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Assessment of the porosity of solids from thermogravimetry and nitrogen adsorption data

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Abstract

Thermal desorption of liquids was investigated for various types of porous solid. The correlation between results obtained using high resolution thermogravimetry and low temperature adsorption of nitrogen is discussed. Pore size distributions and total pore volumes were estimated for the investigated adsorbents.

Keywords: Pore structure; Thermal desorption, Silica gel; Activated carbon

1. Introduction

Thermogravimetric analysis, as a technique for measuring the weight-loss of a sample as a function of temperature or time, is commonly used to study the decomposition and thermal stability of organic and inorganic substances (see, e.g. Refs [1–3]. Ten years ago we had used temperature-programmed desorption for the investigation of pre-adsorbed water and the determination from TG curves of the total pore volumes of silica gel [4]. Recently, temperature programmed desorption (TPD) was applied to the study of porous oxides, organic porous foils, column chromatography packing and microporous carbons by taking advantage of the enhanced resolution provided by controlled transformation rate thermogravimetry (CRTG) in the manner developed by Paulik and Paulik and called, by them, quasi-isothermal heating mode [1,5–14].

Controlled transformation rate thermal analysis (CRTA) was also proposed by Rouquerol [2]. Moreover, by means of Rouquerol's method, the investigations can be

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carried out in vacuum. Quite recently, CRTA was applied to the study of zeolites [15]. Both methods make it possible to maintain as close as possible quasi-equilibrium conditions and hence to increase the resolution of thermal analysis. High resolution thermogravimetry was also applied to the studies of surface and structural heterogeneity of microporous carbon [16].

The aim of this paper is to discuss the correlations between desorption curves obtained using the quasi-isothermal program and nitrogen adsorption—desorption experiment. In other words, the comparison of the desorption performed in quasi-equilibrium conditions and equilibrium conditions is presented.

2. Experimental

Silica gel Si-100 for column chromatography, active carbon, silica gel, Lichrosorb RP-8, with C_8 alkyl groups bonded to the surface (Merck, Germany) and home-made porous glass 62A were selected for investigations. Their main features are reported in Table 1. Porous solids were dried before experiments by prolonged heating at 180°C. These conditions are sufficient to remove the physically bound water and the temperature is low enough to avoid removing surface hydroxyl groups in the case of oxide adsorbents. The fractions 0.1–0.2 mm of porous materials were used.

Benzene, carbon tetrachloride, methanol (POCh, Poland) and *n*-propanol (Merck, Germany) puriss grade were carefully dried and stored over 4 Å molecular sieve. Moreover, the adsorbates were chromatographically tested for the presence of traces of impurities. The additional test of the purity of the liquids are their boiling temperatures registered on TG curves.

The adsorption/desorption isotherms of nitrogen at −195°C were measured with a Sorptomatic 1800 (Carlo, Erba, Italy) automated apparatus. Surface areas were calculated from the linear form of the BET equation. A value 16.2 Å/molecule was used for the cross-sectional area of the nitrogen molecule. The pore distribution curves were calculated by the BJH method [17] with corrections of the pore radii in respect of the surface film thickness t, where $t = 4.3\sqrt[3]{5/\ln(p_o/p)}$. Pore size distribution curves

Table 1
Parameters characterizing the porous structure of the adsorbents investigated

Adsorbent–liquid	Method				
	Nitrogen adsorption			Thermogravimetry	
	$S_{BET}/(m^2g^{-1})$	$V_p/(cm^3g^{-1})$	$r^p/Å$	$V_p/(cm^3g^{-1})$	$r^p/Å$
Activated carbon—*n*-propanol	1104	0.61	< 20	0.62	< 20
Si-100—CCl_4	322	1.10	66	1.05	64
Porous glass 62A—benzene	203	0.69	52	0.67	49
Lichrosorb RP-8—methanol	214	0.83	77	0.74	61

calculated from desorption isotherms were taken into account. Total pore volumes were estimated in the standard manner from adsorption isotherms at $p/p_0 \approx 1$.

Thermogravimetry analysis was performed using a Derivatograph C (MOM Hungary). The samples for the experiment, in the form of pastes, were prepared by adding excess liquid adsorbate to the dry adsorbent; they were placed in a spiral-type platinum crucible. The type of crucible used makes it possible to keep a self-generated atmosphere of liquid vapours over the sample. The samples were outgassed before experiments to facilitate the peneration of pores by the adsorbate. Thermal desorption of liquid was measured using a quasi-isothermal program with a heating rate $\beta = 3$ within linear range.

3. Results and discussion

In Fig. 1 are shown, for illustrative purpose, the desorption curves of benzene for the series of silica gels of different mesoporosity [6]. The liquid loss on desorption is

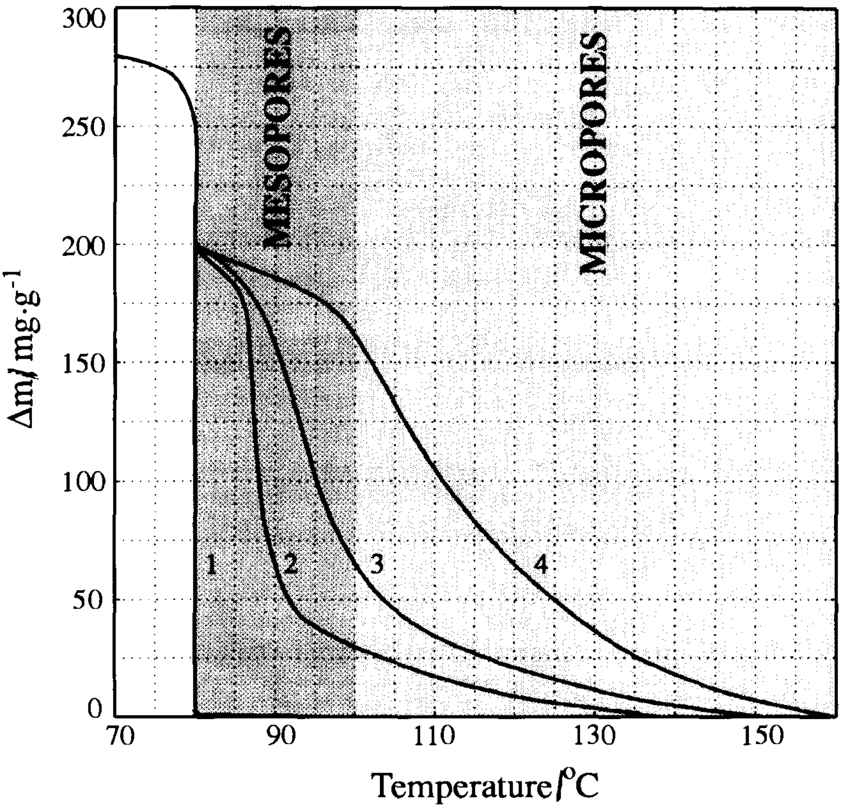

Fig. 1. Thermal desorption of benzene from porous silica gels; (1) evaporation of pure benzene; (2) Si-100 (3) Si-60; (4) Si-40.

reported in mg. In the case of a quasi-isothermal program the heating rate is not constant and changes during the experiment. If evaporation of liquid is slow the fixed weight loss level (in our case $\approx 0.5\,\mathrm{mg\,min^{-1}}$) regulating the run of the program is not exceeded. As a result the linear increase of temperature within measuring range is realized. At a certain temperature corresponding to the temperature of conversion the above mentioned level is exceeded and quasi-isothermal conditions are established for the time during which transformations connected with weight change take place in the sample. In fact, in the case of our experiments, even within the quasi-isothermal range of measurements, temperature increases slightly according to the variation of dimensions of pores evacuated.

As may be expected, the conditions of desorption connected with the heating programme result in process being more or less equilibrium. The influence of various heating rates (from 1.5 to $15\,\mathrm{min^{-1}}$) on the shape of the desorption curves was discussed in Ref. [8]. Textural characterization of the porosity of silica gel by use of various heating programme was also described in Ref. [18]. It follows from these investigations, that the heating rate and consequently rate of desorption strongly influence the time of analysis and does not substantially influence the location of inflection point on the TG curve. Within some time periods, in the case of various quasi-isothermal programme, the changes of temperature are very small. For the smaller heating rate the desorption from pores, having a small share of the total pore volume takes a longer time. For pores with a higher share of the total pore volume the constancy of temperature is satisfactory. The spontaneous stabilization of temperature within the wide range of desorption from pores, independently of the velocity of desorption, indicates that the desorption takes place under quasi-equilibrium conditions. The heating rate ($\beta = 3\,\mathrm{min^{-1}}$) seems to be optimum in our experiments. The curves in Fig. 1 were normalized to the same total pore volume. The initial flat segment represents the evaporation process, the perpendicular segment at the boiling point of liquid corresponds to evacuation of the liquid from the pores. It can be seen that all the curves have an inflection point above the boiling point of liquid which progressively shifts from higher to lower temperatures as the size of the pores increase. Interesting information is provided for temperatures higher than boiling point of the liquid i.e., when the pores are progressively emptied. From the shape of the curve it can be said that a close correlation exists between the porous character of solid and characteristic points of the curves which can be ascribed to the appropriate stages of the desorption process. The upper segments of these curves depend upon particular interactions between the liquid molecules and the adsorbent. Curve 1 in Fig.1 represents the evaporation of pure benzene. This curve illustrates the heating mode realized by using a quasi-isothermal programme for pure liquid. At the end of this curve, after evaporation of last portion of liquid, temperature sharply increase and the curve becomes flat without the extended segment corresponding to desorption from pores and the surface.

The differential curves $\Delta m/\Delta T = f(T)$ for $T \geq 80^{\circ}\mathrm{C}$ are shown in Fig. 2. One can assume that the peaks of these curves represent the mostly intensive evaporation corresponding to emptying of those pores with a greatest share of the total pore volume. The solid line represents the differential curve for pure benzene.

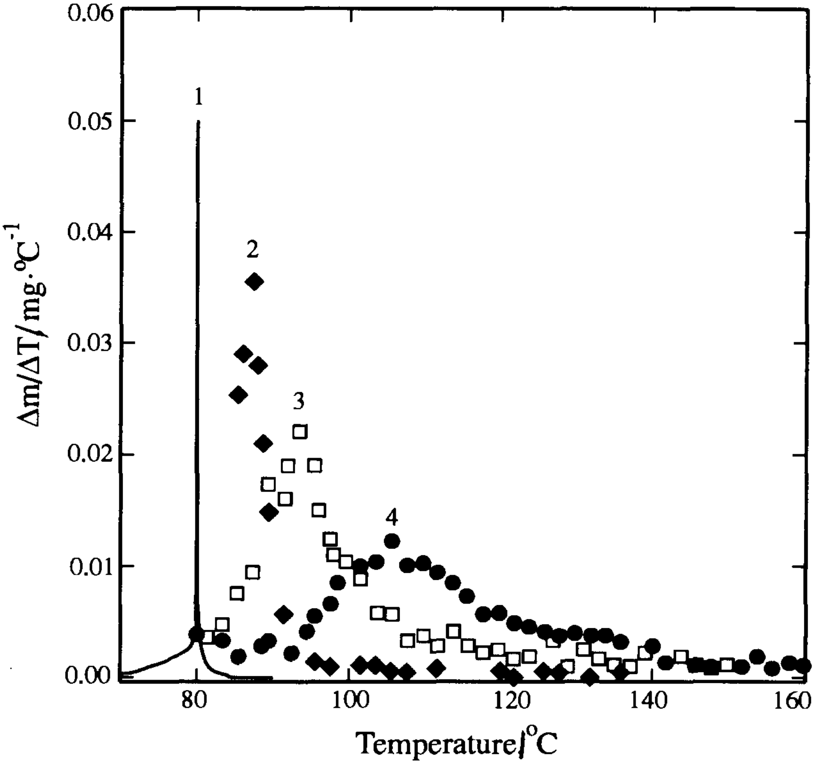

Fig. 2. Differential curves $\Delta m/\Delta T = f(T)$ for: (1) pure benzene (——); (2) Si-100 (◆); (3) Si-60 (□); (4) Si-40 (●).

In Fig. 3 thermodesorption curves (mass against temperature) are shown for various types of porous solid and various liquids. Curve 1 illustrates desorption of carbon tetrachloride from silica gel Si-100; curve 2, desorption of *n*-propanol from active carbon; curve 3, desorption of benzene from porous glass; and curve 4, desorption of methanol from Lichrosorb RP-8. The experimentally obtained curves can be transformed into the dependence of volume loss on pore radius by using the Kelvin equation:

$$\ln \frac{p}{p_0} = -\frac{2\gamma V_M}{r\,RT} \tag{1}$$

Eq. (1) gives the relationship between the saturated vapour pressure of liquid over the curved (i.e. inside the pores) and flat liquid surfaces, p and p_0, respectively; r is the radius of the liquid meniscus, γ is the surface tension of liquid, V_M is the molar and T is absolute temperature. It follows from Eq. (1) that the sharp emptying of the pore of a given diameter occurs under the experimental conditions applied when the liquid vapour pressure becomes equal to atmospheric pressure. For large pore dimensions the evacuation of liquid from the pores occurs at temperatures only a little higher than the

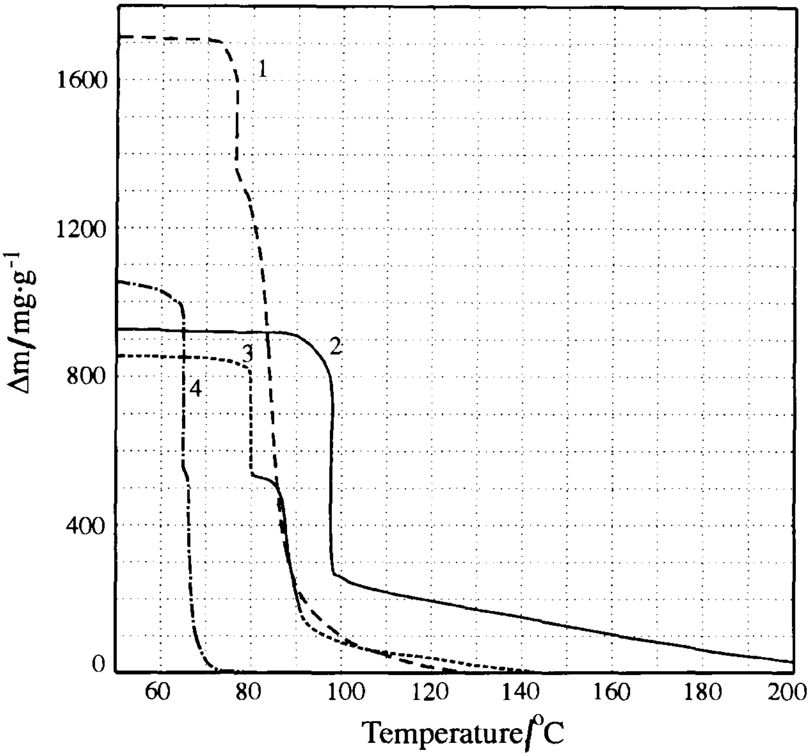

Fig. 3. Thermal desorption curves obtained for: (1) Si-100—CCl_4; (2) active carbon—*n*-propanol; (3) porous glass 62A—benzene; (4) Lichrosorb RP-8—methanol.

boiling point of the liquid. When the pore dimensions decrease a higher temperature is required for their emptying. In our TG experiment the value of p is constant and equal to atmospheric pressure. The values of p_0 are functions of temperature.

It seems interesting to compare the desorption curves obtained from the nitrogen adsorption experiment with those from the TG method. For these purposes, Fig. 4 show the dependences of the amount desorbed on p/p_0 obtained using different techniques. It should be noted that for the adsorption experiment p/p_0 represents the relative pressure at $T=$ *const* and in the case of the TG experiment the p/p_0 values are temperature-dependent. Points represent the adsorption and desorption isotherms of nitrogen. Lines represent the desorption curves from the TG experiment. As is apparent, for silica gel Si-100 (part C) the TG curve starts at lower values of V next goes along the desorption isotherm of nitrogen and at the lowest values tends to zero, which is reached at lower p/p_0 values than for the nitrogen experiment. The different shape of TG curves at the beginning of experiment, when temperature is close to the boiling point of the liquid, is a result of different mechanism of desorption. Near the boiling point of the liquid, part of the liquid present in macropores is desorbed together with

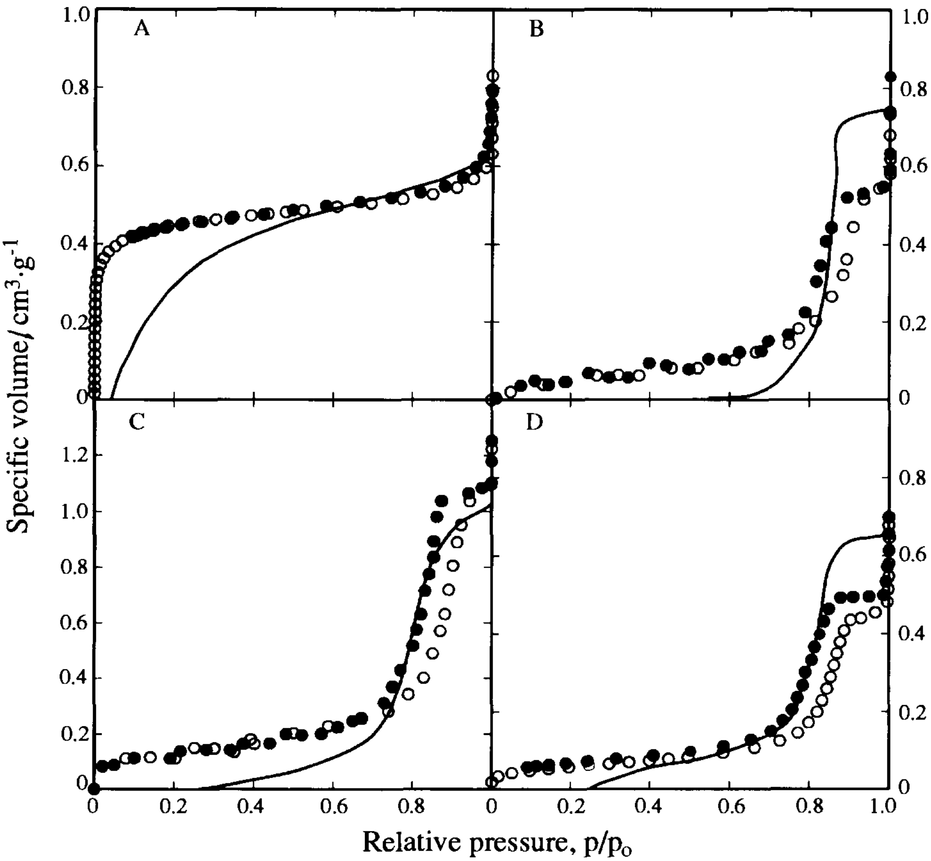

Fig. 4. Adsorption (○)—desorption (●)isotherms of nitrogen (points) and thermal desorption curves (——) for: (A) active carbon—*n*-propanol; (b) Lichrosorb RP-8—methanol; (C) Si-100—CCl_4; (D) porous glass—benzene.

the bulk liquid. The steep segment of the desorption curve is registered under quasi-isothermal conditions and represents desorption from mesopores. At higher temperatures, when desorption from micropores and the solid surface takes place, the fixed weight loss level in the quasi-isothermal programme is not exceeded and the heating mode is linear. Thus, at higher temperatures the desorption from pores is very quick.

Similar, parallel changes of the shape of the desorption curves measured in static, equilibrium conditions and quasi-isothermal conditions of the TG experiment occurs for porous glass (Fig. 4, part D).

Some correlations between the curves measured by using different techniques can be observed for carbon sample (Fig. 4, part A) containing practically only micropores. The TG curve is smooth without the steep segment characteristic of mesopores. Moreover, one can observe that in the case of activated carbon the curve is more extended along

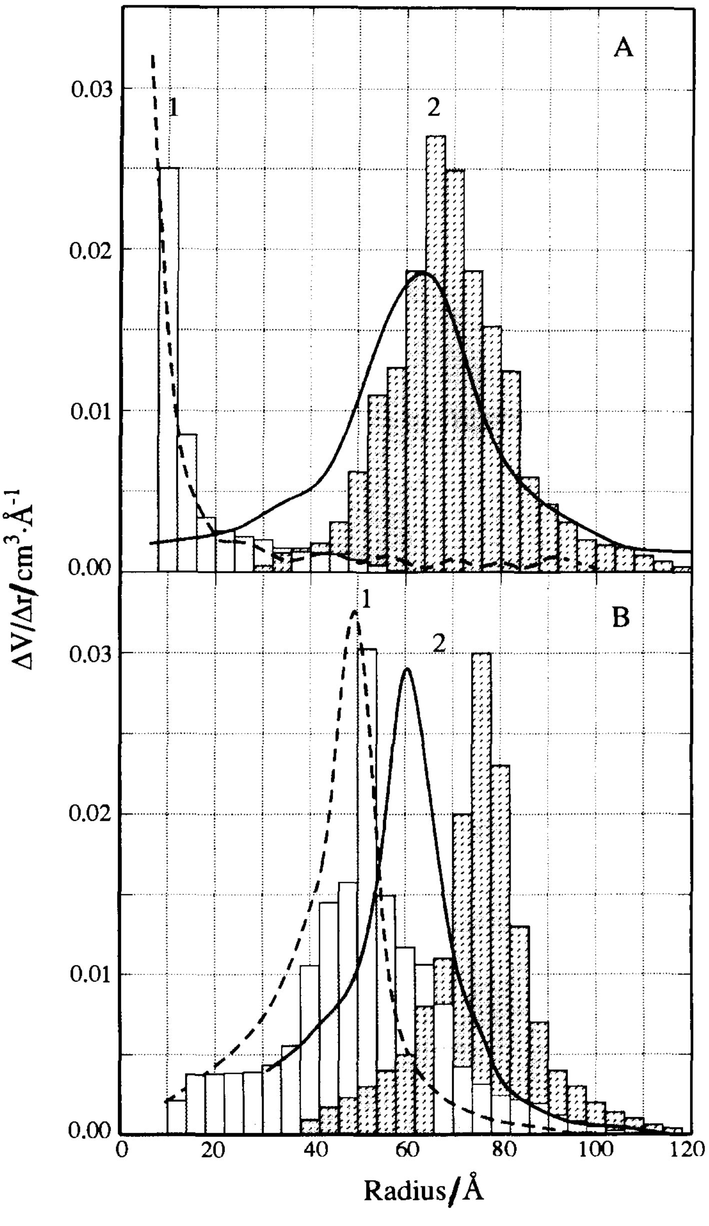

Fig. 5. Pore size distributions curves for: (A1) active carbon—n-propanol; (A2) Si-100—CCl_4; (B1) porous glass 62A—benzene; (B2) Lichrosorb RP-8—methanol; —— and - - - represent PSDs calculated from TG data, bars are PSDs from nitrogen desorption data.

the pressure axis. It should be noted that desorption from micropores requires a higher temperature to which lower p/p_0 values are ascribed.

From the TG data transformed using the Kelvin equation the pore size distribution PSD curves, $\Delta V/\Delta r = f(r)$ were calculated for investigated systems in the manner described earlier [10]. As is seen in Fig. 5, PSD curves derived from TG data (lines) and nitrogen method (bars) are close together except for the Lichrosorb RP-8—methanol system (Fig. 5 B2). Pore radii at the peak of PSD, r^p for both used techniques are included in Table 1. Table 1 also lists total pore volumes (V_p). In the case of the TG method V_p values were calculated from the amount of liquid desorbed between its boiling temperature and the end of the process. Appropriate corrections for changes of liquid density with temperature were introduced. Pore volumes V_p estimated on the basis of the data measured by using different techniques are in good agreement.

From the comparative analysis of experimental data presented above one can conclude that the TG method is accurate and sensitive enough for characterization of the porosity within the mesopores. It is also possible to distinguish whether a given sample contains only mesopores or also micropores.

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