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CHARACTERIZATION OF THE STRUCTURAL AND ENERGETIC HETEROGENEITY OF MESOPOROUS SOLID SURFACES FROM Q-DTG DATA

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Abstract

This paper presents the first evaluation of the pore-size distribution and energy distribution of butanol on a silica gel surface on the basis of one experimental run. The Q-TG mass loss and the first derivative Q-DTG mass loss curves of *n*-butanol thermodesorption from a silica gel sample were made with a Derivatograph Q-1500 D (MOM, Hungary), using an analyser equipped with an automatic ultraslow procedure and a special crucible capable of maintaining the quasi-isothermal heating procedure to increase the resolution of thermal analysis. A numerical procedure was developed for evaluation of the mesopore-size distribution and energy distribution functions of liquids preadsorbed on the mesoporous surfaces from special thermal analysis techniques. This is based on a condensation approximation to treat the kinetics of liquid thermodesorption from solids. A preliminary example is presented of application of the above approach to a quantitative description of the structural and energetic heterogeneities of silica gel surfaces on the basis of a single Q-DTG curve of *n*-butanol thermodesorption under quasi-isothermal conditions.

Keywords: condensation approximation, heterogeneity of solids, pore-size distribution and energy distribution functions, quasi-isothermal method

Introduction

The surfaces of most industrial adsorbents, catalysts and their supports are energetically and structurally heterogeneous. Both the pore-size and adsorption potential distributions of the surface have a great effect on the properties of adsorbed liquid films, viz. their thickness and structure [1]. Methods of characterization of liquid–solid interfaces (parameters of the adsorbed layers, thermodynamic functions of adsorption and adsorption energy distributions) are usually

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based on spectroscopic, adsorption, calorimetric, chromatographic and porosimetric measurements. They consist in evaluation of the parameters of the adsorbate–adsorbent interaction as a function of the surface or pore coverage. These data are used in the following calculations of the adsorption energy and/or pore-size distributions. The above-mentioned methods are time-consuming and the calculations involved are arduous. It is therefore necessary to develop other, more simple and rapid methods for the characterization of structurally and energetically heterogeneous surfaces and their interactions with other, more complex substances (liquids or vapour) than simple gases.

Thermal analysis has been successfully adopted to investigate various liquid–solid interfaces ([2] and references therein). The principal idea of these studies has been to register the changes taking place during the thermodesorption of liquids from the solid surface under quasi-equilibrium conditions. The amount desorbed and the rate of desorption of a liquid are influenced by the strength of the adsorbate–surface interaction, the properties of the adsorbate (its polarizability, polarity and acid/base characteristics), the types of the surface sites, their acid/base properties, topography and concentration, and the porosity (pore volume, size, shape and specific adsorption area). The method consists mainly in measuring the liquid mass loss from the sample during the thermodesorption process carried out under suitable conditions.

The aim of the present study was to develop a numerical procedure for evaluation of the parameters of the mesopore-size distribution and desorption energy distribution of liquid and/or vapour preadsorbed on a mesoporous solid surface from the Q-TG and Q-DTG curves measured under quasi-equilibrium conditions. The example is presented of the application of this approach to a quantitative description of the structural and energetic heterogeneities of the silica gel surface on the basis of a single Q-DTG curve of the preadsorbed vapour of *n*-butanol under quasi-equilibrium conditions.

Theory

Let us assume that the peak and/or its first part in the Q-TG and Q-DTG curves relates to the desorption of a liquid or vapour substance preadsorbed within the pores, together with the film adsorbed on the walls of the pores. We can consider the relationship between the activation energy of desorption of the adsorbate molecules from the mesopores with their radius r_k. In accordance with the Kirchhoff equation, the relationship between the molar enthalpy of the liquid substance and temperature is

$$\Delta H_T = \Delta H_o + \int_o^T [C_p(\text{vap}) - C_p(\text{liq})]\mathrm{d}T \qquad (1)$$

where ΔH_T and ΔH_o are the molar enthalpies of the substance at temperatures T and 0°C, and C_p(vap) and C_p(liq) are the molar heat capacities of the substance in the gaseous and liquid states.

On combining this equation with the Clausius-Clapeyron equation and integrating, we obtain

$$\ln P = -\frac{Q_o}{RT}\int_{o}^{T}\frac{1}{RT^2}\mathrm{d}T\int_{o}^{T}[C_p(\mathrm{vap}) - C_p(\mathrm{liq})]\mathrm{d}T + j_p \tag{2}$$

where Q_o is the vaporization heat and j_p is the constant of buoyancy of the vapour.

If we ignore the temperature dependence of the molar heat capacities, the above equation gives the Kirchhoff-Rankine-Dupre equation:

$$\ln P = a + \frac{\Delta C_p}{R}\ln T - \frac{Q_o}{RT} \tag{3}$$

Let us assume to a first approximation that the terms a and ΔC_p are unaffected in the mesopores. Under the special conditions, the Kelvin equation can be applied to describe the capillary condensation process in the mesopores:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{2\gamma V_M}{r_k RT} \tag{4}$$

where P and P_o are the saturated vapour pressures of liquid inside the pores and the flat liquid surface, respectively, γ is the surface tension of the test liquid, V_M is its molar volume, r_k is the radius of the liquid meniscus in the pores and T is the absolute temperature.

The radius r_k of the mesopores ranges from 1 to 15 nm. Therefore, the Kelvin equation describes the capillary condensation process in the mesopores within this region of mesopore sizes. By combining Eq. (3) with the Kelvin equation (4), we can obtain the following expression:

$$Q_{\mathrm{pore}} - Q_o = \frac{2\gamma V_M}{r_k} \tag{5}$$

where Q_{pore} is the molar vaporization heat of the liquid in the mesopores.

As concerns the kinetics of desorption of weakly physisorbed molecules from the thick liquid film, it may reasonably be assumed that the desorption activation energy (E_d) of a probe approximately corresponds to its condensation enthalpy or to its vaporization heat:

$$E_{d(\mathrm{pore})} = Q_{\mathrm{pore}} = Q_o + \frac{2\gamma V_M}{r_k} \tag{6}$$

The overall desorption rate ($\mathrm{d}V_{\mathrm{pore}}/\mathrm{d}t$) from the structurally heterogeneous solid is given by

$$\frac{\mathrm{d}V_{\mathrm{pore}}}{\mathrm{d}t}=\int_{E_{\mathrm{d\,min}}}^{E_{\mathrm{d\,max}}}\frac{\mathrm{d}V_{\mathrm{i}}(E_{\mathrm{di}})}{\mathrm{d}t}\rho(E_{\mathrm{d}})\mathrm{d}E_{\mathrm{d}} \tag{7}$$

where V_{pore} is the overall relative volume of the mesopores released at time t (at $t\to\infty$, $V_{\mathrm{pores}}=1$), $\rho(E_{\mathrm{d}})$ is the desorption energy distribution of the porous solid, $E_{\mathrm{d\,min}}$ and $E_{\mathrm{d\,max}}$ are the lower and upper limits of the integration of Eq. (7), and $\mathrm{d}V_{\mathrm{i}}(E_{\mathrm{di}})/\mathrm{d}t$ is the kernel of the Fredholm integral equation of the first kind, describing the local first-order rate of desorption of the preadsorbed substance with desorption activation energy E_{di} from the i-th type of pores.

This kernel is determined as

$$\frac{\mathrm{d}V_{\mathrm{i}}(E_{\mathrm{di}})}{\mathrm{d}t}=A_{\mathrm{d}}V_{\mathrm{i}}(E_{\mathrm{di}})\exp\left(-\frac{E_{\mathrm{di}}}{RT}\right) \tag{8}$$

where T is the desorption temperature, R is the universal gas constant, A_{d} is the pre-exponential factor of the desorption reaction, and $V_{\mathrm{i}}(E_{\mathrm{di}})$ is the relative local volume of the pores in which the preadsorbed substance has desorption activation energy E_{di}.

In order to simplify the evaluation of the experimental Q-TG and Q-DTG curves and/or temperature-programmed desorption (TPD) spectrum, it is usually assumed that the pre-exponential factor A_{d} is constant. Many of the methods developed for the theory of adsorption equilibrium and kinetics on heterogeneous surfaces can be extended to the kinetics of desorption from heterogeneous surfaces [3–5]. In the present study, we use the condensation approximation (CA) [6], which gives a simple analytical expression for the distribution function in terms of the desorption rate under isothermal conditions and which does not produce unstable solutions. The CA consists in replacing the kernel of the integral equation ($\mathrm{d}V_{\mathrm{i}}(E_{\mathrm{di}})/\mathrm{d}t$) by the stepped function. Let us assume that in the desorption process the occupied pores are released sequentially, as follows:

$$\frac{\mathrm{d}V_{\mathrm{i}}(E_{\mathrm{di}})}{dt}=\begin{cases}1 \text{ for } E_{\mathrm{di}}>E_{\mathrm{dc}}\\ 0 \text{ for } E_{\mathrm{di}}<E_{\mathrm{dc}}\end{cases} \tag{9}$$

The pores with desorption activation energy E_{dc} are released at temperature T such that the local desorption rate has a maximum. Let us assume that the desorption temperature varies linearly with time, as is usually the case in most TPD and Q-TG experiments, in accordance with the relationship

$$T=T_{\mathrm{o}}+\beta t \tag{10}$$

where T_o is the initial temperature of the desorption and β is the coefficient (in K s^{-1}).

Therefore, the desorption activation energy can be calculated for each temperature T_i in the TPD spectrum and/or Q-TG and Q-DTG curves from the following non-linear equation:

$$\frac{E_{dc(i)}}{RT_i} = \ln\left(\frac{A_d T_i}{\beta}\right) - \ln\left(\frac{E_{dc(i)}}{RT_i}\right) \tag{11}$$

It should be mentioned that Eq. (11) coincides with the Redhead equation for first-order desorption kinetics at initial relative surface coverage Θ_o=1 [7]:

$$\ln\left(\frac{\beta E_d}{RT_M^2} A_d \Theta_o^{n-1}\right) + \frac{E_d}{RT_M} = 0 \tag{12}$$

where T_M is the temperature of the peak maximum (in K), and n is the desorption reaction order.

Equation (12) has the following approximate solution for E_d in the case of first-order desorption kinetics

$$E_d = RT_M\left[\ln\left(\frac{A_d T_M}{\beta}\right) - 3.46\right] \tag{13}$$

The approximate desorption distribution function in the CA, $\rho(E_{dc})$, can be obtained as follows:

$$V_{pore} = \int_{E_{dc\,min}}^{E_{dc\,max}} \rho(E_{dc})dE_{dc} \tag{14}$$

The solution of Eq. (14) will in general differ from the solution of Eq. (7), and for this reason the distribution function $\rho(E_{dc})$ in Eq. (14) has been denoted with the index c. A comparison of the desorption energy distribution functions and pore-size distributions obtained in the CA with those evaluated from Eq. (7) by using a more exact numerical modified regularization procedure or a non-negative least-squares method was performed recently [8, 9]. It was concluded that, for most peaks recorded in the TPD and Q-TG experiments, the CA method yields satisfactory results. Equation (14) gives an adequate description of the distribution function $\rho(E_d)$ provided that the desorption energy spectrum is wider than RT, and $\rho(E_d)$ varies smoothly with E_d.

From Eq. (14), it follows that the decrease in the mesopore filling is related to the increase of the desorption temperature as

$$\frac{dV_{pore}}{dT} = -\rho(E_{dc})\frac{dE_{dc}}{dT} \tag{15}$$

or

$$\rho(E_{dc}) = -\frac{dV_{pore}}{dT}\frac{dT}{dE_{dc}} \tag{16}$$

The first derivative of T with respect to E_{dc} is given by

$$\frac{dT}{dE_{dc}} = \frac{T(RT + E_{dc})}{2RTE_{dc} + E_{dc}^2} \tag{17}$$

If Eqs (10), (16) and (17) are taken into account, an expression can be obtained for the approximate desorption energy distribution from the pores for each temperature T_i in the Q-DTG curve

$$\rho(E_{dc})_i = -\frac{dV_{pore(i)}}{\beta dt_i}\frac{T_i(RT_i + E_{dc(i)})}{2RT_iE_{dc(i)} + E_{dc(i)}^2} \tag{18}$$

Hence, the desorption energy distribution of the heterogeneous surface can be evaluated from a single TPD spectrum and/or from the Q-DTG curve by using Eqs (11) and (18) for each temperature T_i in the non-isothermal experiment, and relating to it the rate of the desorption reaction dV_i/dt_i (the loss in sample mass per unit time in the case of the Q-TG experiment, or the intensity of the TPD spectrum in the TPD MS techniques).

Let us consider the possible relation between the desorption energy distribution, $\rho(E_{dc})$, and the mesopore-size distribution, $\chi(r_k)$. The basic assumption in this approach is that the desorption energy in the mesopores is determined by their sizes. The relationship between the pore size r_k (or, more exactly, the core size) and the desorption energy $E_{dc}(r_k)$ is given by Eq. (6). By using the function $E_{dc}(r_k)$ and the calculated desorption energy distribution $\rho(E_{dc})$, we can evaluate the mesopore-size distribution, $\chi(r_k)$, from the relationship

$$\chi(r_k) = \rho(E_{dc})\frac{dE_{dc}(r_k)}{dr_k} \tag{19}$$

If we take into account Eq. (6) the distribution $\chi(r_k)$ can be calculated as

$$\chi(r_k) = -\rho(E_{dc})\frac{2\gamma V_M}{r_k^2} \tag{20}$$

The pore size related to the desorption temperature T_i can be calculated by substituting the expression for $E_{d(i)}$ (Eq. (6)) into Eq. (11)

$$Q_o + 2\gamma V_M - RT_i r_{k(i)}\ln\left[\frac{RT_i^2 A_d r_{k(i)}}{\beta(Q_o + 2\beta V_M)}\right] = 0 \tag{21}$$

Simpler approximate expressions for $\chi(r_k)$ and r_k can be obtained by using approximate relation (13) for the E_d value

$$\chi(r_k)_i = \frac{2\gamma V_m}{R\beta r_{k(i)}^2} \frac{dV_{pore(i)}}{dt_i} \frac{y_i}{y_i^2 - 1} \tag{22}$$

$$r_{k(i)} = \frac{2\gamma V_M}{RT_i(y_i - 1) - Q_o} \tag{23}$$

where quantity y_i denotes the following function of T_i

$$y_i = \ln\frac{A_d T_i}{\beta} - 2.46 \tag{24}$$

Since the desorption energy distribution in the CA is related to the desorption energy by simple Eq. (14), the dependence of the desorption energy on the relative overall pore volume, $E_{dc}=f(V_{pore})$, can be evaluated directly from the desorption energy distribution $\rho(E_d)=f(E_d)$. Therefore, by using Eq. (6) and the overall absolute pore volume ($V_{overall}$), determined from independent adsorption data or from the loss in substance mass after its complete evaporation from the mesopores, we can obtain the cumulative pore distribution $V_{overall} \times V_{pore}=F(r_k)$, in cm^3. The differential pore-size distribution ($dV_{pore}/dr_k=f(r_k)$, in $cm^3\ nm^{-1}$) can be evaluated from the Q-DTG curve by using Eqs (11) and (18) for E_{dc} and $\rho(E_{dc})$, and substituting these co-ordinates in the distribution energy curve by quantities r_k and $\chi(r_k)$ (Eqs (20) and (21)).

The use of the desorption energy distributions in the first step of the study of the structural and energetic surface heterogeneities seems to be preferable to direct calculation of the pore-size distributions by using Eqs (22)–(24). This arises from the fact that most mesoporous solids are also characterized by the presence of some micropore-size distribution. The adsorption potential in the micropores is greater than that in the mesopores and this leads to an increased adsorption energy and to a shift of the adsorption energy distribution towards large energies. In addition, the reasons for the appearance of the peaks may be the desorption of the substance bound to various types of adsorption sites on the flat energetically heterogeneous solid surface. For the process of desorption of the preadsorbed substance from a non-porous solid surface when its initial surface concentration is equal to or lower than the monolayer coverage, Eqs (11) and (18) coincide, replacing the quantity V_{pore} by the relative surface coverage, Θ, in these equations.

A crucial feature in the application of the above approach to the quantitative description of the structural and energetic solid surface heterogeneities from the Q-TG experiments is the correct choice of the pre-exponential factor A_d. Transition state theory predicts a variation of A_d for monomolecular desorption from 10^{11} to 10^{19} s^{-1} [10]. However, most calculations of A_d from the TPD spectra of water physically adsorbed on silica surfaces by using the most popular Polanyi-Wigner, Kissinger and Freeman-Carroll methods [11] give lower desorption pre-exponential factors, ranging from 0.8 to $3.6\cdot10^{5}$ s^{-1}, than the vibrational frequency, 10^{13} s^{-1} [12]. One of the reasons for such small pre-exponential factors may be the inclusion of readsorption in the overall thermodesorption process. However, this process is favorable from microporous solids [13]. Most silicas (Aerosil, Cab–O–Sil and aerosilogel) undergoing adsorbed water thermodesorption (reviewed in [12]) are non-porous or macroporous. The dramatic decrease in A_d may be explained by limitations of the Polanyi-Wigner, Kissinger and Freeman-Carroll methods for independent A_d evaluation for the process of desorption from solid heterogeneous surfaces. As a rule, the A_d values calculated by using these methods increase with rise of the calculated desorption energy E_d, and at E_d=150÷250 kJ mol^{-1} are in the region for the A_d predicted by transition state theory (10^{11}÷10^{19} s^{-1} [10]). This is exhibition of the 'isokinetic relationship' or 'compensation effect' between the quantities $\ln(A_d)$ and E_d [14]

$$\ln(A_d) = \ln(k_d)_{iso} + \frac{E_d}{RT_{iso}} \tag{25}$$

where T_{iso} is the isokinetic temperature, at which the rates of the similar reactions are equal, and $(k_d)_{iso}$ is the rate constant at this temperature.

Since many parallel adsorption/desorption reactions proceed simultaneously on different active sites of the heterogeneous surface, Eq. (25) may be used for a description. The surface is characterized not only by the adsorption/desorption activation energy distribution, but also by the pre-exponential factor distribution [5]. For heterogeneous surfaces, T_{iso} means the temperature at which all the heterogeneous surface sites have equal reactivities towards gaseous reagent in the adsorption reaction, or the temperature at which all the adsorption complexes have equal stabilities in the desorption process.

A common approach for evaluation of the adsorption activation energy and pre-exponential factor distributions as well as T_{iso} and k_{iso} from kinetic adsorption isotherms recorded at different temperatures is given in [5, 14]. As T_{iso} and k_{iso} for the desorption process may be evaluated in a similar manner, A_d in Eqs (11) and (24) is to be replaced by $(k_d)_{iso}\exp(E_d/(RT_{iso}))$

$$\frac{E_{dc}}{R}\left(\frac{1}{T}-\frac{1}{T_{iso}}\right)+\ln\left(\frac{E_{dc}}{RT}\right)-\ln\left(\frac{(k_d)_{iso}T}{\beta}\right)=0 \tag{26}$$

$$y=\frac{1}{RT}\left(\frac{2\gamma V_M}{r_k}+Q_o\right)+\ln\left(\frac{(k_d)_{iso}T}{\beta}\right)-2.46 \tag{27}$$

It should be mentioned that inclusion of a linear relationship between $\ln(A_d)$ and E_d (Eq. (25)) instead of A_d=constant usually gives an extension of the region of E_d variation, i.e. the calculated desorption energy distribution is much wider than in the case of constant A_d [12].

The following procedure for estimation of the initial (lower) A_d value for desorption of the preadsorbed substance from the mesopores may be proposed. As the temperature of the maximum of the first long narrow peak in the Q-DTG curve for a liquid substance excess on the mesoporous solid surface corresponds to the boiling temperature of this substance, this peak is related to evaporation of the substance from the thick film on the flat surface. The desorption energy in this case corresponds to the vaporization heat of the substance (Q_o). Therefore, a lower value of the pre-exponential factor may be estimated by using a modified Eq. (11)

$$A_{d(lower)} = \exp\left[\frac{Q_o}{RT_b} + \ln\left(\frac{Q_o}{RT_b}\right) - \ln\left(\frac{T_b}{\beta}\right)\right] \tag{28}$$

where T_b is the boiling temperature, in K.

A similar procedure may be used to estimate the upper A_d value relating to desorption of the preadsorbed substance from various adsorption sites of the heterogeneous surface. As the end of the tail in the Q-DTG curve is related to the desorption of the most strongly adsorbed molecules, the desorption energy at this point of T should be similar to the zero-coverage differential adsorption heat of the substance ($q_{d(o)}$), obtained by adsorption microcalorimetry, or to the zero-coverage isosteric adsorption heat ($q_{is(o)}$), which may be evaluated from the temperature dependence of the adsorption isotherms. Therefore, the upper A_d value may be estimated by using Eq. (11) and known zero-coverage heats of adsorption of the substance on the surface under investigation, and the temperature relating to the end of the Q-DTG curve. In such a manner, through use of the values of $A_{d(lower)}$, $A_{d(upper)}$, Q_o and $q_{d(o)}$ or $q_{is(o)}$ data, the coefficients of Eq. (25) may be estimated.

It should be noted that estimation of the A_d value and the region of its variation is very important for correct calculations of the desorption energy and its distribution from the Q-DTG data. In most TPD experiments, the desorption usually occurs in a wide temperature range at high temperatures. The variations in the logarithms for the large A_d values have low effects on the calculated desorption energies and their range. Therefore, in the TPD experiments it is usually assumed that the pre-exponential factor A_d is constant (A_d=10^{13} s^{-1}). In contrast with the above TPD experiments, the Q-TG experiments for the desorption of preadsorbed vapour are usually performed within a relatively narrow temperature range from a temperature below 100°C up to 227°C. The A_d value for the lower temperature peak is less than the vibrational frequency of the adsorbed molecules (10^{13} s^{-1}), and substitution of this value into the Redhead equation gives an overestimated desorption energy.

Experimental

The study was carried out on silica gel with a mean mesopore radius of 2 nm (Merck, Darmstadt, Germany). *n*-Butanol was from Merck. It was distilled several times in vacuo and rendered gas-free by several freeze-pump-thaw cycles. The physicochemical properties of *n*-butanol used in the calculations of the pore-size distribution are presented in Table 1. The silica gel sample was typically thermally treated in air at 250°C already located in the vacuum desiccator, where the relative vapour pressure of the *n*-butanol was $p/p_o=1$. About 0.5 g of the wetted silica gel was placed in the special platinum crucible of the thermogravimetric analyser.

Table 1 Physicochemical properties of *n*-butanol

Property	Unit	Value
Vaporization heat at 25°C	kJ mol^{-1}	43.10
Boiling point	°C	117.9
Surface tension at boiling point	mJ m^{-2}	16.2
Molar volume at boiling point	cm^3 mol^{-1}	102.24
Density at boiling point	g cm^{-3}	0.725

Note: The properties were taken and/or calculated by using relations from [21]

Measurements of programmed *n*-butanol thermodesorption under quasi-equilibrium conditions from the surface of the silica gel was made by means of the simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary) [15]. The apparatus is connected with a computer by the interface and equipped with the Derivat program for calculation of the first derivatives of the mass loss Q-DTG curves with respect to temperature and time. The mass loss Q-TG curves were measured under quasi-isothermal conditions over the temperature range, 20–250°C, using an analyser equipped with an automatic ultraslow heating device and a special crucible, and capable of maintaining quasi-isothermal conditions to increase the resolution of the thermal analysis. The Q-TG and Q-DTG *vs.* temperature and time curves were registered and printed with the help of the computer system. A constant heating rate of 6°C min^{-1} was used in our experiments [16–18].

Results and discussion

As mentioned above, thermoanalytical studies were made of a silica gel sample saturated with *n*-butanol vapour in a desiccator. The thermodesorption process under quasi-isothermal conditions reflects the energy state of the liquid films adsorbed on the studied surface. The Q-TG mass loss curve allows determination of the adsorption capacity of the studied sample surface, the volume of mesopores present on the surface and the amount of liquid bonded with the surface. The first derivatives of mass loss Q-DTG curves with respect to temperature and time are very interesting and useful for accurate determination of inflection points in Q-TG curves relating to a certain proportion of the desorbed liquid [17].

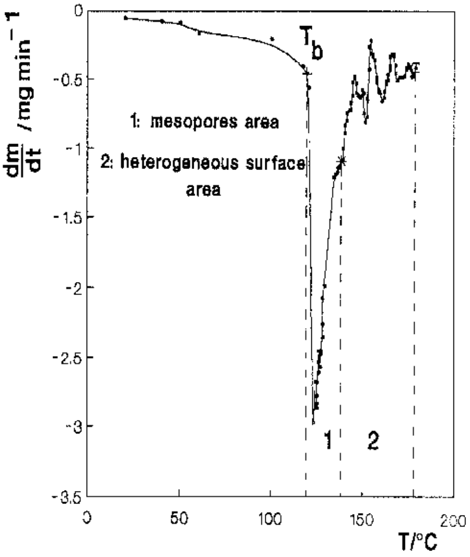

Fig. 1 Q-DTG curve of *n*-butanol thermodesorption from the silica gel surface

The experimental differential mass loss Q-DTG curve in relation to temperature for the preadsorbed vapour of *n*-butanol on the silica gel surface is presented in Fig. 1. It is seen that two parts appear in this spectrum: first a larger peak with its minimum located near 124°C, and a second part with inflections at 135–175°C. Dosing the excess of liquid *n*-butanol on the silica gel surface gives a very long narrow peak with a minimum which corresponds to the boiling temperature of the substance (T_b=117.9°C). Let us assume that the front of the peak in the Q-DTG curve in Fig. 1 is related to the evaporation of the *n*-butanol from the mesopores, whereas the tail of the peak conforms to the thermodesorption of the alcohol molecules bound with the various types of adsorption sites (single, vicinal and geminal OH groups and siloxane bridges) on the silica gel surface. According to the above discussion, the shape and position of the Q-DTG curve reflects the effects of the mesopore-size distribution and adsorption energy distribution of the silica gel surface on the rate of *n*-butanol desorption.

Equation (11) was used in the calculation of A_d for the temperature relating to the point of inflection in the Q-DTG curve (T_b=117.9°C, $E_{d(i)}=Q_o=43.3$ kJ mol^{-1}). This value is equal to $2.2\cdot 10^4$ s^{-1}. The part of the Q-DTG curve from 117.9 to

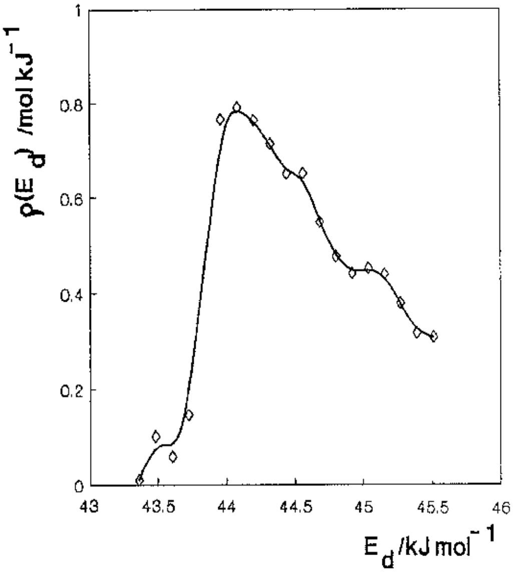

Fig. 2 Energy distribution of *n*-butanol desorption from the silica gel surface, calculated for the first part of the Q-DTG curve, from 117.9 to 135°C

135°C, which corresponds to the probable region of the activation energies of *n*-butanol desorption from the mesopores ranging from 1 to 10 nm, was analysed. The desorption energy distribution is shown in Fig. 2. The pre-exponential desorption factor is $2.2\cdot10^4$ s^{-1}. It is seen that this distribution presents one wide peak with a maximum near 44 kJ mol^{-1}, and two small peaks near 44.5 and 45 kJ mol^{-1}. The dependence of the desorption energy on the relative mesopore volume is plotted in Fig. 3. The E_d value ranges from 43.3 to 45.5 kJ mol^{-1} and increases on release from the mesopores. As may be seen from Fig. 4, the dependence in Fig. 3 can easily be transformed into a cumulative pore-size distribution, by using the measured loss in mass of the sample within this temperature range, the density data on *n*-butanol and relationship (6) between desorption energy and pore radius. The differential pore-size distribution was calculated from the desorption energy distribution curve (Fig. 2) by using Eqs (20) and (21). This pore-size distribution is presented in Fig. 5. It is seen that the pores with radius near 2 nm have the highest intensity in this curve. The concentration of the mesopores decreases with increase of their radius. The observed shape of the pore-size distribution curve is typical for most industrial mesoporous adsorbents. For example, this shape is similar to that evaluated from low-temperature nitrogen adsorption isotherms on various activated carbons [19] by using the Dollimore-Heal method [20].

The calculation of the desorption energy distribution for the second part of the Q-DTG curve (from 135 to 175°C) was performed with the same A_d value

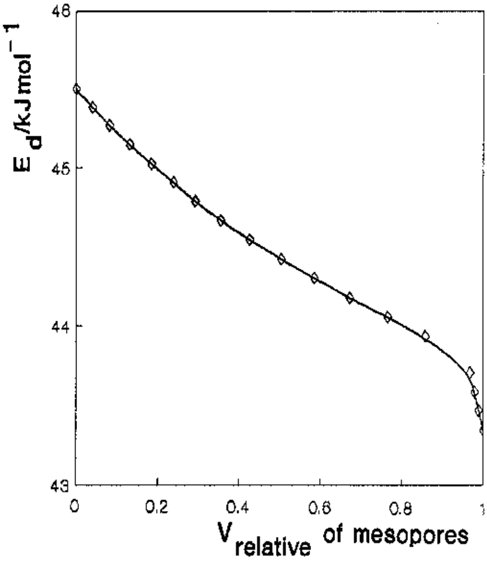

Fig. 3 Plot of energy of *n*-butanol desorption from the silica gel surface *vs*. relative volume of the mesopores. Calculations are performed for the first part of the Q-DTG curve, from 117.9 to 135°C

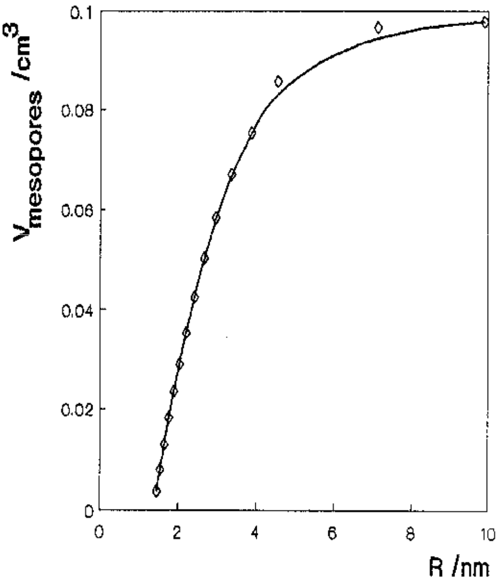

Fig. 4 Cumulative pore-size distribution of the silica gel surface. Calculations are performed for the first part of the Q-DTG curve, from 117.9 to 135°C

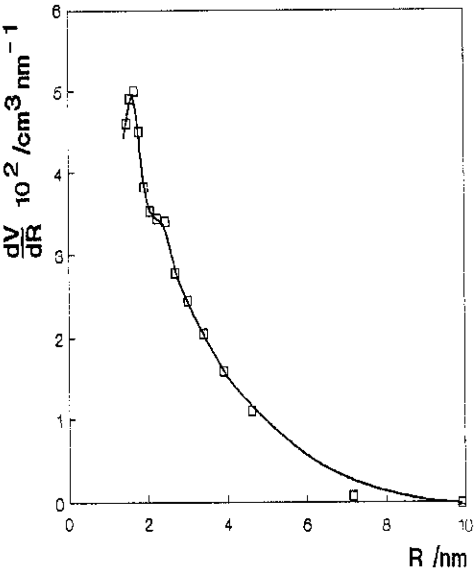

Fig. 5 Differential pore-size distribution of the silica gel surface. Calculations are performed for the first part of the Q-DTG curve, from 117.9 to 135°C

($2.2\cdot10^4$ s^{-1}). The desorption energy distribution curve is presented in Fig. 6. It is seen that this curve has a complex shape. The range of desorption energy varies from 45.5 to 50.5 kJ mol^{-1}, and the concentration of the active surface sites decreases with increase of the desorption energy. Calculation of the plot of desorption energy *vs.* relative surface coverage gives a smoother dependence (Fig. 7). Statistical treatment of this dependence by the least-square method indicates that the desorption energy distribution is described by a power law

$$E_{d(\Theta)} = E_{d(o)} - 6.17\Theta^{0.922} \qquad (29)$$

where $E_{d(o)}$=50.2 kJ mol^{-1} is the desorption energy at zero relative surface coverage.

The number N of points was 40 in the part of the Q-DTG curve. The mean square deviation δ and the correlation coefficient R for relation (29) in logarithmic co-ordinates were 0.054 and 0.998, respectively. Recently, power energy distributions were observed for the reactivity of the silica surface towards various organic compounds [5]. However, the width of the distribution is larger for chemisorption interactions than for the desorption of physically adsorbed *n*-butanol from the silica gel surface. The reason for the observed small range of desorption energy variation may be the limitation of the upper temperature in the Q-TG experiment, when a small fraction of the *n*-butanol molecules bound with the most active sites of the silica gel surface are not desorbed completely at 175°C.

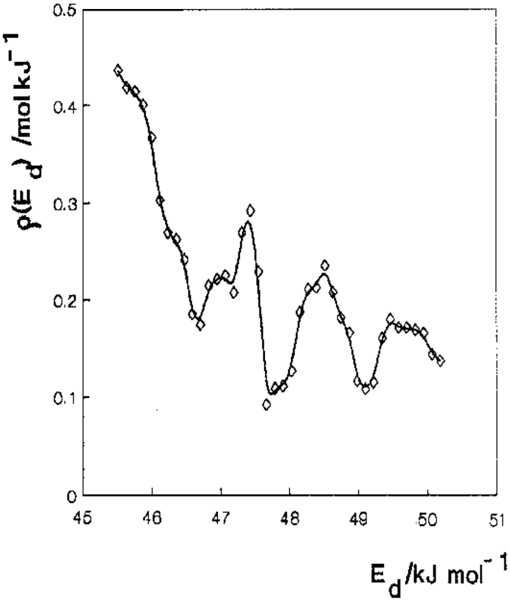

Fig. 6 Energy distribution of *n*-butanol desorption from the silica gel surface, calculated for the second part of the Q-DTG curve, from 135 to 175°C at A_d=2.2·10^4 s^{-1}

Calorimetric data on the adsorption of *n*-butanol vapour on a silica gel surface have not been found in the available literature. It has been reported that the differential molar heat of *n*-butanol adsorption on the silicalite surface ranges from 85 to 93 kJ mol^{-1} [22]. However, such high adsorption heats may arise from the strong interaction of the alcohol with the micropore walls of this solid. Estimation of the *n*-butanol adsorption energy on the non-porous silica surface, taking into account the polarizability, the donor and acceptor numbers of the alcohol and dispersive, and the donor–acceptor characteristics of the silica surface, determined from inverse gas chromatography data at finite concentrations [23], also gives an energy near 90 kJ mol^{-1}. On the other hand, the zero-coverage heat for the adsorption of *tert*-butanol vapour on a non-porous silica surface is 65 kJ mol^{-1} [24].

Since the difference in the vaporization heats of *tert*-butanol and *n*-butanol is 4.1 kJ mol^{-1}, the estimated lower limit of the zero-coverage heat of *n*-butanol adsorption on the silica surface is 69.1 kJ mol^{-1}. This values exceeds $E_{d(o)}$=50.2 kJ mol^{-1} from Fig. 7. This may be explained by the compensation behaviour between A_d and E_d (Eq. (25)). Actually, calculation of the desorption energy distribution at A_d=10^{10} s^{-1} leads to the desired desorption energies, which coincide with the above estimations (E_d varies from 87.5 to 96.5 kJ mol^{-1}). This distribution curve is presented in Fig. 8. The pre-exponential desorption factor is 10^{10} s^{-1}. The shape of the distribution curve is similar to that in Fig. 6. Increase of

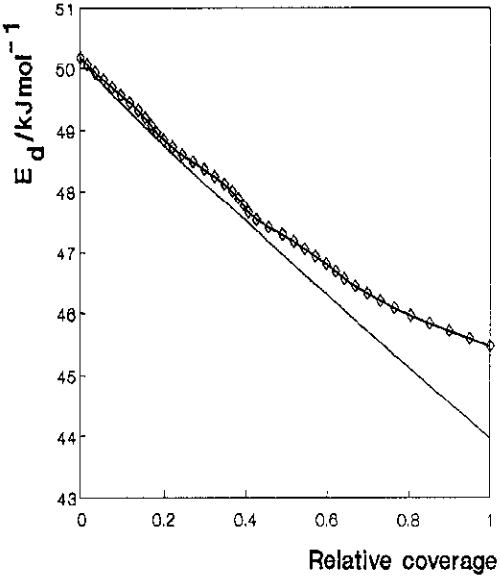

Fig. 7 Plot of energy of *n*-butanol desorption from the silica gel surface *vs.* relative surface coverage. Calculations are performed for the second part of the Q-DTG curve, from 135 to 175°C at A_d=2.2·10^4 s^{-1}

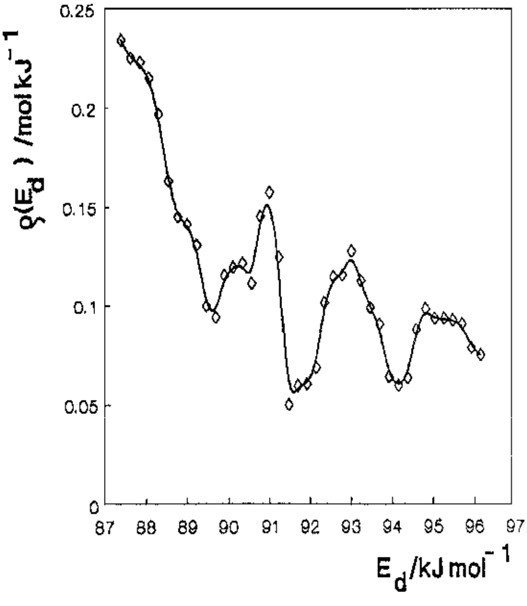

Fig. 8 Energy distribution of *n*-butanol desorption from the silica gel surface, calculated for the second part of the Q-DTG curve, from 135 to 175°C at A_d=2.2·10^4 s^{-1}

the pre-exponential factor leads to a shift in this curve on the high desorption energy side only, and to an increase in the width of the distribution ($E_{d(o)} - E_{d(\Theta=1)}$=8.8 kJ mol^{-1}). The isokinetic relationship between ln(A_d) and E_d should therefore be taken into account in calculations of the desorption energy distributions from the Q-DTG curves.

Conclusions

The present study has demonstrated the extended possibility of using the Q-TG and Q-DTG data on liquid thermodesorption for the quantitative characterization of the structural and energetic heterogeneities of mesoporous solids from one experimental run. This paper is of a preliminary character and is mainly devoted to the theoretical aspects of this problem. The evaluated pore-size distribution and energy distributions of *n*-butanol desorption from the silica gel surface satisfactorily agree with the parameters of the porous structure of the above solid and with known characteristics of alcohol adsorption on the silica gel surface. The extension of the number of silica gels and other adsorbents with different pore sizes, the number of adsorbates possessing different acid/base properties and wettability, and the use of independent spectral, adsorption and calorimetric data to characterize these adsorption processes, provides a possibility for the creation in subsequent studies of a basis for quantitative characterization of the structural and energetic heterogeneities of these solids by means of Q-TG methods.

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