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# FRACTAL DIMENSIONS FROM Q-TG DATA FOR ESTIMATION OF SURFACE HETEROGENEITY

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## Abstract

Programmed thermodesorption of *n*-butanol from Na-, La-montmorillonite, natural and commercial zeolite samples in quasi-isothermal conditions made. The new method of fractal dimension calculations from thermogravimetry data has been presented. On the basis of nitrogen adsorption–desorption isotherms from sorptometry and mercury porosimetry data the fractal dimensions of montmorillonites were calculated. The results from above independent and separated techniques were compared and good correlation were obtained.

**Keywords:** fractal dimensions, montmorillonites, programmed thermodesorption, sorptometry and porosimetry techniques, thermogravimetry, zeolites

## Introduction

The term fractal was introduced for the first time by Mandelbrot while observing stock exchange share fluctuations. Irregular and ragged curves were obtained. The studies showed [1] that many processes and structure difficult to be described by means of traditional Euclidean geometry can be precisely characterized using fractal geometry. While describing physical objects by means of fractal geometry, they are assumed the existence in the three-dimensional space. Fractals can be applied in many areas of science (topology, theory of multiplicity, Brownian motion), art, studies of nature and Galaxy distribution. Using fractals for description of real structures their most important properties are the follows:

- self-resemblance indicating that each object can be divided into parts geometrically similar to the whole object,
- fractal size which assumes fractional values.

Fractal geometry is frequently used to describe macroscopic objects. However, it can also be used for description of microstructure of solids of complex and disordered structure (e.g. adsorbents, polymers, minerals). In this case three main types of fractals can be distinguished: mass, porous and surface ones.

Mass fractal $D_m$ describes mass aggregate build-up of smaller units (primary molecules) which are connected to each other. Mass $M(r)$ of the aggregate in the sphere of radius $r$ is described by the following relationship [2, 3]:

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$$M(r) = M_0 r^{-D_m} \tag{1}$$

where $M_0$ is a constant.

The value $D_m$ ranges $1<D_m<3$. The boundary value $D_m=1$ describes the shape of thin rod without bifurcation but the upper value $D_m=3$ indicates transfer from the branched structure to the pure mass. The increase of dimension means increasing density of the material. Thus thin rod, thin plate and sphere possess fractal sizes of 1, 2 and 3.

Porous fractals $D_p$ often called volume fractals, are a negative of mass fractals. For the object described by the porous fractal size, the change of pore volume $V_p$ depending on the change of their radii $r_p$ can be expressed using the following equation [4]:

$$\frac{dV_p}{dr_p} = K_p r_p^{2-D_p} \tag{2}$$

or

$$V_{p\sim} r_p^{3-D_p} \tag{3}$$

where $K_p$ is the constant.

The values $D_p$ are in the interval $2<D_p<3$. For the values of fractal size 2, pore distribution is homogeneous but for 3 – the material possesses more heterogeneous pores.

Surface fractals $D_s$ have a constant value of density but the objects described by them are confined with rough and corrugated surfaces. The surface area is described by the following equation [2, 3]:

$$S(r) = S_0 r^{-D_s} \tag{4}$$

where $S_0$ is constant, $r$ is the radius of three-dimensional area confined by the surface fractal.

The values $D_s$ are in the interval $2<D_p<3$. The lower boundary value 2 corresponds to the flat surface but the upper value 3 to the corrugated one which fills up the whole space.

Recent studies have shown that using fractal dimensions enables determination of real sizes of pore radii from the data of programmed thermodesorption of liquid and calculations of the pore-size distribution functions [5]. The main aim of this paper is determining fractal dimensions which draw near the shape of studied pores to the real one is their application for calculation of pore radii from the thermogravimetric data. Application of the classical Kelvin equation leads to:

$$\ln\frac{p}{p_0} = \frac{-2\gamma V_m}{rRT} \tag{5}$$

where $\gamma$ is the liquid surface tension, $V_m$ is the liquid molar volume, $R$ is the gas constant, $T$ is the temperature.

Calculation of pore radii from the thermogravimetric data gave unacceptable results because, among others, of the assumption of the cylindrical pore shapes. It does not include parameters that take into account the kinetics of the process and the diffusion of molecules during the thermodesorption of liquid from solid surface (e.g. the change in the relative equilibrium vapour pressure with temperature). The Kelvin equation does not take into account the changes in molar volume and surface tension of the liquid with the variation of temperature, the changes in thickness of the adsorption films on the surface and of the pore radii, or the changes in liquid properties with the variation in distance from the surface during evaporation of liquid in special crucible of the derivatograph. The results obtained from above equation were 10 times smaller than those expected [6]. Therefore, the Kelvin equation does not 'work' and is not suitable for investigation of the above systems by using the method of thermal desorption of liquids under quasi-isothermal conditions. More data and discussions on above problem are presented in papers [6–10].

This paper presents a new method for calculation of surface fractal dimensions based on data of programmed liquid thermodesorption from solid surfaces under quasi-isothermal conditions. The data were compared with those obtained from sorptometry and porosimetry.

### *Apparatus and materials*

Fractal dimensions were calculated from the data of liquid thermodesorption under quasi-isothermal conditions obtained by means of a derivatograph Q-1500 D (MOM. Hungary) [11]. Porosity properties of the samples were estimated using a sorptometer ASAP. 2405 V1.01 (Micrometrics Inc., USA) and mercury porosimeter 4000 (Carlo Erba Instruments, Italy).

The tested materials were Na- and La-montmorillonites from Lago Pellegrini (Argentina) [12]. The substituted samples were obtained by saturation of the ion exchange capacities of the water-saturated clay samples with sodium and/or lanthanium chloride (0.5 M). Finally, the Na- and La-samples were air dried. Moreover, thermodesorption of liquids from natural zeolite-clinoptilolite and zeolite-mordenite (from Ukrainian Transcarpathian region) were made. Before the measurements the samples were saturated with polar (water and *n*-butanol) and apolar (benzene and *n*-octane) vapours of liquids in a vacuum desiccator, where $p/p_0=1$.

## Results and discussion

Determination of fractal dimensions is an important problem for getting to know chemical reactions, diffusion, adsorption and catalysis. Therefore a method has been developed for their calculation from the data obtained by thermal analysis and a comparison was made with the values calculated from measurements by sorptometry and porosimetry. Moreover, the information on structural properties (geometrical heterogeneity) of samples were obtained by means of the above mentioned methods.

Figure 1 shows the isotherms of nitrogen adsorption and desorption at temperature of 77.35 K on the surface of Na- and La-montmorillonite samples obtained by sorptometry. Adsorption isotherms presented on Fig. 1 (II type in classification of BET theory) exhibit a hysteresis loop which indicate the presence of mesopores on

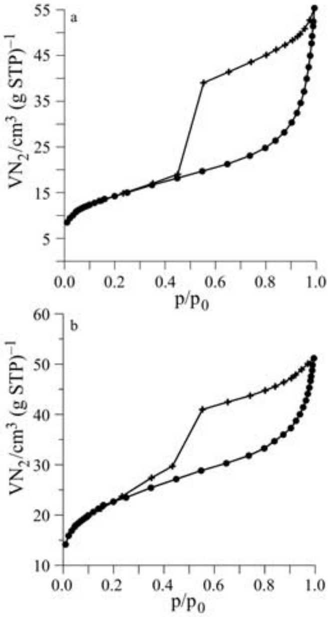

**Fig. 1** Nitrogen adsorption(+)-desorption(o) isotherms on the a – Na- and b – La-montmorillonite samples at 77.35 K

surface of the samples. Figure 1 shows the steps on their isotherms for relative pressure 0.4 and 0.8–1 (condensation steps).

Figures 2 and 3 show the thermogravimetric mass loss Q-TG and differential D-DTG curves in relation to temperature obtained during thermodesorption of *n*-butanol from Na- and La-montmorillonites (Fig. 2) and zeolite-clinoptilolite and zeolite-mordenite (Fig. 3) samples. It is clear from these figures that steps and/or inflections of the thermodesorption process, i.e. evaporation of *n*-butanol from capillary tubes (regions III), pores, interpackets spaces, windows (regions II) and active centres (regions I) of the surface were obtained. From Q-TG and Q-DTG curves the adsorption capacity of samples, number of hydroxyl groups (i.e. active centres), thermodynamic functions (e.g. enthalpy, entropy, activation energy), desorption energy distribution and pore-size distribution functions were calculated before [5–9, 12, 13].

The fractal dimensions were calculated from sorptometry data using the method described in [12, 14] which is based on the theory by Frenkel, Halsey and Hill and also of Kisielev [15]. The fractal dimensions $D_f$ can be calculated from the following equations [2, 12, 16]:

$$D_f = 2 + n_f \tag{6}$$

$$D_f = 3 - \mathrm{d}[\ln a(x)]/\mathrm{d}[\ln(-\ln x)] \tag{7}$$

$$D_f = 2 + \mathrm{d}\left[\ln \int(-\ln x)\mathrm{d}a\right]/\mathrm{d}[\ln(-\ln x)] \tag{8}$$

$$\mathrm{d}V/\mathrm{d}r = A(r) \sim r^{2-D_f} \tag{9}$$

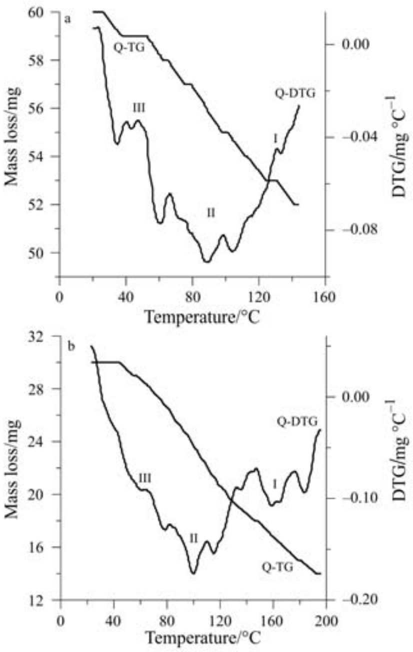

**Fig. 2** The mass loss Q-TG and differential Q-DTG curves of *n*-butanol thermodesorption from a – Na-montmorillonite and b – La-montmorillonite samples immersed in vacuum desiccator

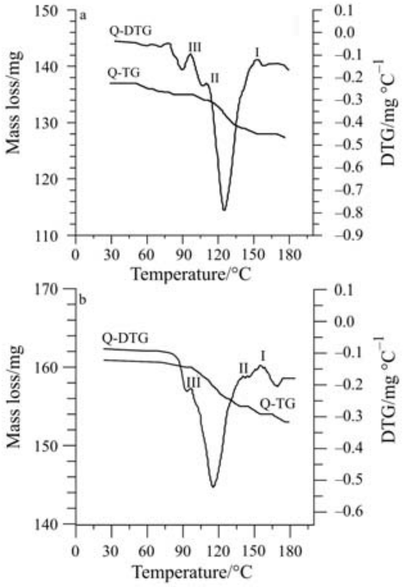

**Fig. 3** The mass loss Q-TG and differential Q-DTG curves of *n*-butanol thermodesorption from a – clinoptilolite and b – mordenite samples immersed in vacuum desiccator

where $n_f$ is a fractional part of the fractal, $a$ is the size of adsorption, $x$ is the segment of experimental isotherm, $V$ and $r$ are the volume and radius of pores. The function $A(r)$ is determined from the experimental data of the adsorption hysteresis.

The dependences $\ln a$ as a function $\ln(-\ln x)$ and $\int(-\ln x)\mathrm{d}a$ as a function $\ln(-\ln x)$ were plotted from Eqs (6) and (7). A good rectilinear dependence was obtained. From the above dependences using an analytical method the fractal dimensions were calculated from Eqs (6)–(9) and presented in the Table 1 for Na- and La-montmorillonites and in Table 2 for zeolite-clinoptilolite and zeolite-mordenite samples. The average values of fractal dimensions $D_f$ for montmorillonites are 2.49 and 2.75, and for zeolites are 2.61 and 2.59, respectively.

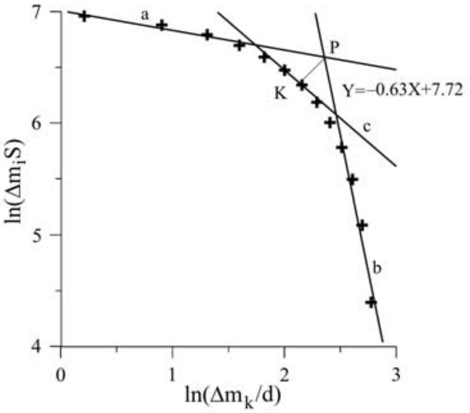

**Fig. 4** Fractal dimension on the basis of Q-TG thermodesorption of *n*-butanol from La-montmorillonite surface under the quasi-isothermal conditions

A new method for calculation of fractal dimensions from the data of programmed liquid thermodesorption from solid surfaces under quasi-isothermal conditions was developed in this work. The curve of *n*-butanol mass loss from the La-montmorillonite sample presented in Fig. 2 was transformed in Fig. 4 into the form of dependence $\ln[(m_0-m_1)S]$ as the function $\ln[(m_1-m_k)/d]$ where $m_0$ is the initial mass of the sample; $m_1$ is the mass of the sample at a temperature $T_i$, $m_k$ is the final mass of the sample, $d$ is the liquid density and $S$ is the specific surface area of the sample. In Fig. 4 point P is obtained from the intersection of tangents *a* and *b*. The straight line perpendicular to the tangent C was made from point P and there was marked point K which corresponds to the minimum on the curve Q-DTG (Fig. 2). The fractal dimension was calculated for this value of *n*-butanol mass loss by an analytical method from the slope of tangent C using the following equation [17]:

$$D_f=(2+3n_f)/(1+n_f) \tag{10}$$

Tables 1 and 2 summarise the values of fractal dimensions calculated from the thermogravimetry desorption of four liquids mass loss data from montmorillonite and zeolite surfaces.

**Table 1** The fractal dimensions of montmorillonite samples calculated from sorptometry, thermogravimetry and porosimetry methods

| Samples | Sorptometry method: $D_f$ calculated from Eq.: | | | | | Thermogravimetry method | | | | Porosimetry method |
|---|---|---|---|---|---|---|---|---|---|---|
| | (6) | (7) | (8) | (9) | Average | water | *n*-butanol | benzene | octane | |
| Na-montmorillonite | 2.59 | 2.62 | 2.34 | 2.78 | 2.49 | 2.44 | 2.42 | 2.44 | 2.50 | 2.88 |
| La-montmorillonite | 2.93 | 2.86 | 2.20 | 2.99 | 2.75 | 2.51 | 2.39 | 2.44 | 2.44 | 2.86 |

**Table 2** The fractal dimensions of zeolite samples calculated from sorptometry, thermogravimetry and porosimetry methods

| Samples | Sorptometry method: $D_f$ calculated from Eq.: | | | | | Thermogravimetry method | | | | Porosimetry method |
|---|---|---|---|---|---|---|---|---|---|---|
| | (6) | (7) | (8) | (9) | Average | water | *n*-butanol | benzene | octane | |
| Clinoptilolite | 2.64 | 2.56 | 2.57 | 2.67 | 2.61 | 2.50 | 2.40 | 2.50 | 2.50 | 2.90 |
| Mordenite | 2.58 | 2.67 | 2.50 | 2.60 | 2.59 | 2.45 | 2.44 | 2.43 | 2.49 | 2.87 |

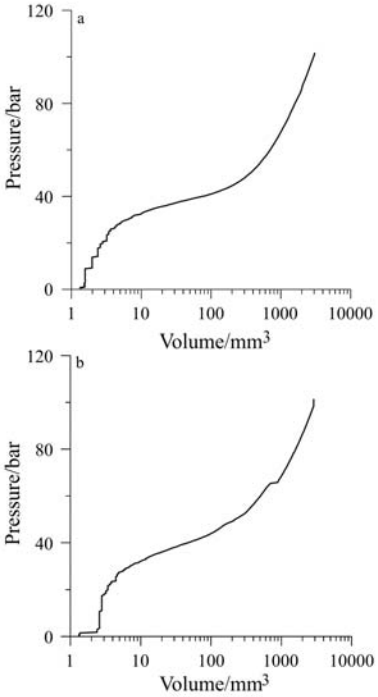

**Fig. 5** The mercury pressure in relation to pore volume of a – Na-montmorillonite and b – La-montmorillonite samples

Fractal dimension from porosimetry data of Na- and La-montmorillonite samples presented in Fig. 5 were calculated from the following equation [18,19]:

$$\frac{\mathrm{d}V}{\mathrm{d}P} \sim P^{D_\mathrm{f}-4} \qquad (11)$$

where $V$ and $P$ are the volume and pressure of mercury.

Fractal dimensions of Na- and La-montmorillonite can be calculated using a simple analytical method from the curves of the dependence of d$V$/d$P$ as a function of $P$ (Fig. 6):

$$\log(\mathrm{d}V/\mathrm{d}P) \sim (D_\mathrm{f}-4)\log P \qquad (12)$$

From the slope of tangents to these curves fractal dimensions were calculated. The values of $D_\mathrm{f}$ are: 2.88 and 2.89 for Na- and La-montmorillonite, and 2.90 and 2.87 for zeolite-clinoptilolite and zeolite-mordenite samples, respectively (Tables 1 and 2).

Tables 1 and 2 show the collected calculations of fractal dimensions from the experimental data of three independent and separate research methods. Comparison of the results show a good agreement. The obtained values $D_\mathrm{f}$ show that the montmorillonite sample modified with lanthanum ions is more heterogeneous than the one modified with sodium ions which confirms the results obtained using a sorptometry (among others, larger specific surface area and smaller radius of the pores of La-

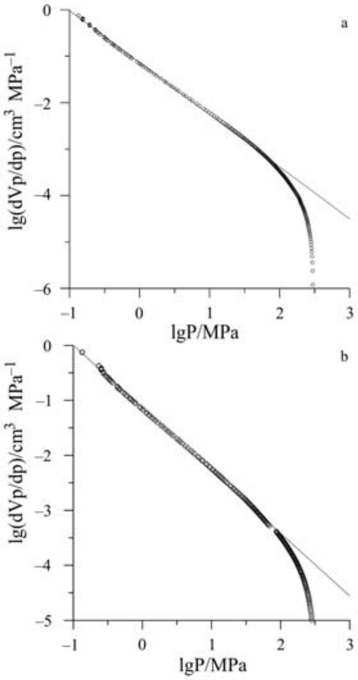

**Fig. 6** The dependences of log(d$V$/d$P$) as a function $P$ calculated from porosimetric data for a – Na-montmorillonite and b – La-montmorillonite samples

montmorillonite sample) [12]. The range of calculated $D_f$ values confirms sorptometry and porosimetry measurements that the surface of the materials studied possesses heterogeneous properties.

## Summary

The new method for determination of the fractal dimensions of montmorillonite and zeolite surfaces using programmed liquid thermodesorption desorption under quasi-isothermal conditions was presented. The obtained results were compared with similar ones from sorptometry and porosimetry data and a good correlation has been obtained. It can be stated that the above analytical method of fractal dimensions calculation from the thermogravimetric data is simple and useful for estimation surface heterogeneity of porous material.

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