

## TOTAL HETEROGENEITY OF $\text{Al}_2\text{O}_3$ SURFACE Programmed *n*-octane thermodesorption under quasi-isothermal conditions

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### Abstract

The paper presents evaluation of energy distribution of *n*-octane and pore-size distribution functions on the alumina oxide surface (e.g. total heterogeneity) of on the basis one experimental run. The Q-TG mass loss and derivative Q-DTG mass loss curves of *n*-octane thermodesorption from the alumina oxide sample were made using a Hungarian derivatograph with an analyser equipped with an automatic ultraslow procedure and a special crucible of maintaining the quasi-isothermal heating procedure to increase the resolution of thermal analysis. A new theoretical and experimental procedure was developed for evaluation of distribution functions of liquid preadsorbed on the mesoporous surface from special thermogravimetry. An example of the approach to quantitative description of the energetic and structural heterogeneities of alumina oxide surface is given.

**Keywords:** desorption of liquid, energy and pore-size distribution functions, quasi-isothermal thermogravimetry, total heterogeneity of solids

### Introduction

The programmed thermodesorption method is commonly used in the studies of surface properties of adsorbents, catalysts, advanced materials and adsorbed liquid films [1–3]. From the experimental mass loss curves and the assumption of adsorption model it is possible to determine kinetic, thermodynamic parameters of the processes and heterogeneous properties of solid surfaces [4–6].

The dependences of temperature maximum  $T_m$  in the programmed thermodesorption on the rate of temperature increase  $\beta$  were studied [7] using Eq. (1)

$$2\ln T_m = \frac{E_{md}}{RT_m} + \ln \frac{E_m V_m \beta}{Rv} \quad (1)$$

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where  $E_{\text{md}}$  – maximum desorption energy,  $R$  – universal gaseous constant,  $V_m$  – molar volume,  $\nu$  – entropy parameter.

Changing the value  $\beta$  in Eq. (1) it is possible to determine the maximum desorption energy  $E_{\text{md}}$ . The value of desorption energy can be also determined from the dependences of desorption rate on temperature assuming the constant value  $\beta$  rate of temperature increase from equations [8]:

$$\ln \left[ -\frac{d\theta}{dT} \frac{1}{(1-\theta)} \right] = \ln \frac{\nu}{\beta} - \frac{E_d}{RT} \quad (2)$$

where  $\theta$  – degree of sorbent coverage.

As shown in paper [8] both ways of determining the parameters  $E_d$  and  $\nu$  give similar results only for the homogeneous surface. However, calculating  $E_d$  and  $\nu$  values on the basis of the shape of the experimental TPD spectrum (with or without taking into account readsorption) from the maxima of peaks on the TPD curve, a perfect result can be achieved which follows from the appearance of surface energetic heterogeneity. In literature the dependence of  $E_d$  on  $\theta$  is associated with both interactions of adsorbate molecules with active centers of different energy and adsorbate-adsorbate interactions. The paper presents the analysis of thermogravimetric curves taking into account surface and energetic heterogeneity and adsorbate molecules interactions.

## Theory

The rate of desorption from the monomolecular layer for the single adsorption sites can be described using the following equation [6]:

$$-\frac{d\theta}{dt} = \nu(1-\theta) \exp\left(-\frac{E_d}{RT}\right) \quad (3)$$

where  $t$  – desorption time and  $T=T_0+\beta t$ .

In such a case desorption rate on the whole surface is described by the following equation:

$$-\frac{d\theta}{dT} = \int_{E_d} \varphi(E_d)(1-\theta) \frac{\nu}{\beta} \exp\left(-\frac{E_d}{RT}\right) dE_d \quad (4)$$

Equation (4) is the Friedholm integral equation of the first order. Energetic heterogeneity of the sorbent surface is shown by the distribution function  $\varphi(E_d)$ . This is the density of adsorption center distribution probability in relation to adsorption energy.

Let us introduce such a distribution function  $\varphi(E_d)$  in which the term  $\varphi(E_d)dE_d$  determines the number of adsorption centers in the interval  $E_d=E_d+dE_d$ . Then one of the tasks to estimate the TPD curves is to determine a form of the function  $\varphi(E_d)$ . Generally it leads to solution of integral Eq. (4) using analytical (e.g. integral calculation method) and numerical methods. However, the form of sub-integral function must be known [9]. The task can be simplified if there is used the numerical, differen-

tiation or tangent method to determine the distribution function  $\varphi(E_d)$  for transformation into the dependence  $\theta(E_d)$ . The function  $\varphi(E_d)$  can be calculated from the transformed equation:

$$\varphi(E_d) = -\frac{dv}{dT} \frac{T(RT+E_d)}{2RTE_d+E_d^2} \quad (5)$$

After assuming a form of the function  $\varphi(E_d)$ , the quantity of adsorption for mesopore adsorbents must be determined in order to interpret and describe TPD curves for type IV isotherms according to BET classification. Moreover, the estimation of specific surface area and pore volume distribution in relation to the radius sizes was made. Essential assumptions of capillary condensation theory were formulated in paper [10]. Its main assumptions about initial laminar filling of pores surface and volumetric filling of pores at the saturated vapour pressure smaller than that for the flat macroscopic surface of phase distribution remains unchanged.

To interpret the dependence between the pressure of saturated vapour in pores and the sizes of pores there is used the Kelvin equation [10]:

$$\ln\left(\frac{p}{p_0}\right) = \frac{2\gamma V_L}{\rho_m RT} \quad (6)$$

where  $p$  – vapour pressure at temperature  $T$ ,  $p_0$  – saturated vapour pressure,  $\gamma$  – surface tension of liquid,  $V_L$  – molar volume of liquid,  $\rho_m$  – average radius of meniscus curvature.

Using this equation assumes a spherical size of gas-liquid distribution for cylindrical pores of the radius  $\rho$  and cylindrical shape in crevice pores of the width  $h$ . This refers to the liquid in the pore core i.e. on the pore walls, which are covered with the adsorption film of the thickness  $t$ . However, the Kelvin equation does not apply for the pores of the widths close to molecule diameters. The reason for this may be the deviation in the values of surface tension and molar volume from the value of normal liquid adsorbate. Under such conditions the concept of meniscus is meaningless [10].

Generally, the value of adsorption work for the whole interval of pore size can be presented in the following form [11]:

$$-A = RT \ln \frac{p}{p_0} = \frac{2\gamma V_L}{\rho - t \left(\frac{p}{p_0}\right)} F(\rho) + U(\rho) \quad (7)$$

where  $F(\rho)$  – function ( $F(\rho)=0$ , when  $\rho=\rho_c$  and  $F(\rho)=1$ , when  $\rho>\rho_c$ ,  $\rho_c$  – critical radius,  $U(\rho)$  – potential energy of adsorbate molecule interactions in pores.

The value of critical radius of pores can be determined in the first approximation as  $\rho_c \approx 5\sigma$ . This condition holds only for the small-energy surface. In the general case  $l/\sigma \approx 5$ , where  $l$  is the characteristic size of pores. It determines precisely properties of the phase, as shown in the left side of the Kelvin equation. In order to use Eq. (4) there should be determined the point of vapour pressure for the monolayer, which for the isotherm of type IV is determined by quantity of relative vapour pressure  $p/p_0 \approx 0.6-0.8$ .

Rightness of the Kelvin equation in the area of adsorbate cluster structure is not determined. The true formula (5) is also very complicated and for practical application one can use the equation:

$$\rho = t \left( \frac{p}{p_0} \right) + \frac{2\gamma(\rho)V_L}{-RT \ln \left( \frac{p}{p_0} \right)} \quad (8)$$

The results of studies on adsorption thermodynamics in these pores carried out using models [12], molecular dynamics [13] and numerical Monte-Carlo methods [14] as well as based on the density distribution function [14] do not provide simple and reliable methods for estimation of changes in adsorption properties in thin pores. Therefore the results presented in [12] are used in this paper. There was introduced the dependence of surface tension at the gas-liquid interface in the free volume and in the pores  $\gamma\sigma^2/\varepsilon_{ff}=f(T/T_c, \rho)$ . Based on paper [15], the dependence  $\gamma/\gamma_\infty$  was introduced that is on the surface tension in the pores of  $\rho$  radius and in the free volume, respectively. Using Eq. (8) one should take into account the increase in the molar volume of the condensed phase. The quantity determined in Eq. (8) is presented with the product  $\gamma(\rho)V_L$ . The decrease in the surface tension value in the pores  $\gamma(\rho)$  after equalization with the surface tension value in the free volume is taken into account. The surface tension at the gas-liquid interface after equalization with the free volume decreases and the extent of decrease depends on temperature. In the first approximation the decrease of surface tension in pores can be estimated according to the formula [15]:

$$\gamma(\rho_m) = \gamma_\infty \left( 1 - \frac{\rho_c}{\rho_m} \right) \quad (9)$$

where  $\gamma_\infty$  – surface tension for free volume,  $\rho_c$  – critical radius.

The value of critical radius  $\rho_c$  in formula (9) corresponds to the critical size of the radius for the function  $F(\rho)$  in formula (7). In transformation of Eq. (8) one should take into account the influence of both quantities –  $\gamma(\rho)$  and  $V_L$ . As mentioned earlier this problem is very complicated. The analysis of mesopores from the adsorption data based on the assumption that density of condensed liquid does not depend on equilibrium pressure of vapour can lead to serious errors. Paper [11] presents also the method of mesopore structure analysis based on the developed capillary condensation theory taking into account the adsorbate state of matter. If the Speedy equation [16] is used in the equation of liquid condensation state, then the relation between the molar volume of the condensed liquid  $V_L$  and the pressure can be presented by the following function [11]:

$$RT \ln \frac{p}{p_0} = (p_m - p_0) V_L \gamma \quad (10)$$

where

$$\gamma = \frac{2}{a^2} \frac{V_L}{V_m} \left[ \ln \left( \frac{V_L}{V_m} \right) + a \right], \quad a = \frac{V_m - V_L}{V_L}$$

and  $p_m$ ,  $V_m$  – pressure and molar volume, respectively.

Values  $p_m$  and  $V_m$  in the first approximation can be calculated from the Van der Waals equation and transforms [17] into the dependence between the value  $p_m$  and the critical pressure of the corresponding adsorbate. Let us consider the properties of the adsorption layer  $t$ . It is the function of the statistic number of monolayers ( $\theta$ ) and the effective thickness of each layer  $\sigma$ :  $t = \theta\sigma$ . On the other hand,  $\theta$  depends not only on the value  $p/p_0$  but also on the ‘pure’ heat of adsorption of adsorbing molecule. As already shown the octane molecule can be considered as a rigid molecule of spherical-cylindrical shape, radius  $r$  and length  $l$ . In this case the thickness of adsorption monolayer depends on molecular orientation towards the surface of pore walls. With the parallel orientation of the molecule this thickness is  $2r$  and with the vertical orientation  $2r+l$ . The radius of octane molecule  $r$  and its length  $l$  can be calculated according to the formula obtained earlier [18]:

$$x = 3\omega \left( 1 + \sqrt{1 + \frac{8}{9\omega}} \right), \quad r = \sigma^3 \sqrt{\frac{1}{6x+8}} \quad \text{and} \quad x = \frac{1}{r} \quad (11)$$

where  $\sigma$  – van der Waals diameter of the molecule,  $\omega$  – Pitzer coefficient [19].

Molecules can be both horizontally and vertically oriented on the surface. Orientation of each molecule depends on the reciprocal ratio of potential and kinetic energy [20]. The number of statistical monolayers is determined according to the BET theory from the adsorption isotherm [10]. Reproduction of the adsorption isotherm according to the experimental curve TPD can be made using equation [21]:

$$p = \frac{V}{C} \exp \left[ - \left( \frac{\nu \beta E_d}{R} I + \frac{E_d}{RT} \right) \right] \quad (12)$$

where  $I$  is calculated using the following formula:

$$I = \frac{\exp \frac{E_d}{RT}}{\left( \frac{E_d}{RT} \right)^2} \left[ \sum_{n=1}^{\infty} (-1)^{n-1} \frac{n!}{\left( \frac{E_d}{RT} \right)^{n-1}} \right]$$

and  $C$  – constant.

Equation (12) at  $E_d/RT > 10$  makes it possible to determine the quantity  $p$  with the relative error up to 10% including five points after comma. It means that in the range of monolayer filling, Eq. (12) can be used for plotting a suitable isotherm. However, with the decrease of the quantity  $E_d/RT$  the order in Eq. (12) changes rapidly. Asymp-

otic approximation of Eq. (12) in the range of multiplayer adsorption has not been sufficiently studied so far.

On the other hand, the adsorption isotherm can be plotted from the curve of mass loss Q-TG and the equation combining 'pure' adsorption heat with the quantity  $p/p_0$ . From the function of pore volume distribution in relation to their radii obtained by the analysis of Q-TG curve of the liquid programmed thermodesorption [6], it is possible to determine the surface fractal size of the adsorbent  $D$  using the following formula [19]:

$$-\frac{dV(\rho)}{d\rho} = \rho^{2-D} \quad (13)$$

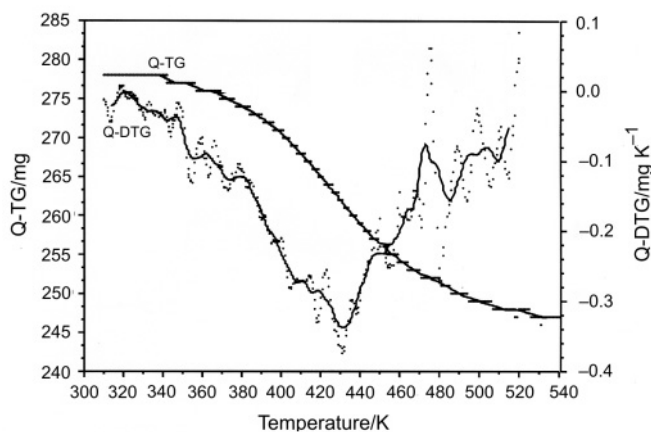
Calculation of mesopores volume distribution in relation to their radii is possible only when the isotherm used is of type IV in the BET classification.

## Experimental

Measurements of programmed thermodesorption under the quasi-isothermal conditions of *n*-octane from the surface of neutral alumina sample were made by means of the derivatograph Q-1500 D (MOM Budapest, Hungary) [3]. The apparatus was connected with a computer by the interface and equipped with the Derivat program for calculation of the first derivatives of mass loss Q-DTG curves with respect to temperature and time. The Q-TG mass loss curves were measured under the quasi-isothermal conditions over a 20–300°C temperature range, using an analyzer equipped with an automatic ultraslow heating device, a labyrinth crucible, and capable of maintaining quasi-isothermal conditions to increase the resolution of thermal analysis. The Q-TG curves were measured over a constant heating rate of 6° min<sup>-1</sup>. Compared with the studies carried out under the classical conditions, the quasi-isothermal method has some advantages, among which are a broader applicability and much greater selectivity. This method is more reliable in the investigations of transformation of overlapping processes [5]. This paper presents the results of *n*-octane thermodesorption from the porous adsorbents – neutral aluminum oxide samples (Aluminum Co. of America, AL-COA Center, PA, USA). The samples were thermally treated in air at 250°C already located in the vacuum desiccator, where the relative vapour pressure of *n*-octane was  $p/p_0=1$ . About 0.5 g of the wetted alumina oxide was placed in the special platinum crucible of the thermogravimetric analyser.

## Results and discussion

Figure 1 presents the Q-TG mass loss and the Q-DTG differential mass loss curves with respect to temperature of *n*-octane thermodesorption from neutral porous Al<sub>2</sub>O<sub>3</sub> saturated with vapour in desiccator. It follows that the presented curves are characterized by a few inflections (on Q-TG) and peaks (on Q-DTG) resulting from successive stages of evaporation of *n*-octane being in different energetical stages on the alumina surfaces. The thickness of the adsorbed layer can be controlled by altering the mode



**Fig. 1** The Q-TG and Q-DTG curves of *n*-octane thermodesorption from the surface of neutral alumina sample

of immersion of the samples. Thus, immersion in *n*-octane vapours in a desiccator with  $p/p_0=1$  saturates all adsorption sites as well as surface and capillary forces. Under such conditions the surface and capillary forces are compensated as in the McBain balance static adsorption method. The samples prepared in this way do not contain excess bulk liquid, which would affect the kinetic and mechanism of thermodesorption by lateral interactions between molecules. The Q-DTG curves are a characteristic 'spectrum' of the thermodesorption process and reflect an energetic state of *n*-octane molecules on the surface of alumina with various heterogeneous properties. The shape of Q-DTG curves result from the discontinuous properties of adsorbed layers and disruption of the adsorbate–adsorbate and adsorbate–adsorbent bonds. The adsorption energies of *n*-octane result from dispersive interactions.

The interpretation of *n*-octane thermodesorption from alumina surfaces can be explained as follows. The first stage is the evaporation of liquids from capillaries (desorption of the liquid film in the region of capillary condensation on the adsorption isotherm). In next stages, thermodesorption of liquids takes place from mesopores and finally from the surface and active sites of the samples. Using the single Q-TG and Q-DTG curves it is possible to determine the adsorption capacity (e.g. thickness of adsorbed film), pore volume (i.e. geometrical heterogeneity), discontinuous change of adsorbed layer properties, mechanism of wetting process and energy interactions between the liquid molecules and the solid surfaces (i.e. energetical heterogeneity) [6].

Analyzing the curve it is possible to separate seven distinct peaks, corresponding values of their maximum temperature, (in K): 306.2, 352.2, 393.2, 431.6, 453.2, 485.2, 511.2. The numerical analysis of separated values  $T_m$  from Eq. (1) confirms the presence of seven different types of adsorption centers on the surface. Further analysis of the curves Q-TG and Q-DTG was made using the models described in paper [8]. From the experimental spectra of Q-TG and Q-DTG the dependence was calculated:

$$\ln \left[ -\frac{d\theta}{dT} \frac{1}{(1-\theta)} \right] = f \left( \frac{1}{T} \right) \quad (14)$$

The obtained curve presented in Fig. 2 is characterized by great non-linearity as confirmed by a large extent of surface energetic heterogeneity.

Graphical analysis of dependence (14) by means of the tangent method makes it possible to separate seven intervals with different values  $E_d$  on the curve presented in Fig. 2.

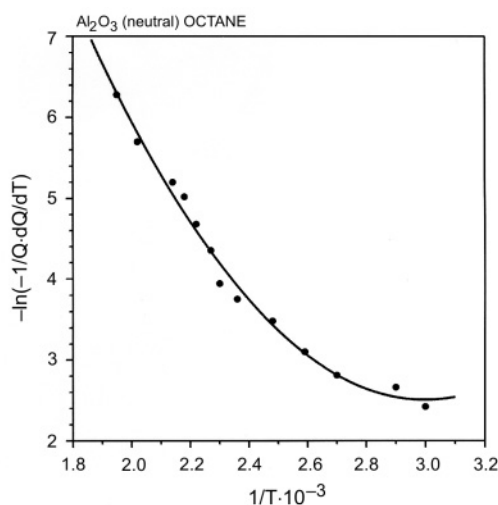


Fig. 2 The dependence of  $\ln \left[ -\frac{d\theta}{dT} \frac{1}{(1-\theta)} \right]$  on inverse temperature

From the numerical analysis of the dependence

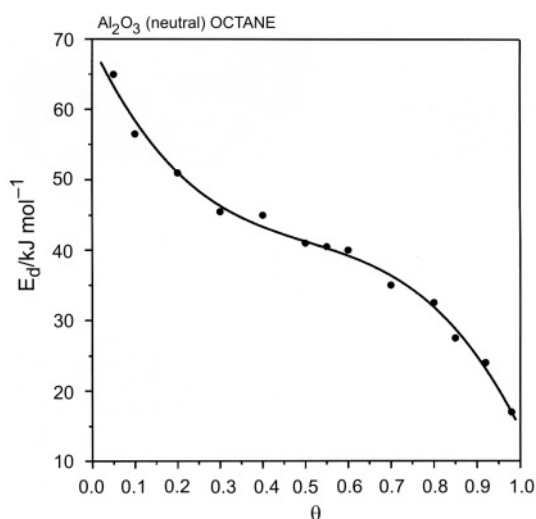
$$\ln \left[ -\frac{d\theta}{dT} \frac{1}{(1-\theta)} \right] = f \left( \frac{1}{T} \right)$$

using the method given in papers [2, 3] the following dependences of desorption energy on temperature were obtained:

$$\begin{aligned} E_d &= 0.18T - 38 \text{ kJ mol}^{-1} && \text{for the interval } 0 < T < 403.2 \text{ K} \\ E_d &= 0.31T - 91 \text{ kJ mol}^{-1} && \text{for the interval } 403.2 < T < 520 \text{ K} \end{aligned} \quad (15)$$

The dependence of  $E_d$  on temperature is shown by the curve composed of two straight lines whereby the intersection point of straight lines corresponds to  $T=403.2$  K. The boiling point of octane is  $T_b=398.9$  K [19]. Equation (12) shows two ranges of dependences  $E_d=f(T)$  on the surface of the process of different character. Analogous dependence of desorption energy on the extent of coverage  $\theta$  of the surface is presented in Fig. 3.





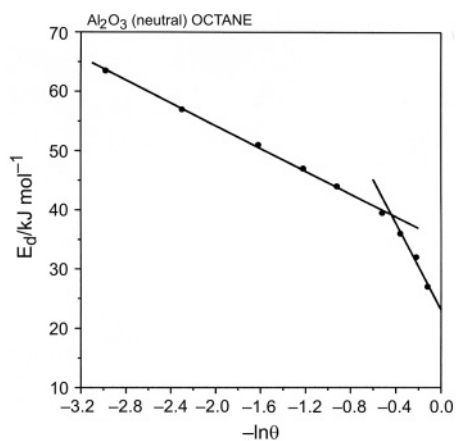
**Fig. 3** The curve of dependence of desorption energy on the coverage value  $\theta$  of the surface of neutral alumina sample

$$E_d = 35.5 - 9.24 \ln \theta \quad \text{for the interval } 0 < T < 403.2 \text{ K} \quad (16)$$

$$E_d = 21.5 - 45.21 \ln \theta \quad \text{for the interval } 0 < T < 403.2 \text{ K}$$

Figure 3 indicates that for the thermodynamic system adsorbate - adsorbent the dependence of energy  $E_d$  on the coverage  $\theta$  is of exponential character. Figure 4 presents the diagram of the dependence of  $E_d$  on  $\ln \theta$ . One can see two sections with the intersection point at  $T = 403.2$  K. The boiling point of octane corresponds to the intersection point.

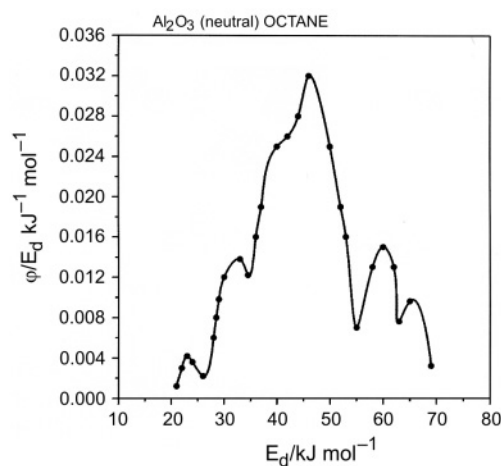
The dependence of entropy coefficient on desorption energy is presented by the following equation:



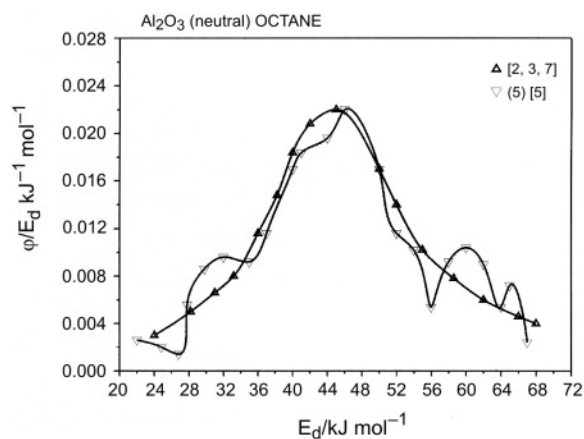
**Fig. 4** The plot of the dependence of desorption energy  $E_d$  on the  $\ln \theta$  value for neutral alumina sample

$$\frac{1}{\beta}v=0.21\exp(1.1\cdot 10^{-4} E_d) \quad (17)$$

Calculation of the function of desorption energy distribution was made using formula (5). The obtained diagram presented in Fig. 5 is qualitatively in agreement with the mass loss curve whereby the peaks in Figs 1 and 5 are in agreement with the accuracy of error calculation.



**Fig. 5** Energy distribution curve of octane thermodesorption from the surface of neutral alumina sample, calculated using formula (5)



**Fig. 6** Energy distribution curves of octane thermodesorption from the surface of neutral alumina sample, calculated from Eq. (5) – curve 2; and using methods [8] – curve 1

Figure 6 presents normalized values of distribution functions calculated from Eq. (5) (curve 2) and, for comparison (curve 1) using the method given in papers [8, 22].

Both distribution functions were calculated from the Q-TG curves. The agreement of the results calculated using the above methods is observed only for the interval of the mesopores.

The value of the radius of mesopores was calculated from the Q-TG and Q-DTG data. Formula (8) is used to calculate the radius of pores taking into account thickness of the adsorption layer  $t$ . The diameter of octane molecule is 0.75 nm. Calculations using formula (11) give thickness of the layer for horizontal positions of molecules equal to 0.49 nm and for the vertical position of molecules –1.33 nm. It seems that starting from the second layer the dependence between kinetic and potential energy of molecule interactions is favorable for vertical orientation of spherical–cylindrical molecules of octane. It should be noted that approaching the point of multilayer saturation of the surface, mobility of molecules in the layer increases causing its ‘swelling’. It was assumed in the calculations that in the first layer the molecules are oriented horizontally and in the next ones vertically. The thickness of adsorption layer was calculated.

Figure 7 presents the dependence of thickness of the layer  $t$  as a function of  $p/p_0$ . The obtained dependence is in agreement with the analogous one in the case of  $n$ -hexane adsorption on active carbon [10]. Slightly greater values of the quantity  $t$  are due to the increase of  $\sigma$  value for octane and differences in orientation of molecules.

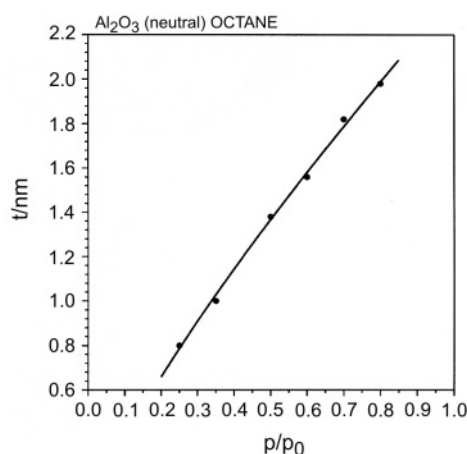
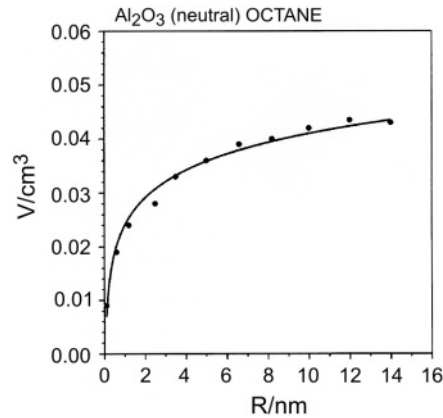


Fig. 7 The plot of the dependence of the thickness of adsorption layer  $t$  on  $p/p_0$

Sizes of pore radii were calculated from Eq. (8). Volumes of mesopores were calculated from the molar volume of the volumetric liquid. The error in the size of molar volume is essential only for the pores smaller than 7 nm. The preliminary calculations showed that the increase of  $n$ -octane molar volume in the area of radii of mesopores close to the critical radii for  $n$ -octane  $\rho_k \approx 3$  nm does not exceed 15% but for the pores of the diameter larger than 7 nm the change of molar volume can be neglected.

Figure 8 shows the dependence of mesopores volume quantity on their radii. To confirm the calculations of the radius of pores  $\rho$ , the coefficient of core volume con-



**Fig. 8** The relationship between pore volume and pore radius for neutral alumina oxide sample

version into the volume of pores ( $Q$ ) was determined which was calculated for the cylindrical pores using the equation:

$$Q = \left( \frac{\rho}{\rho - t} \right)^2 \quad (18)$$

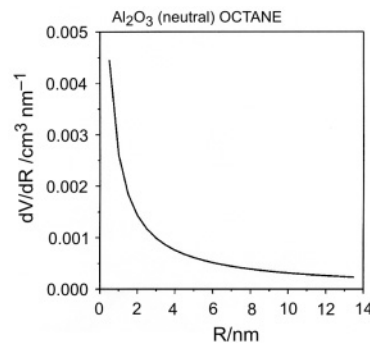
The calculations show that the quantity  $Q$  changes from the value 1.95 for  $p/p_0=0.4$  to the value 1.35 for  $p/p_0=0.8$ . The size order for the value  $Q$  in this case is in agreement with the values calculated for *n*-hexane [10]. For the dependence of pores volume on their radii presented in Fig. 8 it was obtained:

$$V(\rho) = 0.023 \rho^{0.28} \quad (19)$$

The function of mesopore volume distribution in relation to their radii calculated from Eq. (18) can be given in the form:

$$\frac{dV(\rho)}{d\rho} = 6.44 \cdot 10^{-3} \rho^{2-D} \quad (20)$$

where the surface fractal dimension:  $D=2.72$ .



**Fig. 9** Pore-size distribution function curve for neutral alumina sample

The values of mesopores volume and radii and the value of the fractal size  $D$  are convergent, as for the size order, with the corresponding values obtained during the studies of the structure Al<sub>2</sub>O<sub>3</sub> [23]. The pore-size distribution function is presented in Fig. 9. It is seen that the pores with the radius near 2 nm have the highest intensity in this curve. The concentration of the mesopore decreases with the increase of their radius. The observed shape of the pore-size distribution curve is typical of most commercial mesoporous adsorbents. For example, this shape is similar to that evaluated from the low-temperature nitrogen adsorption isotherms on various activated carbons by using the Dollimore–Heal method [24].

## Conclusions

Based on the studies using quasi-isothermal thermogravimetry, it can be stated that the presented method is useful and effective for quantitative characterization of the structural and energetic heterogeneities of mesoporous solids from one experimental run. The evaluated energy distribution and the pore-size distribution functions of  $n$ -octane on the alumina oxide surface (e.g. total heterogeneity) are in good agreement with the parameters of porous structure of the above solid and with the known characteristics of  $n$ -alkane adsorption. The increase of a number of adsorbents and other materials with different pore sizes and adsorbates possessing different acid/base properties and wettability provides possibility for creating in further studies total heterogeneities of these solids by means of quasi-isothermal thermogravimetry.

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