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COMMENTS ON SURFACE STRUCTURE ANALYSIS BY WATER AND NITROGEN ADSORPTION

E. Robens[1*], *A. Dąbrowski*[2] *and V. V. Kutarov*[3]

[1]Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, Duesbergweg 10-14, D-55099 Mainz, Germany
[2]Wydziatu chemii, Uniwersytet Marii Curie-Skłodowskiej, Pl. Marii Curie-Skłodowskiej 2, PL-20-032 Lublin, Poland
[3]Physical Research Institute, University of Odessa, 27 Pastera St. Odessa 270100, Ukraine

Abstract

Specific surface area and pore size distribution are determined usually from adsorption isotherms at low temperatures using nitrogen or noble gases. These are not absolute parameters and the measuring methods are fraught with serious difficulties. General problems of sorption measurements and recent developments are discussed. To obtain information for practical purposes these measurements need to be supplemented by investigations of the sorbate/sorbent system used in practice. Results of the measurement of nitrogen and water vapour adsorption on different materials are compared.

Keywords: adsorption, fractality, nitrogen, surface, water vapour

Introduction

Adsorption methods are usually used to characterise dispersed or porous solids in relation to their processing by chemical treatment, application as reactant, adsorbent or catalyst. These methods are adequate because they make use of the same physical phenomena as used in the practical application of the material. The surface is subjected to adhering molecules. The extent of the surface and its structure is calculated by counting the molecules which are required to cover the surface or to fill a group of pores. The cross-sectional area or volume of the molecules, respectively, is used as yardsticks.

Usually adsorption isotherms are measured with nitrogen at 77 K or noble gases at 77 or 90 K [1] using gravimetric or volumetric/manometric apparatus. From the isotherm the specific surface area can derived by means of the standardised [2, 3] two-parameter equation of Brunauer, Emmett and Teller (BET) [4]:

$$n_\mathrm{a}=\frac{n_\mathrm{m}C(p/p_0)}{(1-p/p_0)[(1+(C-1)p/p_0)]} \tag{1}$$

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[*] Author for correspondence: E-mail: erich.robens@t-online.de

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where n_a is the number of molecules measured as a function of the pressure, p, related to the saturation pressure of the gas, p_0, n_m is the number of molecules in a monolayer covering completely the surface and C is the BET number. From n_m the specific surface area can be calculated assuming a value for the cross-sectional area of the adsorbed molecules. A molecular cross sectional area of 0.162 nm^2 is recommended for nitrogen at 77 K and 0.125 nm^2 for water at 298 K [5].

The thickness of adsorbed layers, t, as a function of the relative pressure is important [6]. Although it has been proved that the idea of a universal standard isotherm of a special adsorbate at any sorbent is unsatisfactory, deviations from an ideal curve form a basis of discussion. A reasonable value for a unimolecular layer thickness, t_m, of nitrogen at 77 K is 0.345 nm and of water at 298 K 0.30 nm. The t-curves are less dependent on temperature. At high densities, for example, near saturation pressure, significant deviations may exist.

Usually a modified Kelvin equation [7] is used to derive the pore size distribution (cumulative or differential adsorbed volume as a function of the pore diameter) from the isotherm in the mesopore range. The procedure of Barrett, Joyner and Halenda (BJH) has been adopted as the international standard [8–11]. The molecular volume is derived from liquid density, neglecting divergences in layers near the solid surface, in particular in small pores.

Problems of sorption measurement

We emphasise that all methods devoted to the characterisation of the surface structure yield no absolute results. On account of the fractal nature of the surface structure, the results depend on the size of the yardstick used for the measurement [12–17]. Furthermore, in the range of nanostructures we find no reliable limits at which the yardstick could be placed.

In adsorption measurements what is recorded is not exactly the adsorbed amount, because adsorption is always accompanied by other interfering physical phenomena, for example, buoyancy in gravimetric or dead space in volumetric measurements. The result of both volumetric and gravimetric measurements is the quantity

$$m^* \equiv m - \rho_f V_s \qquad (2)$$

where m is the adsorbed mass, ρ_f is the density of the adsorptive, and V_s is the solid volume of the sample, which is not accessible for the adsorptive gas. Thus, in both cases we need a second, independent measurement or calibration procedure.

Down to very low temperatures the adsorbate in the two to three layers nearest the surface is quasi-liquid. Because the density of the adsorbate, ρ_a, cannot be measured directly, the liquid density at the triple point can be used as a good approximation. Near the saturation pressure, however, significant differences may occur.

A notable effect is the hysteresis loop between adsorption and desorption curves. The pore size distribution calculated from the adsorption and desorption branches are substantially different and there is no clear theoretical explanation as to which one should be employed. We are faced with special problems if the volume of the sample or its pore structure is varied by the influence of the adsorbate, for example, by swelling.

The weak physical bond between the sorbate molecules and the sorbent is somewhat specific for each sorbate/sorbent system. However, nitrogen and noble gases have been proved to be less specific. By far, nitrogen is preferred for the characterisation of surfaces, although the quadrupole moment and the orientation of the dumb-bell shaped molecule may cause significant errors. The chemical nature of the surface plays an important role in the adsorption of polar molecules, and especially of water vapour. For this reason, surface characterisation using water vapour is not commonly used.

The most serious objection to measurements using nitrogen or noble gases is that the conditions are far from real when compared with those in everyday applications. Whereas laboratory measurements are made at low temperatures and pressures, most industrial adsorption processes occur at ambient or high temperature, ambient or high pressure and with reactive gases.

Progress in the determination of surface parameters

The two-parameter BET Eq. (1) is based on a very simple molecular model of adsorption and many attempts were made to improve it. Recently Kats and Kutarov [18] suggested extending this equation by considering a limited number of possible adsorbate layers and taking into account the fractal nature of the surface. In this way, besides specific surface area, values of the mean number of adsorbed layers and of the surface fractal dimension are obtained.

Several methods exist for the determination of the pore size distribution in the mesopore range [1, 6]. Progress is notable in the investigation of micropores [19–21]. Successful attempts were made in the area of molecular level modelling of capillary condensation. The methods of grand canonical Monte Carlo simulations (GCMC) [22], molecular dynamics (MD) [23] and density functional theory (DFT) [24] are capable of generating hysteresis loops for sorption of simple fluids in model pores. Non-local DFT can be employed for the characterisation of nanopores [25]. The methods of Horvath–Kawazoe [26] and Saito–Foley [27, 28] are already being standardised. Such methods need, however, properly chosen parameters of fluid/fluid and fluid/solid intermolecular interactions. Very interesting results are obtained in investigating microporous structures using CO_2 at ambient temperature and at sub-atmospheric pressure [29].

Several attempts were made to apply thermogravimetry in order to determine the pore size distribution. Recently, Staszczuk *et al.* [30] succeeded in investigating the heterostructure and the fractal dimension of high-temperature superconductors using quasi-isothermal thermogravimetry.

We discuss below the usefulness of measuring water vapour adsorption as a supplement to the classical measurements using nitrogen.

Instrumentation

Nitrogen sorption isotherms at 77 K on wool and cement were measured using volumetric/manometric techniques using Quantachrome instruments [31]. Water vapour isotherms on hair and wool at 298 K were determined by means of a Gast microbalance [32] manufactured by Sartorius [33]. For water vapour measurement on cement a gravimetric instrument of Surface Measurement Systems was used as shown in Fig. 1 [34]. Constant humidity is established by means of a humidified carrier gas which passes through the sample. In this way the humidity may be varied stepwise from zero to one hundred percent. Isotherms were plotted using the program Rt-Plot [35].

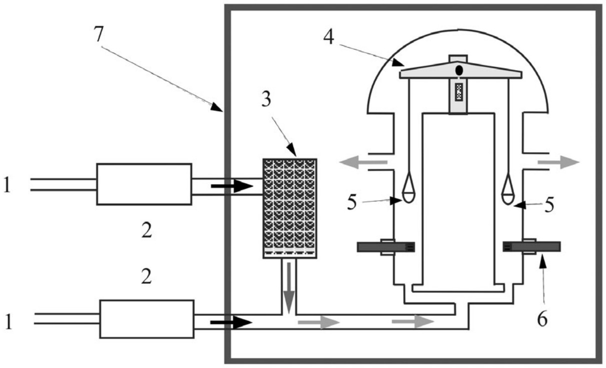

Fig. 1 DVS sorption measuring apparatus. 1 – admission of dry gas; 2 – dosing device; 3 – humidifier; 4 – microbalance; 5 – sample/reference sample; 6 – temperature and pressure probe; 7 – thermostated chamber

Measurement of nitrogen and water sorption isotherms

The measurement of a water vapour isotherm on hardened cement paste is shown in Fig. 2 [36, 37]. It is to be noted that measurements were not made at equilibrium! After a pre-set time or after pre-set equilibrium conditions the apparatus switches to the next pre-set humidity value. If operated manually the measurement is usually interrupted at one’s own discretion and corrections applied. Such procedures can result in significant errors if slow and fast adsorption processes are overlapping. Also in such cases, numerical extrapolation or curve fitting may fail. Measurement can be shortened with some reliability by extrapolation of the equilibrium values according to a procedure introduced by Jäntti [38–41]. This method is based on a molecular adsorption model and the kinetics is described by the Kohlrausch-equation [42].

The isotherm (Fig. 3) cannot be fitted into the IUPAC classification; this occurs very often with water vapour. The isotherm reveals a swelling process. Unexpectedly, water adsorption is far lower than nitrogen adsorption. This may be due to hydrophobicity of components of the heterogeneous material.

The nitrogen isotherm at 77 K (Fig. 4) is of type II of the IUPAC classification and can be treated in the usual manner for the calculation of the specific surface area and the pore size distribution. But there is no possibility to predict the behaviour of the material with water. For that purpose the nitrogen isotherm is irrelevant.

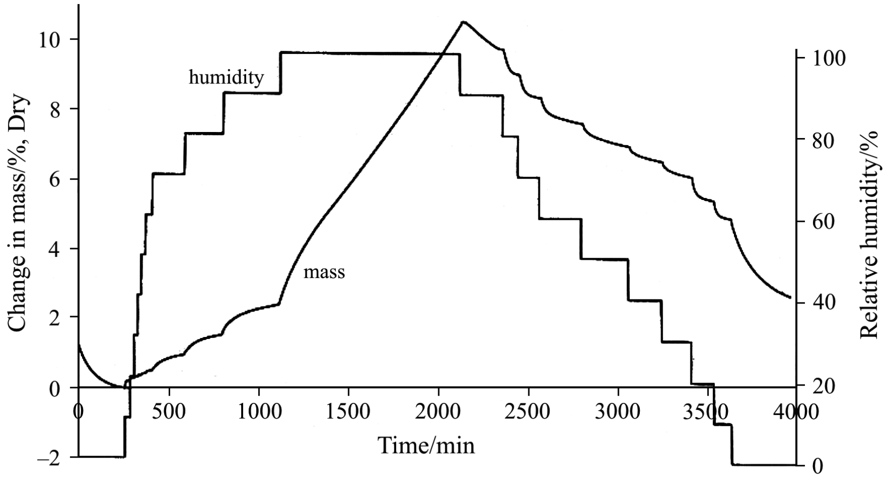

Fig. 2 Measurement of a water vapour adsorption isotherm at 298 K on hardened cement paste. As a function of time the stepwise changed humidity is depicted (right hand scale) and the resulting mass change of the sample (left hand scale). In the interval 0 to 260 min the sample is dried, then water vapour is adsorbed up to 2150 min and subsequently desorbed

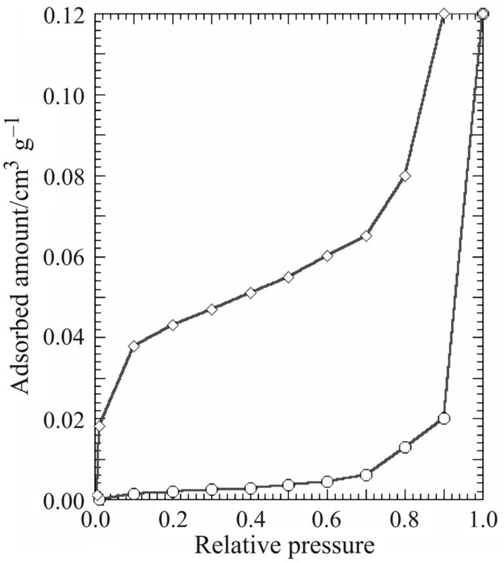

Fig. 3 Water vapour isotherm at 298 K on hardened cement paste (Dyckerhoff white); ○ – adsorption; ◇ – desorption. The amount refers to liquid adsorbate

In Fig. 5 the nitrogen isotherm of activated carbon is compared with the water isotherm [43]. Likewise, in this case, no predictions are possible. However, the total pore volumes, the so-called Gurwitsch volumes, are in good agreement (upper end of the isotherms). The water isotherm is typical for hydrophobic surfaces: There is practically no adsorption at the surface but condensation in pores starts at about 40%

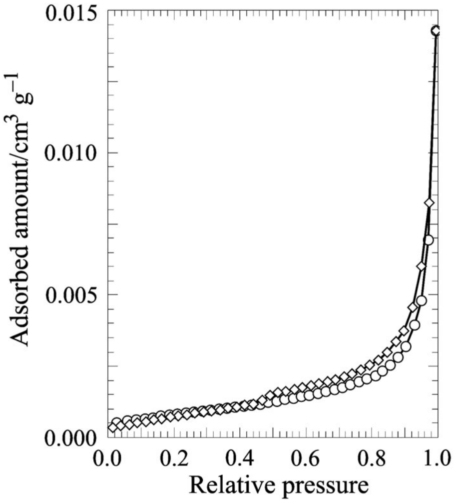

Fig. 4 Nitrogen isotherm at 77 K on hardened cement paste (Dyckerhoff white); △ – adsorption; ▽ – desorption. The anmount refers to liquid adsorbate

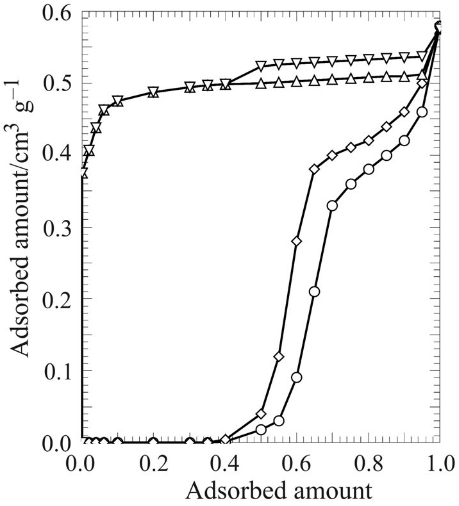

Fig. 5 Nitrogen △ – adsorption and ▽ – desorption isotherm at 77 K and water vapour ○ – adsorption and ◇ – desorption isotherm at 298 K on activated carbon according to Juhola. The amount refers to liquid adsorbate

relative humidity. Such an isotherm may be evaluated well by means of a modified Kelvin equation.

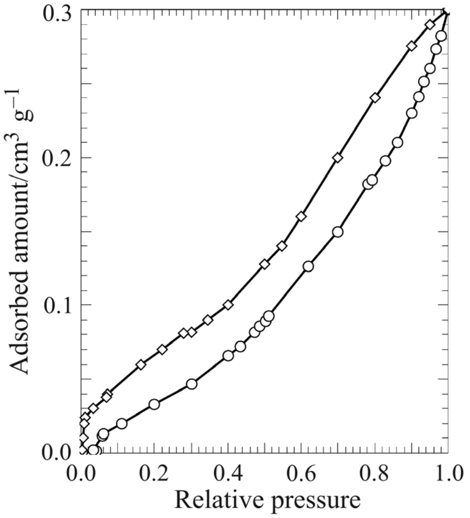

Fig. 6 Water vapour ○ – adsorption and ◇ – desorption isotherm at 298 K on washed raw wool. The amount refers to liquid adsorbate

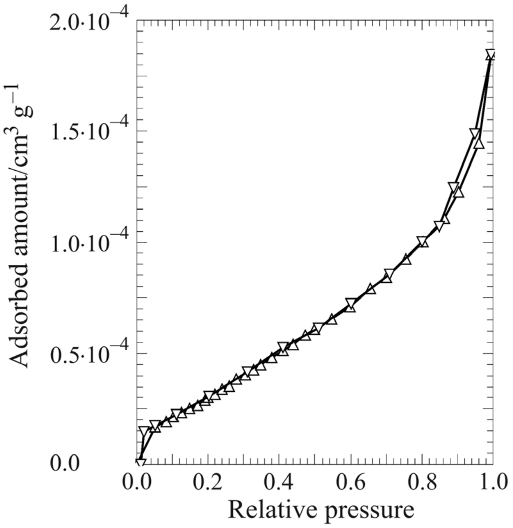

Fig. 7 Nitrogen △ – adsorption and ▽ – desorption isotherm at 77 K on washed raw wool. The amount refers to liquid adsorbate

Conspicuous differences are observed between water vapour (Fig. 6) and nitrogen isotherms (Fig. 7) on washed raw wool. The nitrogen isotherm is of type II of the

IUPAC classification and the specific surface area can be evaluated in the usual manner. Also water vapour adsorption is reversible. The isotherm, however, shows a hysteresis loop down to zero relative pressure. Evidently a swelling process has taken place. Each branch is strictly reversible and the calculation of a pore size distribution appears to be possible.

In Fig. 8 a water vapour isotherm is depicted on woman's hair – a material used earlier in de Saussure's hair hygrometer [44]. In contrast to the relation of the length of the hair (as measured in the hygrometer) the adsorbed amount as volume or mass varies with relative humidity somewhat linearly. Thus, a gravimetric hair hygrometer would be much better than the conventional instruments based on the measurement of length changes.

Figure 9 shows water vapour isotherms on various non-porous substrates, where the adsorbed amount is converted to layer thickness, *t* [6, 45]. These isotherms are of the common type II of the IUPAC classification. For the calculation of *t*-curves only hydrophilic, ionic solids can be used. However, the surface of such materials may be composite: partly hydrophilic, partly hydrophobic. The ions of the surface cause orientation of the dipoles of the water molecules, and thus, the area occupied by a water molecule at different adsorbents is different. Furthermore, as for other adsorbates, the thickness of the adsorbed film at a given relative pressure depends on the heat of adsorption, expressed, for example, by the BET-number *C* in Eq. (1). That means, that for each adsorptive, the *t*-curve, which matches the heat of adsorption on the adsorbent to be analysed, should be used.

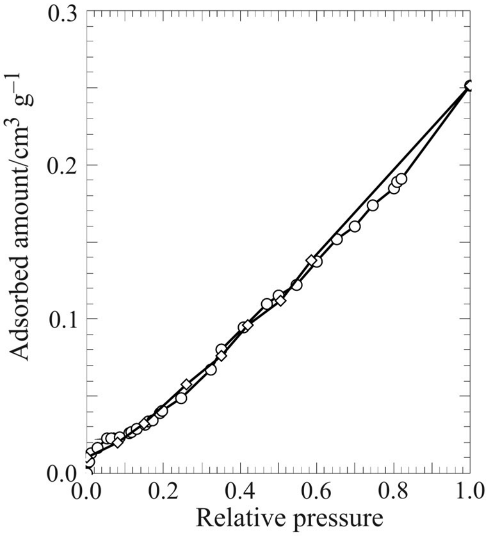

Fig. 8 Water vapour ○ – adsorption and ◇ – desorption at 292–297 K on woman's hair. The amount refers to liquid adsorbate

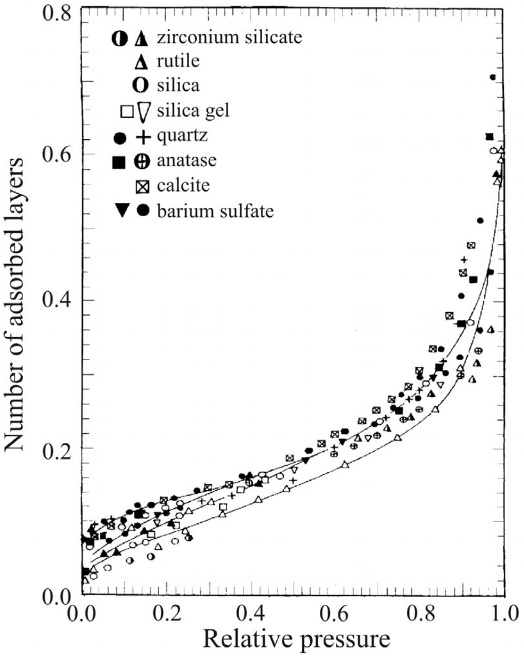

Fig. 9 Water vapour isotherms (*t*-curves for pore structure analysis according to Hagymassy, Brunauer and Mikhail)

Conclusions

The most important adsorbate in nature and in everyday life is water, either as a useful reactant or as an interfering impurity. Nevertheless, instruments to measure water adsorption have appeared on the market only recently. The reason is that measurement of water adsorption is sophisticated and fraught with difficulties. The highly polar molecule causes a hydrophobic or hydrophilic effect, depending of the chemical nature of the solid surface. Only hydrophilic surfaces allow for a common calculation of the specific surface area. Thus, water vapour is not suitable as a standard adsorbate for the investigation of surface structure. However, the isotherms give additional and quite different information of the adsorption properties than nitrogen or noble gas isotherms. For the evaluation of water vapour isotherms, new procedures should be developed.

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