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The method of standard porosimetry
1. Principles and possibilities

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Abstract

A new porosimetric method is described which allows the investigation of all kinds of porous materials including soft or frail materials and powders. The method is relatively simple and nondestructive, and can be used for measurements in a wide range of pore sizes from 1 to 10^6 nm. This method can also be used for the evaluation of wetting angles and of the water wettability of multicomponent porous materials. This method is now widely used for investigation of battery components: porous electrodes, membranes, etc.

Introduction

The structural and surface properties of porous bodies used in different electrochemical devices (electrodes, separators, membranes, catalysts, amongst others in batteries, fuel cells, electrolyzers, sensors, etc.) have a great influence on the performances of these devices. The knowledge of structural properties is important also for many other materials: ceramics, powder-metallurgical products, soils, oil- or gas-bearing strata and rocks, building materials, etc.

The porous structure can be described by integral or differential porosimetric curves or porograms, i.e., curves of pore volume V (e.g., in units cm^3/g) or relative porosity θ (ratio of pore volume and overall volume of the sample) distribution in terms of the pore radii. The following methods for measuring porograms are well known: mercury porosimetry — mercury intrusion into materials nonwettable by mercury [1]; low-angle X-ray scattering [2]; electronic or optical microscopy; centrifugal porosimetry [3]; displacement of wetting liquids from the pore volume by gas pressure [4], and capillary condensation [5].

Each of these methods has its possibilities and its limitations. Low-angle diffraction can be used only for pore radii from 2 to 50 nm and often leads to ambiguous results. The centrifugal, optical microscopy and displacement methods are practically useless for $r<10^3$ nm. Measurements by electronic microscopy are connected with difficulties in pretreatment of the samples and in interpretation of the results. The method of capillary condensation can be used in the pore-size range from 1 to 50 nm.

The widest spectrum of measurable pore radii (from about 2–5 to 10^4–10^5 nm) is found in the method of mercury porosimetry (MMP). A disadvantage of this method is the necessity to apply high pressures of mercury (up to thousands of atm), which can lead to a deformation or even destruction of the samples and to a distortion of the porograms [5–7]. Other difficulties connected with this method are: distortion of

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the results owing to amalgamation of most metals [8]; different values of the mercury wetting angle for different materials [7]; complexity of the equipment, and toxicity of the mercury.

In the A.N. Frumkin Institute of Electrochemistry a new method — the method of standard porosimetry (MPS) — was developed in which most of these disadvantages are eliminated and which gives the possibility of measurements in a large range of pore sizes and with different kinds of materials including soft or frail materials or materials amalgamated by mercury [9–18].

Principles of the method

The method is based on the laws of capillary equilibrium. If two (or more) porous bodies partially filled with a wetting liquid are in the state of capillary equilibrium then the values of the capillary pressure p_k of the liquid in these bodies are equal. The capillary pressure can be represented by the Laplace equation:

$$p_k = -2\sigma \cos \theta / r_m \qquad (1)$$

where σ is the surface tension (interfacial tension) of the liquid, θ the wetting angle, and r_m the maximum radius of pores filled with the liquid (this equation holds only for pores of a cylindrical shape, but in porosimetry it is also used as an approximation for pores of other shape).

If for one of the porous bodies (the standard sample) the pore-size distribution is known, then by determining (for different overall volumes V_0 of the liquid) the distribution of the liquid between all porous bodies (volume of liquid V_k in the body k) the pore-size distribution for the other bodies (test samples) can be calculated. In Fig. 1 an example for the distribution of a liquid in two porous bodies is given. In the left part curve 1 represents the experimental dependence of the volume V_s in the standard sample on the volume V_t in the test sample. In the right part the integral pore-size distribution curves — dependence of pore volume on log r — are shown. Curve 2 is the known curve for the standard sample. Let us assume, for simplicity, that the wetting angles of the liquid for both bodies are equal. For a definite overall volume of the liquid V_0' the volumes of liquid in both bodies V_s' and V_t' are represented

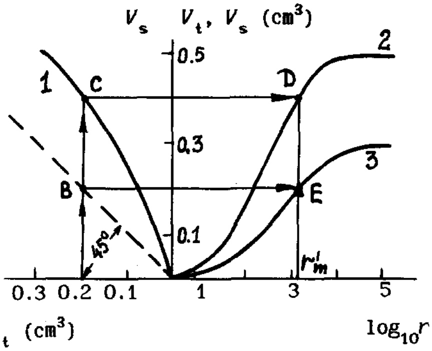


Fig. 1. Example of determination of pore-size distribution curves by MSP: (1) V_s vs. V_t; (2) pore-size distribution curves for the standard sample, and (3) for the test sample.

by the coordinates of point C. This point corresponds to point D on curve 2 and to a definite value r'_m of the maximal radius of filled pores. In the case of a capillary equilibrium (under the assumption made) the maximum radius of filled pores in the test samples will be the same. As in this sample the volume of liquid is represented by point B (the dashed line is drawn at an angle of 45°) the point E corresponds to a point on the pore-size distribution curve for the test sample. In a similar manner by changing the value of V_0 the whole distribution curve 3 for the test sample can be determined.

Method of measurement

The amount of liquid in the samples is determined by weighing. As working liquid usually hydrocarbons are used (octane, decane) which completely wet most of the materials ($\theta \approx 0°$). Thus the assumption of equal wetting angle is fulfilled. In some special cases other liquids are used, e.g., water.

The porous standard and test samples are prepared in the shape of discs with a thickness of 0.1 to 3 mm. They are washed, dried, and weighed; then they are filled (under vacuum) with the liquid. The stack of porous samples is assembled in a special clamping device (Fig. 2) in which the samples are tightly pressed to each other. In the case of readily compressible (soft) materials the pressure must be controlled (e.g., by sylphon bellows). In the assembly the test samples (1) are usually placed between two standard samples (2).

From this assembly a small portion of the liquid is evaporated through the open surface (3) by heating and/or vacuum treatment or by a flow of dry inert gas. When a certain amount of liquid is removed the open surface of the samples is closed up with a plug and the assembly is stored for a certain time (1–30 min) to allow the establishment of a new capillary equilibrium. Afterwards the stock is disassembled, the samples are placed into individual glass bottles and weighed. The stock is then reassembled and all listed operations are continued periodically until all the liquid has almost completely evaporated from the test samples.

There exist also other possibilities for changing the overall volume of liquid, e.g., by repeatedly contacting the test sample with the standard sample, containing different amounts of liquid.

The attainment of capillary equilibrium can be controlled by the use of two standard samples, one of which is placed at the open surface of the stack (where the

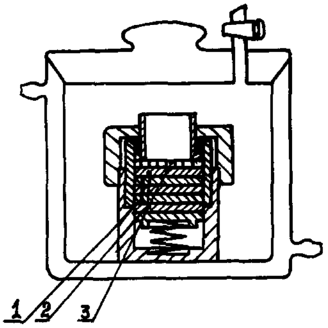


Fig. 2. Clamping device: (1) test samples; (2) standard samples, and (3) open stack surface.

liquid evaporates) and the other one at the closed surface. If during the experiment the amount of liquids in both standard samples correspond to their (known) distribution curves then an equilibrium is established throughout the whole stack.

In the case of samples with small pores (<10 nm) the disassembling of the stack is performed in a dry box in order to prevent absorption of humidity from the air. When making measurements involving large pores ($>10^4$ nm) the stack is disassembled in a box saturated with vapour of the measuring liquid in order to avoid drying out of the stack.

With this method porograms can be measured also for powdered materials. These materials are placed between two sheets of filter paper. Other samples of filter paper without powder are also assembled in the stack. By substracting the porograms of the 'empty' filter paper samples from the porograms of the test sample the pore volume distribution curve of the powder can be determined.

The capillary equilibrium between different porous samples can also be established through the vapour phase (without a direct contact of the samples) — method of contactless standard porosimetry. But in this case the time for the establishing of the equilibrium rises sharply.

The pore-size distribution for the standard samples must be determined by other methods, e.g., by mercury porosimetry. For these samples materials are used that are sufficiently strong and are not deformed or amalgamated by mercury, e.g., nickel or ceramic materials. The standard samples must fulfill the following condition: their pore volume in the corresponding pore-size range must be sufficiently high as to allow an accurate measurement of the mass increase during flooding of these pores.

The time needed for the measurement of a porogram depends on the pore characteristics of the sample (which influences the time of establishment of the equilibrium) and varies between 2 and 10 h (for microporous materials even more).

Limits, accuracy and sensitivity of the method

The method of standard porosimetry with suitable standard samples and working liquids (not interacting with the samples) can be used for measurements of pore sizes in the range from 1 to 10^5–10^6 nm.

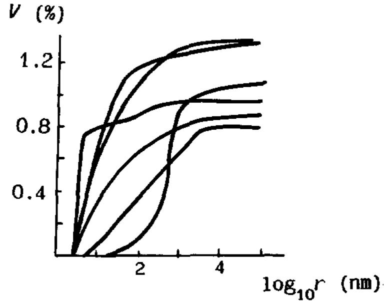


Fig. 3. Integral porograms for different carbonate rocks of the Vuktyl region [19].

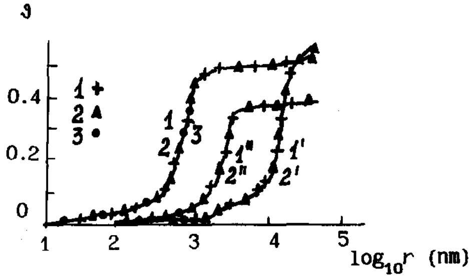


Fig. 4. (1, 1′, 1″) Integral porograms obtained by MSP; (2, 2′, 2″) by MMP, and (3) by contactless MSP for porous electrodes prepared from a mixture of carbonyl and Raney nickel (1–3), from carbonyl nickel (1′, 2′) and from titanium (1″, 2″) [18].

The accuracy of MSP depends primarily on the accuracy of measuring the pore-size distribution curve of the standard samples. By MMP this curve can be measured with an accuracy of about 1% of the total pore volume. As was shown by special statistical measurements performed by six different people during more than four years, under suitable conditions the error (nonreproducibility) of the results due to MSP itself is about 1%.

The sensitivity of the method is illustrated in Fig. 3 which represents the results for different almost monolithic samples of carbonate rocks for which the open porosity (porosity due to interconnected pores) was less than 1%. When referred to the overall volume of the sample the sensitivity in this case was 0.05 to 0.07%.

In Fig. 4 the porograms measured by MSP and by MMP for different types of electrodes are shown. It can be seen that there is a good agreement between the results obtained by these two methods.

Porosimetry of deforming samples

Sometimes MMP is used for investigation of samples with a low mechanical strength [6, 7]. To reveal the influence of high mercury pressures the results of measurements by MMP and MSP for such samples were compared. The effect of deformation depends on the nature of the material. As an example in Fig. 5 differential porograms are shown for a fibrous filter material FPIAN-5 which is used as a separator in batteries. It can be seen that the deformation changes the shape of the curves: the number and the position of the maxima on these curves are different. They coincide only in the pore-size range 10^2 to 10^3 nm; this points to a rigid microporous structure within the fibres.

MSP gives the possibility to perform measurements of samples at fixed levels of compression, i.e., in conditions in which they are used in different devices. By measuring porograms at different levels of compression additional information on the properties of the porous structure can be obtained.

It should also be noted that MSP allows repeated measurements on the same sample, which gives the possibility to investigate structural changes under the influence of different external factors, e.g., the structure of one and the same electrode at different depths of charge or discharge. Indeed, even for soft or frail materials there is no deteriorating influence of the measurement on the sample (in contrast to MMP) and after drying up it fully retains its previous structure.

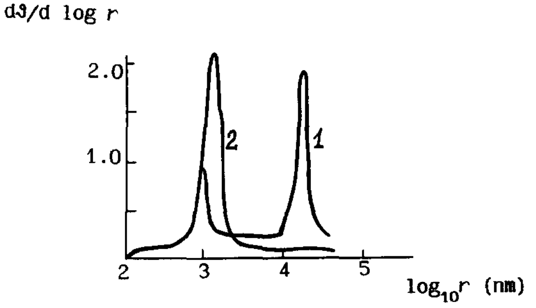


Fig. 5. Differential porograms obtained by (1) MSP, and (2) MMP for FPIAN-5 filters [18].

Measurement of the total pore volume

When measuring the total porosity of porous bodies an error is often introduced due to a thin liquid film on the surface of the sample or to a deficiency of liquid after attempts to remove this film. On the base of MSP a method was developed [18] with a new procedure of filling the sample with the wetting liquid. The test sample is contacted with an auxiliary sample whose volume of coarse pores V_2 is higher than the total volume of the test sample V_1. Then a volume of liquid is added to the samples which is greater than V_1 but lower V_2. Under these conditions the pores of the test sample will be completely drowned without formation of a film on its surface.

Investigation of samples with corrugated pores

The corrugation of pores influences to a great extent processes of mass and heat transfer and of current flow in porous materials. For such materials the porograms measured in forward and reverse directions usually do not coincide and it is difficult to evaluate the true shape of the porogram. MSP gives the possibility to measure the true pore-size dependence not influenced by pore corrugation [15, 18]. The quantitative description of such a porous structure is given by the statistical distribution function of the volume of the trapped (blocked) pores V_{tr} in terms of both their radii r_{tr} and the radii of the blocking pores (necks) r_b:

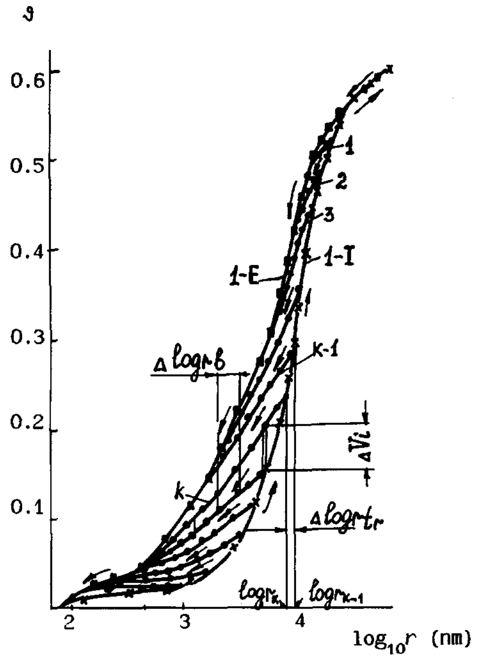


Fig. 6. Integral porograms for electrodes made from carbonyl nickel measured by MSP via: (1-I) capillary impregnation; (1-E) evaporation starting with complete flooding, and (1, 2, ... $k-1$, k) evaporation starting with different degrees of flooding [18].

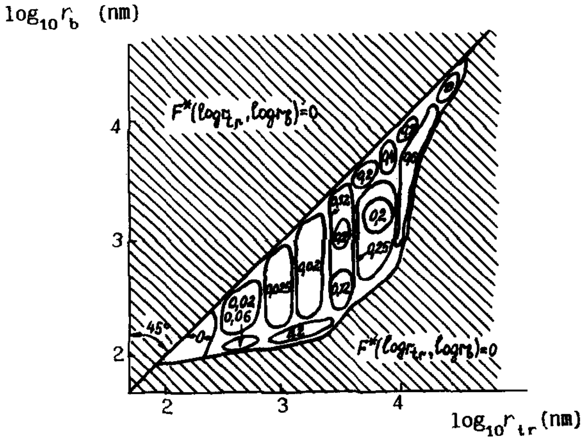


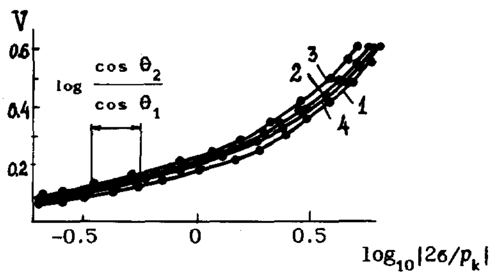
Fig. 7. The volume-distribution function of blocked pores in terms of the logarithms of their radii (r_{tr}) and of the logarithms of the radii of blocking pores (r_b) calculated from the porograms shown in Fig. 6 [18].

$$F(r_{tr}, r_b) \equiv \partial^2 V_{tr} / \partial r_{tr} \partial r_b \tag{2}$$

To evaluate this function it is necessary to measure the porograms by two methods: (i) by filling the pores with liquid, and (ii) by evaporation of the liquid beginning from different degrees of filling. In Fig. 6 such a set of porograms for an electrode from carbonyl nickel is shown. In Fig. 7 in coordinates log r_b, log r_{tr} the lines connect points with equal values of the distribution function (dimensionless, for the relative porosity). The line at an angle of 45° is characteristic for pores without corrugation. It follows that the pores of this electrode can be divided into three groups: (1) coarse pores with radii 30 to 70 μm and with a low degree of corrugation (formed by special pore-forming agents); (ii) pores in the range 2 to 15 μm with a high corrugation degree (located between individual particles of the carbonyl nickel), and (iii) a low volume of pores <1 μm with a low degree of corrugation (located inside the nickel particles). Such a kind of distribution functions has not been described in literature up to now.

Measurement of wetting angles

The measurement of wetting angles for porous materials is connected with difficulties especially if these materials cannot be prepared with a smooth surface (e.g., carbons, soil samples, building materials etc.). MSP gives such a possibility for liquids with wetting angles of $\theta_t < 90°$. For this purpose porograms with the test liquid and with a standard liquid with a known wetting angle (e.g., hydrocarbons with $\theta_s \approx 0°$) are measured. The results of measurements are plotted as indicated above, i.e., without taking into account the change of the value of cos θ. In this case the curves for the two liquids will be shifted along the log r-axis. For a given amount of liquid $\tilde{V}'$ the capillary pressure (the value of cos θ / r) in both cases will be the same. Therefore, the value of the shift will be $\log(\cos \theta_t / \cos \theta_s)$, or, when $\theta_s \approx 0°$, log cos θ_t. If the value of θ_t for the sample is not constant but depends on the pore size, then there



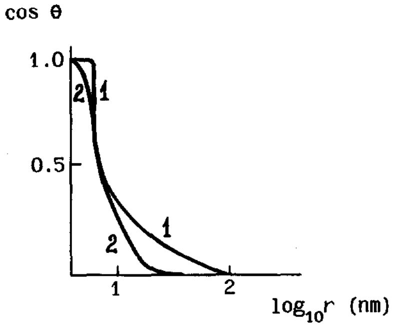


Fig. 8. Integral porograms of a porous PTFE sample measured by MSP with: (1) cyclohexanone; (2) isopropyl alcohol; (3) decane, and (4) measured by MMP [10].

Fig. 9. Wetting angle of water vs. pore size for (1) active carbon adsorbents SKN-1K, and (2) SKN-4M [21].

will not only be a shift but also some deformation of the porogram. From the values of the shift for different values of V_t the dependence of θ on the pore size can be found.

In Fig. 8 porograms are shown for a porous sample of pressed PTFE powder measured with cyclohexanone, isopropyl alcohol and decane. It can be seen that there is an almost parallel shift of the curves without deformation. Assuming that for decane $\theta_s \approx 0°$ we find for cyclohexanone $\theta_t = 52°$ and for isopropyl alcohol $\theta_t = 20°$. These values are close to those measured on a smooth PTFE surface [20].

The situation is different for samples of activated carbon. In Fig. 9 porograms for carbon samples SKN-1 and SKN-4M are presented which were measured with decane and water. It can be seen that the micropores are almost hydrophilic. With increasing pore radius up to 10 nm the wettability with water decreases (wetting angle θ_t increases). Almost all the pores with $r > 10$ nm are hydrophobic.

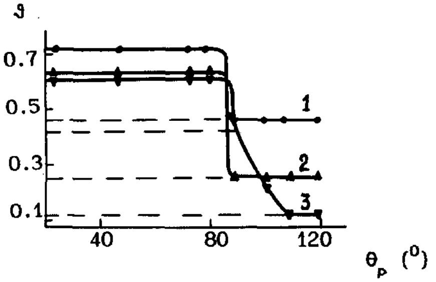
Investigation of multicomponent porous bodies with mixed wettability

Multicomponent porous materials with a mixed water wettability (hydrophobic-hydrophilic materials) are widely used as electrodes in fuel cells and other electrochemical devices, as well as in other fields (glass-reinforced plastics, composite materials, etc.). MSP gives the possibility to obtain information on the structure and surface properties of such kind of materials. For this purpose, measurements are performed with several liquids with a different wettability of each component of the material.

Let us consider a two-component system of a catalytic active electrode consisting of platinum black and PTFE particles. Let us denote the wetting angle of water with the hydrophilic and hydrophobic component as θ_1 and θ_2, respectively. Such a material contains purely hydrophilic pores (between platinum particles), purely hydrophobic pores (between PTFE particles) and mixed pores which are filled with water only in the case when for the mean value of cos θ the condition:

$$\overline{\cos\theta} \equiv ((1-\rho)\cos\theta_1 + \rho\cos\theta_2) > 0 \qquad (3)$$

is fulfilled [22]; ρ is the fraction of the pore surface occupied by the hydrophobic material.



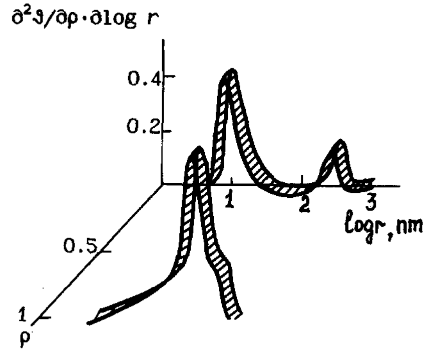


Fig. 10. Flooding degree vs. the wetting angle with different liquids for electrodes of: (1) platinum +6% PTFE; (2) platinum +16% PTFE, and (3) nickel +4.8% PTFE [17].

Fig. 11. Differential pore-distribution function in terms of radii and in terms of hydrophobicity factors ρ for a platinum electrode containing 16% PTFE [17].

In order to evaluate the structure type of this electrode, the dependence of the amount of liquids in the electrode as function of their wetting angle with PTFE, θ_p, was measured by hydrostatic weighing of the electrode in different liquids well-wetting platinum ($\theta_m = 0°$). It can be seen from Fig. 10 that this dependence is step-shaped. In the range of θ_p between 24 and 90° the amount of liquid remains unchanged at a value equal to the electrode's total porosity. At about 90° this value drastically drops and remains unchanged as θ_p increases further (curves 1 and 2). This result shows that in the case considered the amount of mixed pores is small. In the case of an electrode containing carbonyl nickel and PFTE there is a sloping section of this dependence indicating the existence of mixed pores (curve 3).

From the porograms measured with different liquids differential distribution functions of the pore volume in terms of pore radii and ρ values, $\partial^2 V/\partial\rho \cdot \partial \log r$, were calculated (Fig. 11 for a layer containing 16% PTFE). It can be seen that this function has three maxima — two for hydrophilic and one for hydrophobic pores. Such a kind of functions has not been described in literature up to now.

Absorption isotherms

The ability of highly dispersed (colloidal) porous systems to absorb or to release liquids can be investigated by the method of capillary condensation and is usually characterized by absorption isotherms, i.e., equilibrium relations between the amount of liquid bound in the body and the relative vapour pressure of the liquid $\tilde{p} = p_s/p_o$, where p_s is the vapour pressure of the liquid in the system and p_o is its saturated vapour pressure. The upper limit for this method is at a pore size of about 50 nm, where $p_s \approx p_o$.

By using standard porosimetry measurements it is possible to extend the notion of absorption isotherms to a broader range of porous systems. For this purpose it is convenient to use the parameter 'free binding energy liquid-sample' A (capillary potential, differential work of wetting). This parameter is related to the structural (r)

and surface properties (θ) of the system which can be determined by MSP and also to the relative vapour pressure (method of capillary condensation) via the Kelvin equation:

$$A = -RT \ln(p_s/p_o) = \frac{2\sigma \cos \theta \, V_m}{r} \tag{4}$$

Absorption or desorption isotherms expressed as the dependence of the amount of liquid in the system on the free binding energy allows the comparison of the behaviour of any kind of porous systems, investigated by different methods, even of systems with strong interactions between the porous material and the working liquid (adsorption, solvatation, etc.) and of lyophobic systems for which the values of A are negative.

By MSP primarily the distribution function for the parameter A is measured. The calculation of the pore radii from the values of A is based on eqn. (4) which is valid only for radii $r \geqslant 1$ μm. In the case of strong interactions the results cannot be interpreted through the radii r. In order to investigate the geometric (undisturbed) structure in MSP working liquids are used which do not chemically interact with the porous materials, e.g., hydrocarbons, perfluoralkanes, etc.

A number of water desorption isotherms are presented in Fig. 12 as plots of the volume of drowned pores versus A, and, for comparison, versus $\tilde{p}$ and versus r. Very diverse samples have been examined including hydrophilic, hydrophobic and mixed materials, typically porous samples and samples of colloidal type (pine wood, peat). The spectrum of A values measured is rather wide: six orders of magnitude in the hydrophilic region and three orders of magnitude in the hydrophobic region. It can be seen that the isotherms measured by MSP give a very complete information concerning the uptake of liquids by porous systems.

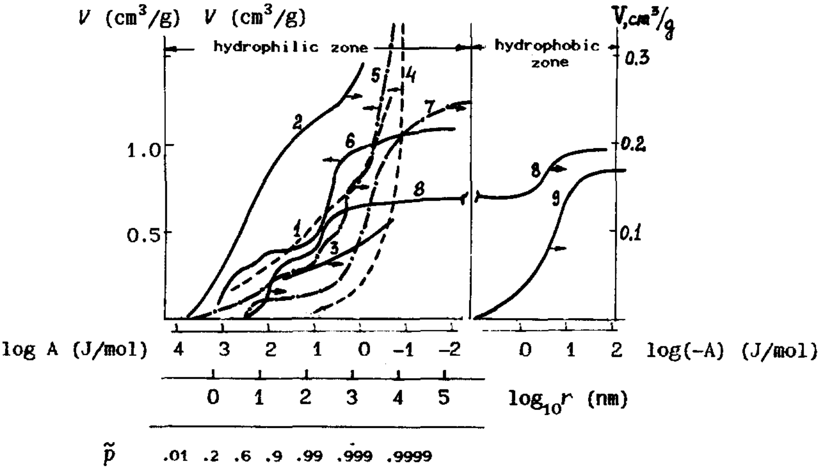


Fig. 12. Integral water volume-distribution curves in terms of quantities log A, log r, and $\tilde{p}$ for: (1) milled peat; (2) red clay; (3) pine wood; (4) quartz sand; (5) filter paper; (6) an electrode of activated carbon; (7) a porous nickel electrode, (8) a porous platinum electrode with PTFE, and (9) a PTFE filter [18].

Automation of measurements

The described MSP includes a great amount of manual operations: multiple assemblage and disassemblage of the stack, weighing of the individual test and standard samples, etc. In order to reduce the amount of operations a mechanical device was designed which allows an automatic assemblage and disassemblage of the stack, partial evaporation of the working liquid and the subsequent transfer of the samples to an electronic balance. The results are accumulated and processed in a PC. In the near future the production of such devices is planned (together with Sartorius from Germany).

Another possibility for simplifying the measurements is the use of special standard samples of nonconducting materials in which two platinum electrodes are inserted. A saturated solution of a salt with low solubility is used as the working liquid. The measured resistance between the electrodes depends on the amount of liquid in the standard sample. The amount of liquid in the test sample is found as the difference of the overall amount of liquid (measured by weighing the whole assembled stack) and the amount of liquid in the standard sample.

Conclusions

A porosimetric method was developed which allows the investigation of all kinds of porous materials including soft or frail materials and powders. This method is nondestructive and allows repeated measurements on one and the same sample. The method can be used for a wide range of pore sizes from 1 to 10^6 nm. The accuracy of this method corresponds to the accuracy of mercury porosimetry. The use of different working liquids allows the evaluation of wetting angles and wettability of multicomponent porous materials. No complex devices and high pressures are needed.

The method of standard porosimetry is now widely used in many scientific and industrial laboratories throughout Russia and other states of the CIS for the investigation of porous materials used in electrochemical devices (electrodes, membranes), and elsewhere.

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