

Porosity of sol-gel silica glasses doped by ruthenium bipyridyl as measured by positron annihilation lifetime spectroscopy and nitrogen adsorption

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The porous structure of glasses incorporated by ruthenium tris bipyridyl chloride (further Rubpy) and adsorbed by Rubpy is studied by positron annihilation lifetime spectroscopy and liquid nitrogen adsorption method. The first method provides the radius of the pores in the range of 0.6–4 nm and their distribution. The second method provides the radius of the pores in the range of 1–150 nm, their total volumes, size distribution and specific surface area. In the first method both closed and opened pores can be seen when the measurements are made on bulk samples as in this work. When thin films are measured, one has to use a capping material to prevent backscattering. The dimension of the pores can be controlled by the catalyst used for sol-gel formation. When Rubpy is prepared by adding its salt to precursor solution catalyzed by HCl, the pore size increases because of stress exhibited by large molecules. The pore size decreases with adding of Rubpy in precursor solution, catalyzed by HF and HNO₃. Glass doped by Rubpy is less sensitive to the type of catalyst, than undoped glasses. A comparative study was performed on undoped glasses prepared by the identical method. We shall discuss the similarities and differences of the two methods.

Keywords: porous glasses, ruthenium tris bipyridyl chloride, pore size, liquid nitrogen adsorption method, positron annihilation lifetime spectroscopy.

1. Introduction

Porous glasses play an important role as starting materials for the incorporation of a large number of active molecules which may be applied in tunable lasers [1], active waveguides, chemical and biological sensors and nonlinear molecules [2–7]. The formation of porous glasses by the sol-gel method resulting from hydrolysis and polycondensation of alkoxy silane precursors involves many parameters [8–10].

The main parameters that influence the hydrolysis and polycondensation are temperature, pH, type of alcoxide precursor, solvent and catalyst. Reactions of

hydrolysis are more rapid and complete when catalysts are employed. Many authors report that mineral acids are more effective catalysts than the equivalent concentration of a base [8, 9].

At low pH levels, at acidic conditions (slow hydrolysis), the silica tends to form linear molecules that are occasionally cross-linked. Those molecular chains entangle and form additional branches resulting in gelation. As the chains impinge on each other they deform and form a dense gel structure. In these weakly cross-linked systems, which are transparent, a high density low-pore volume gel is formed.

Under basic conditions (faster hydrolysis) more highly branched clusters form that are not interpenetrable before drying and thus behave as discrete species, gelation occurs by linking the clusters. On impingement the polymers will not deform as readily due to the removal of solvent from within the polymer. As the solvent is removed, individual clusters undergo shrinkage and rearrangement to achieve a higher coordination number. Shrinkage stops at an earlier stage of drying due to the stiffness of the impinging clusters. As a result we get larger pores. In this case low density high-pore volume opaque gels are obtained [10].

In the presence of hydrofluoric acid (HF) as a catalyst, the process of gelation is distinguished from usual acidic conditions. Anion F^- is about the same size as OH^- and has the ability to increase the coordination of silicon above four, for example in $(OR)_3Si-F_2^-$. So fluorine anion increases the coordination of silicon from four to five and six just as in the case of the anion OH^- . Because fluorine is more electron withdrawing than the hydroxyl group, thus HF substitution for OH^- reduces the electron density of silicon making it more susceptible to a nucleophilic attack [9]. Therefore, the choice of a catalyst allows us to control the glass porosity.

The sol-gel method applied in this work is a low-temperature technique for creating solid glass bulks. The relatively gentle synthetic conditions allow for the addition of various dopants such as organic dyes or inorganic ions, which convert the resulting glass/dopant combination into an active material which may be used in various optical or sensing applications.

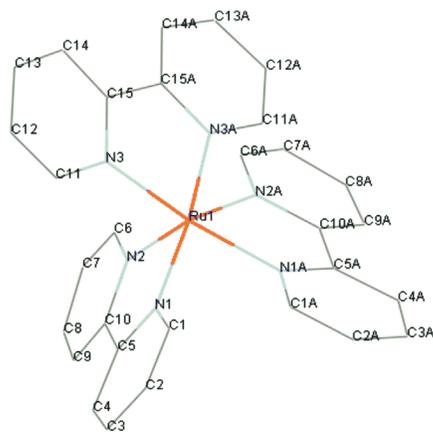


Fig. 1. Ion of ruthenium tris bipyridyl.

For instance, it has been shown that solid state laser can be prepared by incorporating optically active molecules into glass obtained by the sol-gel method. The impregnation of porous glasses after the bulk has been formed and treated at high temperature with laser dyes allows us to prepare tunable solid state lasers [2, 11–14].

The characterization of porous silica materials (measurements of pore size, surface area, pore volume and pore distribution) by such physical methods as liquid nitrogen (LN) adsorption and positron annihilation lifetime spectroscopy (PALS) has been carried out [1,7,15–18]. It was shown that HCl catalysed sol-gel forms the high density micropore network and HF with HNO₃ catalysts results in mesopore silica sol-gel with pore diameter 4–5 nm.

The purpose of the present paper is the elucidation of the structure of porous glasses, obtained by sol-gel process, and the influence of a large molecule, *i.e.* Rubpy, on the porous structure. This large molecule can then serve as a model for preparation of doped materials either by its addition to the precursor solution or by adsorption of prepared glasses.

The molecules of Rubpy (Fig. 1) with the radius of about 2 nm and octahedral coordination as quite common for transition metal ions were used as doped and adsorbed material for the high porous and low porous silica sol-gel bulks.

2. Theoretical background

The texture of sol-gel materials is defined by the geometry of the void and pore space. Porosity characterizes the pore space in a material. An open pore is a cavity or channel exposed at the surface of dense species as opposed to a closed pore. Void is the space between dense species.

The classification of the pore size according to International Union of Pure and Applied Chemistry (IUPAC) is given as follows [19]: micropores are of a dimension less than about 20 Å (2 nm), mesopores – from about 20 to 500 Å (2–50 nm), macropores – greater than 500 Å (50 nm).

The difference in physical properties and morphology between various silicates are related to the pH of reaction mixture, addition of various substances such as inorganic salts and surfactant to sol-gel reacting mixture, temperature, aging time, and drying process.

For full characterization of physical properties of the sol-gel matrix prior to practical use, four parameters are sufficient: specific surface area, specific pore volume, pore size and pore area distribution.

In the present research two methods are used for the estimation of those parameters: liquid nitrogen adsorption method (LN method) and spectroscopic method – positron annihilation lifetime spectroscopy (PALS method)

2.1. LN method

In this method the adsorption-desorption isotherms of nitrogen are measured at 77°C. Surface area is calculated from the linear form of BET equation [20]. The pore size

distribution is calculated from the desorption branch using BJH method [21]. The appropriate equations are given in the Appendix.

2.2. PALS method [18]

This method is based on positron behavior in the medium.

Positron emitted from a radioactive source (usually ^{22}Na) entering the sample can annihilate directly with one of the electrons of the medium, or it can create a bound state e^+e^- called positronium (singlet state – para-Ps, or triplet state – ortho-Ps) which locates in the regions of low electron density, called free volume. In vacuum para-Ps decays with a mean lifetime value $\tau_S = 0.124$ ns, lifetime of free annihilation does not exceed 0.5 ns, and ortho-Ps decays with $\tau_T = 142$ ns. Due to the negative work function, Ps is ejected into the vacuum, or locates in the regions of negligible electron density (in voids and empty spaces) as in the case of bulk samples used in this work. The ortho-Ps trapped in a void have an additional possibility of annihilation (*i.e.*, with one of electrons from surrounding bulk material). This kind of two-quantum annihilation is called a pick-off process. The rate of pick-off annihilation is proportional to the probability to find ortho-Ps inside the bulk (*i.e.*, to the overlap of ortho-Ps wavefunction with wavefunction of electrons). Such probability can be calculated using simple model proposed by TAO [22] and ELDRUP *et al.* [23]. In this work to investigate porous media, the model was extended by assuming capillary geometry (one dimension infinite) and population of the excited states of the particle (ortho-Ps) in the potential well [24].

3. Experimental

Five types of silica sol-gel glasses were prepared and measured by LN and PALS methods (the numbers are in order to experimental numbering):

1. High density silica sol-gel glasses: 5, 6 (catalyst HCl);
2. Low density silica sol-gel glasses: 3, 4, 2 (catalysts HF and HNO_3);
3. Silica sol-gel glasses doped by Rubpy: 10, 13 (catalyst HCl);
4. Silica sol-gel glasses doped by Rubpy: 11, 12 (catalyst HF and HNO_3);
5. Silica sol-gel glasses (catalyst HF and HNO_3) adsorbed by Rubpy dissolved in ethanol: 9, 8, 7.

All the silica sol-gel bulks were formed by hydrolyzing tetraethoxysilane (TEOS).

The following precursors were used for the preparation: TEOS (from Aldrich); ethanol, nitric acid, hydrochloric acid (from Flutarom); analytical grade; ruthenium tris/2,2'-bipyridyl/chloride (from ICN Pharmaceuticals) and triply distilled water. In all the cases the starting solution contained: TEOS, water and ethanol with the molar ratio 1:4:4 and catalysts such as HNO_3 , HF (0.06 and 0.09 mol%, respectively) and HCl (0.02 mol%).

The glasses doped by Rubpy ($c = 10^{-5}$ mol%) were formed by adding of the complex dissolved in ethanol to the precursor solution, catalyzed by HCl (3) or HF and HNO_3 (4). The samples with adsorbed Rubpy were prepared as following: the low

density bulks, prepared with catalysts HF and HNO₃ (2) were placed in solutions of Rubpy in ethanol with concentration of Rubpy: i) 3.75×10^{-5} mol%, ii) 1.25×10^{-5} mol% and iii) 0.62×10^{-5} mol%.

The bulks were dried in a thermostat for 24 hours and treated at $T = 150^\circ\text{C}$ for 30 minutes.

The hydrolysis was carried out by mixing the starting materials into a homogenous solution under vigorous stirring for about 30 minutes, after which this sol was transferred to a sealed plastic vessel (a few holes should be pierced in the lid using a needle) and allowed to gel and age. The gelation and aging temperature was $20\text{--}25^\circ\text{C}$ for a period of 3–4 weeks. During hydrolysis and aging processes the gel had lost approximately 50% of its initial volume. The volume change arises primarily from the loss of ethanol which is used as a co-solvent and which is a product of the hydrolysis reaction. The wet gel was dried in a thermostat (40°C) for a period also of 3–4 weeks to give silica gel monolith. The last step of the preparation was a thermal treatment ($200, 300$ and 600°C) needed to improve mechanical properties of gel.

3.1. LN method

The adsorption-desorption isotherms of nitrogen at 77 K were measured with a volumetric adsorption analyzer ASAP 2010 (Micromeritics). Surface areas S_{BET} were calculated from the linear form of the BET equation over the range of relative pressures between 0.05 and 0.25, taking the cross-sectional area of the nitrogen molecule to be 16.2 \AA^2 . The pore size distributions were calculated from the desorption isotherm by the BJH method. The total pore volumes V_p for the samples under study were determined from a single point adsorption at a relative pressure of 0.98 by converting the value of the adsorbed gas to the volume of the liquid adsorbate [15].

3.2. PALS measurements

PALS measurements were performed using a ^{22}Na positron source and a classic lifetime spectrometer. Lifetime spectra were measured at room temperature under the pressure of ~ 0.5 Pa. The distribution of the time between the birth of positron and its annihilation was recorded in 8000 time channels covering the range of $1 \mu\text{s}$ (for long-lived component searching) or 100 ns in the case of typical measurements. The appearance of positron was signaled by 1274 keV γ quantum following the β decay (start signal), and its annihilation by 511 keV photon (stop signal) [7].

The set of lifetimes τ_i and respective intensities I_i were decomposed from spectrum by LT program [25]. From the obtained lifetimes and their distributions the radii of pores and their distribution were calculated using cylindrical model presented elsewhere [24].

4. Results

The nitrogen adsorption-desorption isotherms (presented in the conventional form: the amount adsorbed V_a (cm^3) at standard conditions of temperature and pressure-STP,

i.e., 0°C and 760 torr, versus the relative pressure p/p_0) allow to conclude about the structure of different samples by comparing their shapes with the literature value [1, 18, 26].

The undoped samples 5 and 6 catalyzed by HCl have very low porosity as shown in [1] and the isotherms could not be measured. Also isotherms for glasses doped by Rubpy and catalyzed by HCl (samples 10, 13) could not be obtained.

The nitrogen adsorption-desorption isotherms and pore size distribution for some investigated samples are shown in Figs. 2–7.

Figure 2 presents the adsorption-desorption isotherms of samples 3, 4, 2 of pure silica glasses catalyzed by HNO_3 and HF prepared at three temperatures: 200, 300 and 600°C, respectively. The adsorption isotherms for samples 3, 4, 2 rise rapidly in the intermediate zone and show a wide hysteresis loop, indicating the presence of mesopores in the samples. Evaporation from the pores of the samples 3, 4 and 2 is a different process than the condensation within them.

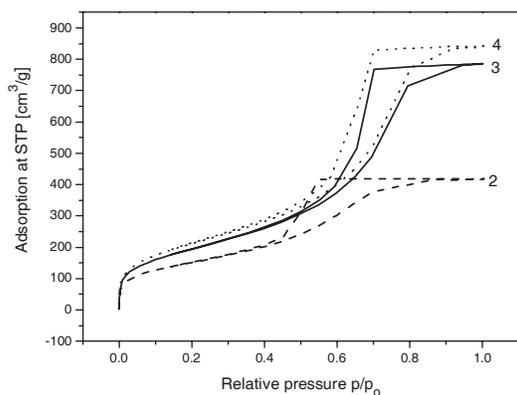


Fig. 2. Adsorption-desorption isotherms of nitrogen at 77 K for sol-gel glasses catalyzed by HF, HNO_3 and treated at: 200°C (sample 3), 300°C (sample 4) and 600°C (sample 2).

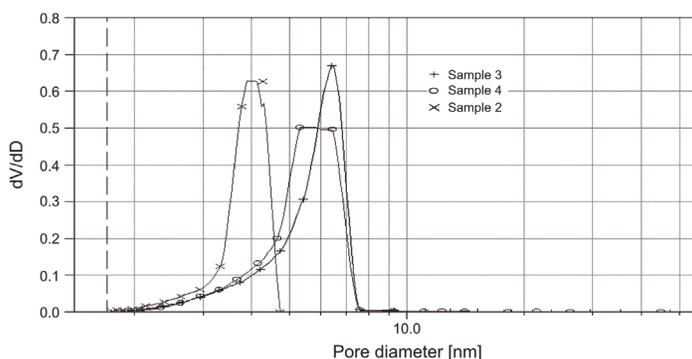


Fig. 3. Pore size distribution for samples 3, 4 and 2 according to BJH method. Sol-gel glasses catalyzed by HF, HNO_3 and treated at: 200°C (sample 3), 300°C (sample 4) and 600°C (sample 2).

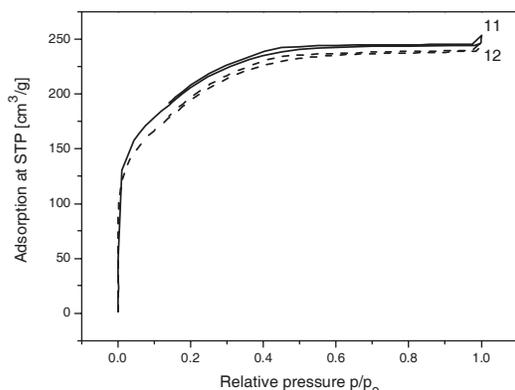


Fig. 4. Adsorption-desorption isotherms of nitrogen at 77 K for sol-gel glasses, catalyzed by HF, HNO₃, doped by Rubpy and treated at: 200°C (sample 11) and 300°C (sample 12).

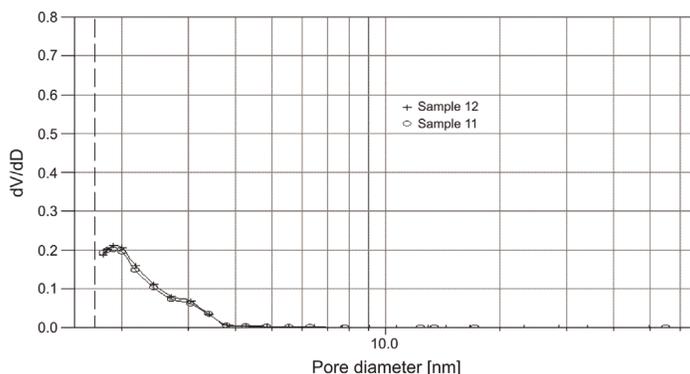


Fig. 5. Pore size distribution for samples 11 and 12 according to BJH method. Sol-gel glasses, catalyzed by HF, HNO₃, doped by Rubpy and treated at: 200°C (sample 11) and 300°C (sample 12).

The adsorption isotherms of sample 2 are lower than adsorption isotherms of samples 3 and 4, which is an evidence of the lower pore volume (porosity).

Those adsorption-desorption isotherms show one clearly visible condensation jump at $p/p_0 = 0.6-0.7$ for samples 3 and 4 and at $p/p_0 = 0.5-0.7$ for sample 2. The pore size distributions of samples 3, 4, 2 are given in Fig. 3.

Figure 4 presents the adsorption-desorption isotherms of samples 11, 12, catalyzed by HF, HNO₃, doped by Rubpy and treated at 200 and 300°C. The hysteresis loop is slightly visible. The isotherms can be assigned to supermicropores. By comparing the pore size of pure silica glasses (samples 3, 4) and glasses doped by Rubpy (samples 11 and 12) we see that the pore sizes decrease in comparison with undoped glasses. The pore size distributions of samples 11, 12 are given in Fig. 5.

Adsorption-desorption isotherms and pore size distribution of glasses adsorbed by Rubpy from solution (samples 7, 8, 9) are presented in Figs. 6 and 7. The shape

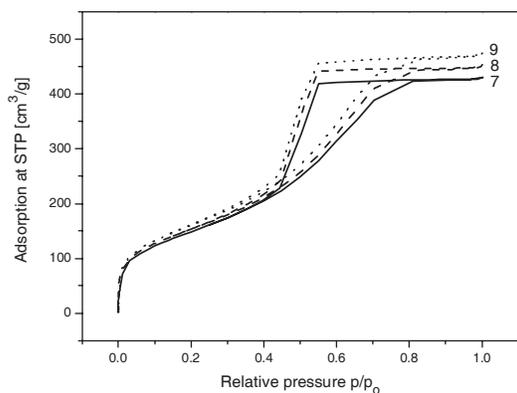


Fig. 6 . Adsorption-desorption isotherm of nitrogen at 77 K for sol-gel glasses, catalyzed by HF, HNO₃ adsorbed by Rubpy at concentrations: 3.75×10^{-5} mol% (sample 7), 1.25×10^{-5} mol% (sample 8) and 0.62×10^{-5} mol% (sample 9).

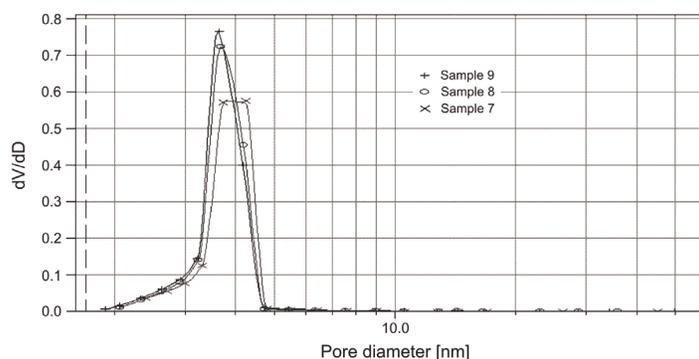


Fig. 7. Pore size distribution for samples 7, 8 and 9 according to BJH method. Sol-gel glasses, catalyzed by HF, HNO₃ adsorbed by Rubpy at concentrations: 3.75×10^{-5} mol% (sample 7), 1.25×10^{-5} mol% (sample 8) and 0.62×10^{-5} mol% (sample 9).

of adsorption-desorption isotherms shows the mesopores structure. The isotherm of sample 9 is slightly higher than isotherm of sample 7.

The results of LN and PALS measurements are summarized in the Table. It is shown that samples 11 and 12 prepared by doping of precursor solution by Rubpy and catalyzed by HF and HNO₃ give the same results, obtained by the two methods. The samples consist of submicropores which are open. There were difficulties in measuring the pore size of sample 13, catalyzed by HCl, treated at 300°C by LN method as the pores were probably closed and would be seen only by PALS method which can detect the close pores. Sample 10 gives unrealistic value of radii 1.5 nm as opposed to 0.77 nm, using PALS method, which brings us to the conclusion that only the surface of the pore was observed.

Table. Comparison of pore size and ranges, obtained by two methods.

Groups of samples	Material	Number of sample	Nitrogen adsorption		Positron annihilation lifetime spectroscopy	
			R_{pores}^{***} [nm]	Range _{pores} [nm]	R_{pores} [nm]	Range _{pores} [nm]
I	Si, HCl, Rubpy, s; 200°C	10	1.5	< 1.5	0.77	0.64±0.88
	Si, HF, Rubpy, s; 200°C	11	1.15	< 2.0	1.16	0.98±1.37
	Si, HF, Rubpy, s; 300°C	12	1.2	< 2.0	1.13	0.98±1.3
II	Si, HCl, Rubpy, s; 300°C	13	Not measured	Not measured	0.74	0.62±0.85
	Si, HF, Rubpy, a**; 3.75×10 ⁻⁵	7	1.9	1.75–2.25	2.75	1.72±5.2
	Si, HF, Rubpy, a; 1.25×10 ⁻⁵	8	1.85	1.75–2.25	2.89	1.73±5.8
III	Si, HF, Rubpy, a; 0.62×10 ⁻⁵	9	1.85	1.75–2.25	3.1	2.4±6.8
	Si, HF, 600°C	2	1.9	1.75–2.25	4.01	2±12
	Si, HF, 200°C	3	2.75	2.75–3.75	4.24	2.4±12
IV	Si, HF, 300°C	4	2.7	2.25–3.75	4.02	2.3±10
	Si, HCl, 200°C	5	Not measured	100–150	0.64	0.5±0.76
	Si, HCl, 300°C	6	Not measured	100–150	0.64	0.53±0.76

* sample, doped by Rubpy;

** sample with adsorbed Rubpy;

*** BJH desorption pore radii corresponding to the peak of pore size distribution from nitrogen data.

Samples 7, 8 and 9 in which the Rubpy was adsorbed from solution show the larger pore size obtained by PALS method, since PALS can observe both closed and open pores.

Samples 5 and 6 have extremely small pore size that can be enlarged by the introduction of Rubpy (sample 10, 13). They can be measured by PALS and LN methods. The results, obtained from undoped samples catalyzed by HCl, can be measured as explained above only by PALS because the pores are smaller than 1 nm.

5. Conclusions

Applying LN and PALS methods of measurement of pore size, pore distribution, surface area and pore volume to glasses doped and adsorbed by large molecules of Rubpy allows us to clarify the texture of the glasses.

An addition of ruthenium complex to the glasses catalyzed both with HF, HNO₃ and HCl reveals different behavior to undoped glasses. The complex increases the size of the pores in HCl catalyzed sample by pushing out the glass forming SiO₄ tetraheder because of its large size, on the other hand in samples catalyzed by HF, HNO₃ the complex fills out the pores decreasing their size. Pore size is also decreased when the glass is heated to higher temperature.

In the case of undoped glasses with HF and HNO₃ catalysts the pore sizes obtained by PALS method are bigger than those obtained by LN adsorption. Those results can be explained as follows:

- The LN method measures only the open pores while the PALS method measured the closed pores in addition the open pores;
- By comparing the doped with undoped glasses, we come to the conclusion that the pores have a cylindrical shape slightly enlarged at the bottom where the nitrogen cannot penetrate;
- By looking at the results of adsorbed Rubpy from solution, we see that the pore sizes obtained by LN method are smaller than those obtained by PALS and this is due to the diffusion of the Rubpy complex into the depth of the pores, which is facilitated by the ethanol in which the complex is dissolved.

Appendix

LN method

Surface area information S_A may be derived from the lower region of the isotherm [18]. The specific surface area is usually calculated from the linear form of adsorption isotherm, represented by the Brunauer–Emmert–Teller (BET) equation:

$$\frac{p/p_o}{V_a(1 - p/p_o)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} (p/p_o)$$

where V_m is the quantity of gas adsorbed when the surface is entirely covered with a monomolecular layer, V_a is the quantity of gas adsorbed at pressure p , C is a constant representing the difference of heat of adsorption of the first layer and heat of liquefaction of the adsorptive.

Constant C value should be positive and indicates the magnitude of the adsorbent-adsorbate interactions energy. A plot of the left-hand side versus p/p_o should yield a straight line with intercept $1/V_m C$ and slope $(C - 1)/V_m C$. Thus the values V_m and C may be obtained from a plot of a straight line.

The specific surface area S_{BET} of 1 g of the adsorbent is then calculated according to the expression:

$$S_{\text{BET}} = \frac{V_M \sigma N_A}{m V_o}$$

where m is the mass of the sample, and σ is the area of a single nitrogen molecule ($16.2 \times 10^{-20} \text{ m}^2$), N_A is Avogadro's number.

The surface area of the sample can be determined using the area occupied by a single adsorbate molecule. This area may be expressed under the assumption of a close packing of spherical molecules at the surface by the formula [18]

$$\sigma = 1.091 \left(\frac{M}{N_A d} \right)^{2/3}$$

where σ is the mean area per molecule, M is the molecular weight, N_A is Avogadro's number, d is the density of the liquid adsorbate, 1.091 is the coefficient ascribed to spherical shape and hexagonal close packing of molecules. The accepted value of the monolayer thickness of N_2 at 77 K is 0.354 nm.

Characterization of mesopore and macropore size distribution generally follows the procedure described by the Barrett, Joyner and Halenda (BJH method) [21] having the following form:

$$\ln \frac{p}{p_o} = \frac{-2 \gamma V_M \cos \Theta}{R_k R T}$$

where p is equilibrium pressure, p_o is pressure of vapor over a flat surface at the same temperature, γ is the liquid surface tension, V_M is molar volume of the condensed adsorptive, Θ is the contact angle between the solid and condensed phase, R_k is the mean radius of curvature of the liquid meniscus, R is gas constant, T is temperature. For nitrogen, $V_M = 34.68 \text{ cm}^3/\text{mol}$ and $\gamma = 8.72 \times 10^{-3} \text{ N/m}$, respectively.

Contact angle $\Theta = 0$ ($\cos \Theta = 1$) is assumed. This assumption is probably reasonable for many systems in which a solid is perfectly wetted by adsorption.

PALS method

At thermal equilibrium the decay rate (reciprocal of the lifetime) of ortho-Ps is expressed by the weighted average

$$\lambda = \lambda_T + \lambda_{po} = \frac{\sum_i \lambda_i g_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)} + \lambda_T \quad (1)$$

where λ_i , E_i and g_i are the decay rate of ortho-Ps in the i -th state, the energy of that state, and statistical weight, respectively, λ_T is the intrinsic decay rate of ortho-Ps in vacuum, T is temperature, and k is the Boltzmann constant. Summation is over all states existing in the potential well accommodating positronium.

The decay rates λ_i from particular states i in a cylindrical well are (assuming the Tao–Eldrup concept [23] of infinite well depth and replacing the real wave-function penetration depth with respective broadening of the well by ΔR)

$$\lambda_{po}^{nm} = \frac{2 \int_{Z_{nm}R/(R+\Delta R)}^{Z_{nm}} J_m^2(r) r dr}{\int_0^{Z_{nm}} J_m^2(r) r dr} \quad (2)$$

where $J_m(r)$ are cylindrical Bessel function and Z_{nm} are their n -th zero crossing points, R is the radius of capillary (one dimension infinite), $\Delta R = 0.19$ nm. Summation in Eq. (1) extends over the noticeably populated states, *i.e.*, the region where energies are comparable to kT . For $R \leq 1$ nm one can limit the sum to the first term, the larger R is, the more levels should be included, as their spacing diminish like $1/R^2$.

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