil DD3R is an all-silica material. The crystal size was found to be about 5 µm. This leads to an estimation of the value of the outer surface of the crystals $s_1 \approx 1$ m^2 g^{-1}.

Apparatus and procedures. The adsorbed amount of redistilled water has been measured using a gravimetric vacuum apparatus. Samples of 100 to 150 mg were placed on glass pans and suspended on quartz spirals with a sensitivity ranging from 1.1 to 1.7 mg mm^{-1}. The extension of the spirals has been measured by means of the cathetometer with the accuracy of ±0.01 mm. The pressure of the sorbing species was measured using an U-manometer. A more detailed description of the apparatus is given elsewhere[6].

Prior to a series of adsorption measurements, the samples were activated at 393 K and 9 mPa for 24 h and then at 650 K and 9 mPa for 48 h.

The measurement of the adsorption was performed under constant pressure conditions. Liquid water was placed into a small polyethylene vessel and sealed into the glass apparatus. Water was then kept at constant temperature with an accuracy of ±0.05 K. The polyethylene material used prevented a crash of the apparatus when water was frozen.

Adsorption isotherm of N_2 on DD3R has been measured at 77.3 K by a routine volumetric method after outgassing the sample at 448 K.

RESULTS AND DISCUSSION

Data Treatment, Model Statement and Testing

Using a classical gravimetric apparatus with a quartz spiral, we achieved for water vapour adsorption a satisfactory measurability only in the relatively narrow temperature region from 303 K to 333 K. The upper limit of the relative pressure of water vapour used in the present paper is 0.75. Due to a low hydrophilicity of the adsorbent, adsorbed amounts measured exhibited a considerable scatter. This drawback has been compensated by repeating the measurements of the adsorption isotherms in several series of adsorption and desorption runs.

The results of all the sorption measurements for water are summarised in Fig. 3 which represents a plot of the adsorbed amount of water a (mg g^{-1}) *vs* the partial pressure of water vapour at four temperatures. Figure 4 shows the adsorbed amount a plotted against the relative pressure $P = p/p_s$ of water vapour (p_s is the pressure of saturated vapour at the sorbent temperature).

The primary experimental findings with respect to the adsorption of water are as follows:

a) The maximum adsorbed amount a_{max} observed in this investigation was estimated to about 15.5 mg g^{-1} ($\approx$ 1.5 wt.%). It occurred for $p/p_s = 0.75$ at $T = 303$ K).

b) The adsorption isotherms exhibit only an insignificant variance with temperature, *cf*. Fig. 4 where all the experimental points of Fig. 3 tend to be condensed into a narrow stripe along the solid line which represents the best fit of the plot by Eq. (*3*).

$$a = \frac{AP}{(Q - P)(1 + BP)} \tag{3}$$

In Eq. (*3*) *A*, *B* and *Q* represent empirical constants $A = 125.39$ mg g^{-1}, $B = 15.48$ and $Q = 1.25$.

c) Adsorption isotherm described by Eq. (*3*) belong to the type II (according to the Brunauer *et al.*[7] classification). There is missing a characteristic feature of highly hydrophobic adsorbents *i.e.* that the adsorption isotherms for water vapour on such ad-

F$_{IG}$. 3
Plot of adsorbed amount of water, *a*, *vs* partial pressure, p_{H_2O} for water vapour sorption on DD3R; ○, ● $T = 303$ K; Δ, ▲ $T = 313$ K; ▫, ■ $T = 323$ K; ▽, ▼ $T = 333$ K; empty symbols: adsorption, filled symbols: desorption
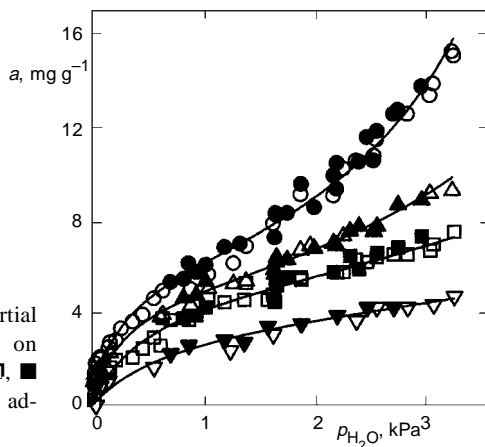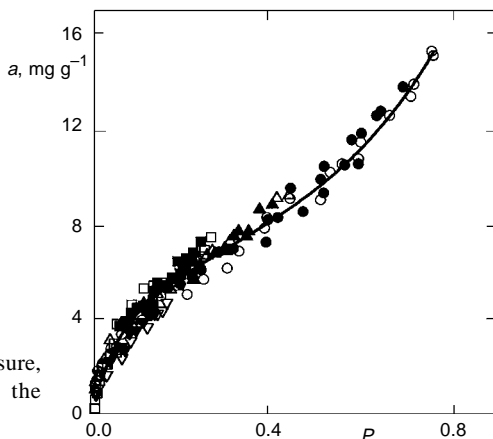
F$_{IG}$. 4
Plot of adsorbed amount, *a*, *vs* relative pressure, *P*, for water vapour sorption on DD3R; the nomenclature is the same as in Fig. 3

sorbents are in their initial region concave with respect to the axis of adsorbed amount (this property is an attribute of isotherm types III and V). Following the nomenclature by Gregg and Sing, one can characterise this isotherm as the isotherm with sufficiently sharp "knee" (ref.[8]) in other words, an estimation of inflex position on the curve would be possible with a sufficient accuracy.

d) The character of the distribution of adsorption and desorption points along the solid line on Fig. 4 does not indicate the existence of a hysteresis loop.

e) The adsorption isotherm of nitrogen does not seem to exhibit any hysteresis for $p/p_s > 0.4$ (*cf.* Fig. 5).

Expressed in terms of bulk liquid water, the maximum adsorbed amount of water $a_{max} = 1.5 . 10^{-2}$ ml g^{-1}. Comparing this quantity with the limited accessible volume of the intracrystalline space which has been estimated on the basis of N_2 sorption as 0.15 ml g^{-1}, one can see that the degree of volume filling $\Theta_v = 0.102$. The number of water molecules N_{H_2O} per 19-hedron cavity is obtained as adsorbed amount of water vapour a (mg g^{-1}) multiplied by the factor $F = 6.5 . 10^{-2}$ (molecule mg^{-1}) (g cage^{-1}). This leads to $(N_{H_2O})_{max} \approx 1$ molecule cage^{-1}. Theoretically, the 19-hedron cage could accommodate about 10 water molecules.

The form of the sorption isotherm (type II) is consistent with BET models valid for free surfaces or fine capillaries with no constraints imposed on the adsorption from the opposite pore walls. The opposite case would result in the existence of a saturation plateau for high values of *P*. We cannot exclude this situation to occur in our system in the vicinity $P \to 1$ which would result into the isotherm of the type IV.

It should be noted that the BET model is preferentially applied to the adsorption on non-porous or macro/mesoporous solid systems, while the sorption in microporous
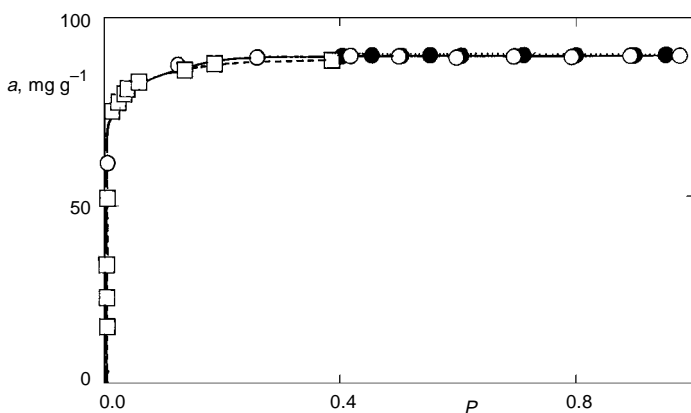
Fig. 5
Plot of adsorption isotherm for N_2 on DD3R at 77.3 K. 1st adsorption run ◯ (———); desorption run ● (· · · ·); 2nd adsorption run ☐ (– – – –)

solids represents an application domain for volume filling theories (*e.g.* the Dubinin–Radushkevich isotherm[8]), for different variants of cell theories based on statistical thermodynamics or for models involving the treatment of energetic heterogeneity of the sites. The Dubinin–Radushkevich or Dubinin–Astakhov isotherm[8] would, however, give rise to an isotherm of the type II only when adsorption in micropores acts in superposition with capillary condensation in a mesoporous system (*cf.* analysis in ref.[8]).

In our unconsolidated beds of DD3R crystals used for gravimetrical sorption measurements there is no developed mesoporous structure in the intercrystalline space. A rough estimate of the size of the intercrystalline pores is about 2 μm (estimated on the basis of the crystal size) and the specific surface of the intercrystalline pores is about 1 m^2 g^{-1}. Thus, the prevailing portion of the intercrystalline space consists of macropores and only a small portion of that space formed by constrictions around crystal contacts can be considered as mesopores. In this respect there are relevant equilibrium sorption measurements of water vapour on granulated 4A and 5A zeolites performed by Dubinin *et al.*[9]. These materials are strongly hydrophilic with smaller pores of intercrystalline space (only 6% of the intercrystalline pore volume is formed by pores with a diameter larger than 0.7 μm) as compared with our DD3R beds. The corresponding isotherms for water adsorption given in ref.[9] start to be concave with respect to the axis of adsorbed amount approximately for $P > 0.9$. We suspect that with a weakly hydrophilic material of greater pore size in the intercrystalline space, the capillary condensation will not occur even at higher P.

The N$_2$ adsorption did not show any hysteresis in the relevant region of P which excludes a significant volume of mesopores. We can conclude that the adsorption isotherms in Figs 3 and 4 reflect only the water behaviour in the micropores of DD3R.

We adopt as a working hypothesis the assumption that a layer-by-layer adsorption takes place on an array of hydrophilic adsorption sites in cages. A generally accepted concept of a co-operative process for micropores filling consisting of a rapid succession of stages: monolayer formation, condensation, promoted condensation[8] seems to be inadequate for the investigated system.

Another model which also disregards the stage of promoted condensation has been developed by Dubinin and Serpinsky to describe adsorption of water vapour in microporous carbonaceous adsorbents[10].

Our hypothesis is supported by a scarce population of hydrophilic sorption sites in DD3R which follows from the low value of a_{max}. When less than one hydrophilic sorption site exists per 19-hedra for stochastically distributed sites, the lateral water–water interactions between molecules residing on neighbouring hydrophilic sorption sites might be absent and the above step of promoted condensation would be prevented. For a regular arrangement of hydrophilic sites an optimum co-operation between sites might exist for sites located in 8-membered oxygen rings shared by neighbouring cages. In the latter case, the upper limit to adsorbed amount with no lateral interactions

might be lower *i.e.* the adsorbed amount should be less than 0.5 molecule per cage. For both the above situations the adsorption may be consistent with BET models in that water chains or columns are formed on the first adsorbed molecule. One can complete the above assumed molecular picture by the assumption that for $P < 0.75$ no constraints from the opposite walls act on building the molecular multilayer in cages.

The above hypothesis may be tested using a simple variant of the BET model which is valid for free surfaces. When doing so, one has to keep in mind that an application of simple BET model is in our case connected with averaging a potentially nonuniform energy distribution of hydrophilic sites over all the hydrophilic sites on the surface. The mathematical description of the BET model used (ref.[11]) is given by Eq. (*4*):

$$a = \frac{k\sigma_0 P}{(Q - P)[1 + (k-1)P/Q]} \ .$$

(*4*)

In this equation σ_0 denotes the sorption capacity of the monolayer expressed in the same units as adsorbed amount *a*. The parameter $Q = q/p_s$ and the quantity *q* has a dimension of pressure. (Generally $q \neq p_s$, for the case $q = p_s$ Eq. (*4*) reduces to the most common form of BET equation.) For the quantity *k* de Boer gives the following expression[11]:

$$k \approx \exp\left[\frac{Q_a - Q_l}{RT}\right] \ .$$

(*5*)

Q_a and Q_l denote the heat of adsorption of the sorbing species on the clean adsorbent surface and its heat of condensation, respectively.

To examine the above hypothesis, we applied in a separate way an optimisation process to individual isotherms plotted in co-ordinates *a vs P*.

The results of the data optimisation are given in Table I.

The strength of the hydrophilic sites. The quantity $Q_a - Q_l$ which enters Eq. (*5*) is frequently termed net heat of adsorption[12]. Hydrophilicity of a solid material can rigorously be treated in terms of Helmholtz or Gibbs energy. As an adequate characteristic for practical applications one can also define a hydrophilicity scale using some enthalpic function. In the present study, the net heat of adsorption and the parameter

$$\delta = \frac{Q_a - Q_l}{Q_l} 100$$

(*6*)

 will be used as quantitative characteristics of hydrophilicity.

The adequacy of the net heat of adsorption to characterise the hydrophilic character of solid surfaces has been shown *e.g.* by Goldmann and Polanyi[13] who demonstrated

that $Q_a - Q_l$ is identical with the differential heat Q_w of wetting. Q_w is also accessible from calorimetric measurements of heat effects during wetting of a solid material by an appropriate amount of liquid or from the results of immersion measurements if heat effects are measured using a sufficient excess of wetting liquid. The primary calorimetric data are integral and the most straightforward information of that kind is the immersion heat Q_{im} measured in dependence on the degree of preadsorption. Thus, the differential net heat of adsorption Q_w is the measure of hydrophilicity strength of those sites which are occupied within the region of adsorbed amounts a and $a + da$. An average strength of hydrophilic centers which adsorb water in a finite interval of adsorbed amount a_1, a_2 with $a_1 < a_2$ can be expressed as:

$$\overline{Q_w} = \frac{\int_{a_1}^{a_2} (Q_a - Q_l)\, da}{a_2 - a_1} \ . \tag{7}$$

Overall characteristics of material hydrophilicity. As an overall characteristic of material hydrophilicity, one can use either the above immersion heat measured with an initially clean sample surface *i.e.* $Q_{im,0}$ or the corresponding integral net adsorption heat $Q_{w,int}$. Both the effect of hydrophilicity strength of the adsorption sites and that of their number are involved and the heat is then related to the unit of solid surface or mass. The thermodynamic basis of wetting phenomena is given *e.g.* by Harkins and Jura[14] and by Zettlemoyer and Narayan[15]. Using our nomenclature, one can write the following relation between the immersion and adsorption heat:

TABLE I
Results of data fitting by Eq. (*4*)

Parameter	*T*, K			
	303	313	323	333
p_s, kPa	4.242	7.376	12.33	19.92
Q_l, kJ mol^{-1}	43.702	43.295	42.858	43.436
k	22.44	22.00	23.73	21.47
Q	1.177	0.910	0.628	0.383
q, kPa	4.994	6.712	7.745	7.628
σ_0, mg g^{-1}	5.78	5.26	4.57	2.91
$Q_a - Q_l$, kJ mol^{-1}	7.84	8.04	8.50	8.49
δ, %	17.9	18.6	19.8	20.0

$$Q_{im,0} = \int_0^{a_s} Q_w \, da + h_l = \int_0^{a_s} Q_a \, da - a_s Q_l + h_l \ . \tag{8}$$

Equation (8) is applied mostly to unconsolidated non-porous powders. For such samples, the adsorbed amount a is related to the surface of the materials, a_s being the adsorbed equilibrium amount which corresponds to the saturation in gas phase at vapour pressure p_s. The term h_l represents the heat evolved when a solid preadsorbed in the gas phase in contact with vapour pressure p_s is immersed into liquid sorbate. It is often assumed for non-porous sorbents that h_l represents the surface enthalpy of liquid sorbate film formed at the solid surface at saturation of the adsorbent to a_s. Equation (8) will be used to define a hydrophilicity scale of sorbents based on immersion heats of non-porous solids in water.

For DD3R, the values of the net heats of adsorption and parameters δ are summarised in Table I. The temperature dependence of the parameters over the temperature interval is not very strong. The average values of these parameters over the temperature interval investigated, are

$$Q_a - Q_l = 8.2 \text{ kJ mol}^{-1} \quad \text{and} \quad \delta = \frac{Q_a - Q_l}{Q_l} \, 100 = 19.1 \ [\%] \ .$$

This result confirms a dominating role of water–water interactions in adsorption layer (along a direction "perpendicular" to the surface of the cage) as the net heat of adsorption for water on DD3R amounts to less than 20% of the condensation heat.

The number of hydrophilic adsorption sites. The average value σ_0 for the considered temperature interval was estimated to be $\sigma_0 = 4.63$ mg g^{-1}. Thus, the number of hydrophilic adsorption centres per 19-hedron equals to about 0.3 centres per cage. Apparently the occurrence of hydrophilic adsorption centres is not necessarily due to some regular points in the framework of DD3R but rather to a presence of some stochastically distributed defects. We cannot exclude the other possibility that water adsorption starts at constrictions of 8-membered rings but at this stage of investigation we consider this model as less probable.

Comparison of DD3R with Other Weakly Hydrophilic Materials

To complete the above picture, a comparison of properties of other weakly hydrophilic materials is given. A review on the water sorption on silica is given in ref.[8]. Similarly as in the case of carbonaceous sorbents, the type of isotherm and the amount of water adsorbed depend on the amount of oxygen surface species which are represented by silanol OH groups, whereas the Si–O–Si segments of the framework are considered to be hydrophobic. In the dependence on silica treatment, the material can be dehydroxylated and again rehydroxylated and thus there exists still a proportion between physi-

and chemisorbed water. For silica gels there is continuous transition of the isotherm type IV to type V when the temperature of silica gel pretreatment increases and the material becomes less hydrophilic. This behaviour has been observed *e.g.* by Naomo *et al.*[16] for both the silica gels and porous silica glasses. The nature of SiOH–H_2O complexes on partially hydrophobic non-porous silicas have intensively been investigated using near-infrared spectra by Klier *et al.*[17]. For a submonolayer region the complex has been evidenced in which SiOH is a donor and H_2O an acceptor of the hydrogen bond.

Relevant are also the adsorption measurements for water on annealed (at 973 K for 48 h) and unannealed quarz silica performed by Hackerman and Hall[18]. The isotherms are of type II and fully reversible *i.e.* on these types of non-porous silicas no chemisorbed water due to material rehydroxylation contributed to the water adsorption. This oc- curred because the annealed samples were carefully rehydrated prior to sorption meas- urements. Using the water isotherms treated by a simple BET model, the authors estimated the areas per water molecule in the monolayer as 0.132 nm^2 and 0.117 nm^2 for unannealed and annealed quartz, respectively. Based on the volume of the 19-hedra cage 0.35 nm^2 we have made for a comparison a rough estimate of the area per water molecule in the monolayer of DD3R. It amounts to about 8 nm^2. For silica materials, the isosteric adsorption heats were also estimated from adsorption isotherms[18]. They amount at a half monolayer coverage to about 58 kJ mol^{-1} and 56 kJ mol^{-1} for annealed and unannealed quartz, respectively. There is a steep decrease of the sorption heat with increased adsorbed amount so that when two monolayers are filled, the sorption heat values are 47.5 kJ mol^{-1} and 46.0 kJ mol^{-1} for annealed and unannealed sample, respectively. Another measurement of water adsorption on quarz has been reported by Sarakhov[19]. Although the form of the isotherms is essentially the same as in ref.[18] (type II), an irreversible behaviour of sorption isotherms has been found.

Scale of hydrophilicity. The scarce population of hydrophilic sites and the assump- tion on the absence of the promoted condensation stage makes it possible to disregard the difference between the surface of non-porous and microporous solids and to con- struct a hydrophilicity scale based on the net integral adsorption heat values for water adsorption on non-porous powders. Using Eq. (*8*) we have derived this scale from the literature data on immersion heats of various materials in water measured in the tem- perature region between 298 and 303 K. For h_1 we used the value 0.1195 J m^{-2}, calcu- lated according to the Gibbs–Helmholtz equation which, applied to the free energy of the unit of liquid surface, gives:

$$h_1 \approx u_1 = \gamma - T \frac{d\gamma}{dT} \ . \tag{9}$$

In this equation, u_1 is the internal energy of the unit of liquid surface at the temperature T and γ is the surface tension of the liquid. For water at temperature 300.5 K, $\gamma =$

$71.575 \cdot 10^{-3}$ J m^{-2} and dγ/d$T = -0.1595 \cdot 10^{-3}$ J m^{-2} K^{-1} (*cf.* ref.[20]). Using the above data, one obtains for $h_l = 119.5 \cdot 10^{-3}$ J m^{-2} and we used this value to convert the scale of immersion heats into the scale of integral net adsorption heats in accordance with Eq. (*8*). The hydrophilicity scale is presented in Fig. 6 and it can be seen that displacement of the scale given by the actual value of h_l is not negligible at the low hydrophilicity end of the scale. This had been pointed out in the fundamental paper on the thermodynamics of immersion by Harkins and Jura[14], particularly, one can see that in accordance with the above analysis, teflon and carbonaceous materials with low content of surface oxygen species are located at the negative values of the scale.

Location of the DD3R on the scale has been found using Eq. (*10*):

$$Q_{w,int} = 0.055 \, (Q_a - Q_l) \frac{\sigma_0}{A_s} \, , \tag{10}$$

where A_s is an estimate of the total geometric surface of all the 19-hedra in 1 g of the DD3R:

$$A_s = \frac{6A_{19\text{–hedra}}}{V_{UC} \, \rho_c} \, , \tag{11}$$

where $A_{19\text{-hedra}}$ represents an estimate of the geometric surface of one 19-hedra cage. Based on the volume of the cage of 0.35 nm^3, the estimate of A_s is 1 230 m^2 g^{-1} and $Q_{w,int}$ reaches the value $1.8 \cdot 10^{-3}$ J m^{-2}. Important is that an error of about 100% in estimation of A_s does not affect significantly location of DD3R on the hydrophilicity scale.

A question may arise whether a sign of $Q_{w,int}$ and Q_w determines the hydrophilic/hydrophobic character of the material and sites, respectively. We can accept the convention
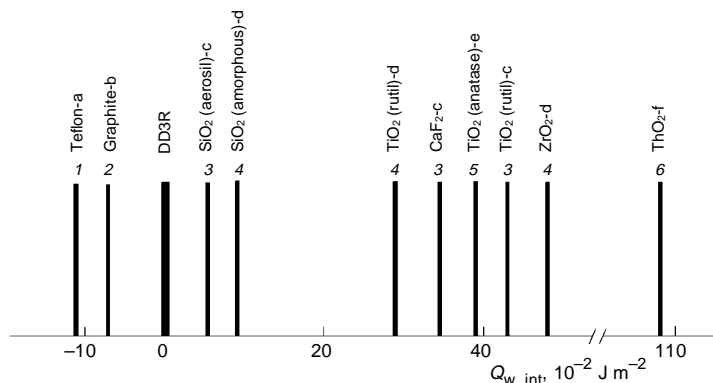

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Scale of hydrophilicity: *1* Ref.[21], *2* ref.[22], *3* ref.[23], *4* ref.[15], *5* ref.[24], *6* ref.[25]

reported in ref.[17] that materials with $Q_w > 0$ are hydrophilic and *vice versa*. Then it can be concluded that DD3R is just at the frontier between hydrophobic and hydrophilic materials. When considering, however, only microporous sorbents, DD3R seems to represent a material of a very high hydrophobicity among zeolites and their analogues. For these materials separate scales based on the net adsorption heat on one side and on the Polanyi adsorption potential on the other can be constructed.

This limiting behaviour of DD3R may be attributed to the choice of 1-aminoadamantane as a template for clathrasil synthesis. This molecule is present in the synthesis mixture mostly in a non-protonated state so that only a very minor part of template should be electrostatically compensated by negative charge in the clathrasil framework.

CONCLUSIONS

Hydrophilicity of clathrasil DD3R has been quantified by estimating the number and the strength of hydrophilic sites from adsorption isotherms of water. The population of hydrophilic sites has been found to amount to 0.3 sites per 19-hedron cage. Such a scarce population of hydrophilic sites enabled us to locate DD3R on a hydrophilicity scale based on net adsorption heats of water adsorption on non-porous powders of various nature. The net integral heat of adsorption for water on DD3R was estimated to amount less than 20% of the corresponding condensation heat. Thus, the hydrophilicity of DD3R is just at the border between hydrophobic and hydrophilic materials.

SYMBOLS

a	adsorbed amount, mg g^{-1}
A	parameter in Eq. (*3*), mg g^{-1}
A_s	surface area of all 19-hedra in 1 g of sorbent, m^2 g^{-1}
a, b, c	dimensions of UC, nm
B	parameter in Eq. (*3*)
h_l	surface enthalpy of liquid sorbate film, J m^{-2}
k	parameter in Eq. (*4*) defined be Eq. (*5*)
M	molal mass, mol g^{-1}
N_A	Avogadro number, mol^{-1}
p	partial pressure of sorbing species, kPa
p_s	pressure of saturated vapour at the temperature of sorption, kPa
P	relative pressure of sorbing species
q	parameter in Eq. (*4*), kPa
Q	parameter in Eqs (*3*) and (*4*) (short for q/p_s)
Q_a	differential heat of adsorption on clean surface of adsorbent, kJ mol^{-1}
Q_l	heat of condensation of sorbing species, kJ mol^{-1}
Q_w	differential heat of wetting (equal to the net heat of adsorption $Q_a - Q_l$), kJ mol^{-1}
$Q_{w,int}$	integral wetting heat, J m^{-2}
Q_{im}	immersion heat, J g^{-1}
s_l	outer surface of crystals, m^2 g^{-1}
T	temperature, K

V_{UC}	volume of UC, nm^3
u_l	internal energy of liquid surface, $J\ m^{-2}$
γ	surface tension of the liquid, $J\ m^{-2}$
δ	fraction of net adsorption heat in condensation heat, %
ρ_c	apparent density, $g\ cm^{-3}$
ρ_s	crystal density, $g\ cm^{-3}$
σ_0	sorption kapacity of monolayer, $mg\ g^{-1}$
Θ_v	degree of pore volume filling

REFERENCES

1. Gies H.: Z. Kristallogr. *175*, 93 (1986).
2. Gunawardane R. P., Gies H., Liebau F.: Z. Anorg. Allg. Chem. *546*, 189 (1987).
3. den Exter M. J., Jansen J. C., van Bekkum H. in: Stud. Surf. Sci. Catal. (J. Weitkamp, H. G. Karge, H. Pfeifer and W. Holderich, Eds), Vol. 84, Part B, p. 1159. Elsevier, Amsterdam 1994.
4. den Exter M. J., Zikanova A., Jansen J. C., van Bekkum H.: Unpublished results.
5. Alma-Zeestraten N. C. M., Darrepaal J., Keijsper J., Gies H.: Zeolites *7*, 81 (1989).
6. Zikanova A., Kocirik M.: Collect. Czech. Chem. Commun. *36*, 1225 (1971).
7. Brunauer S., Deming L. S., Deming W. S., Teller E.: J. Am. Chem. Soc. *62*, 1723 (1940).
8. Gregg S. J., Sing K. S. W.: *Adsorption, Surface Area and Porosity*. Academic Press, London 1982.
9. Dubinin M. M., Vishnyakova M. M.: Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk *1961*, No. 3.
10. Dubinin M. M., Serpinsky V. V.: Carbon *19*, 402 (1981).
11. de Boer J. H.: *The Dynamical Character of Adsorption*. The Clarendon Press, Oxford 1953.
12. Lamb A. B., Coolidge A. S.: J. Am. Chem. Soc. *42*, 1146 (1920).
13. Goldmann F., Polanyi M.: Z. Phys. Chem. *132*, 321 (1928).
14. Harkins W. D., Jura G.: J. Am. Chem. Soc. *66*, 919 (1944).
15. Zettlemoyer A. C., Narayan K. S. in: *The Solid–Gas Interface* (E. A. Flood, Ed.), Vol. l, p. 145. Dekker, New York 1967.
16. Naono H., Fujiwara R., Yagu M.: J. Colloid Interface Sci. *76*, 74 (1980).
17. Klier K., Shen J. H., Zettlemoyer A. C.: J. Phys. Chem. *77*, 1458 (1973).
18. Hackerman N., Hall A. C.: J. Phys. Chem. *62*, 1212 (1958).
19. Sarakhov A. I.: Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk *1956*, No. 2, 150.
20. *Handbook of Chemistry and Physics* (C. D. Hodgman *et al.*, Eds), Vol. II, p. 1989. Chemical Rubber Publishing Co., Cleveland 1954.
21. Chessick J. J., Healey F. H., Zettlemoyer A. C.: J. Phys. Chem. *60*, 1345 (1956).
22. Bartell F. E., Suggit R. M.: J. Phys. Chem. *58*, 36 (1954).
23. Zetllemoyer A. C., Chessick J. J., Hollabaugh C. H.: J. Phys. Chem. *62*, 489 (1958).
24. Wade W. H., Hackerman N.: J. Phys. Chem. *65*, 1682 (1961).
25. Holmes H. F., Fuller E. F., Jr., Secoy C. H.: J. Phys. Chem. *70*, 436 (1966).