Journal of Thermal Analysis, Vol. 53 (1998) 597-616

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

THE STUDIES OF THE HETEROGENEOUS PROPERTIES OF SOLID SURFACES BY MEANS OF THE DERIVATOGRAPH Q-1500 D

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Abstract

A simple method has been adopted to obtain an important information on the heterogeneous properties of materials studied, adsorbed liquid films and liquid-solid interactions. The method utilizes Q-TG mass loss and the first derivative Q-DTG mass loss curves with respect to temperature and time obtained during programmed liquid thermodesorption in quasi-isothermal conditions. The values of the adsorption capacity, total porosity of material, the value of active centers, desorption energy distribution and mesopore-size distribution functions obtained by this method are in good agreement with those estimated on the basis of independent methods. The theoretical and experimental results provided novel and unique data on the heterogeneity of solid surfaces, properties of liquid adsorbed films and thermal stability of the liquid/solid interfaces.

This paper presents the more important results obtained so far in the studies the liquid/solid systems by means of the Paulik's classical and quasi-isothermal techniques.

Keywords: adsorbed liquid film properties, classical and quasi-isothermal methods, heterogeneity of solid surfaces, liquid-solid interactions, thermodesorption of liquids

Introduction

Special techniques of TA have been adopted to study the liquid/solid systems [1]. The effects taking place in the processes opposite to adsorption, i.e. in the thermodesorption of liquids from solid surfaces were registered and used in practical calculations of the physicochemical parameters. The mass loss and the first derivatives mass loss curves in respect to temperature and time obtained under classical [2, 3] and quasi-isothermal [4–12] conditions have been applied. During thermodesorption process of adsorbed liquid films from solid surfaces the physical bounds (first of all hydrogen bounds, which are 10 times weaker that chemical ones) are disrupted. For that reason, liquid evaporation effects (i.e.

1418–2874/98/ $ 5.00
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change of sample mass loss and heat effects) are subtle and very small. Therefore, it was necessary to use more sensitive and special methods of TA in registration of the fine peaks and/or inflections on obtained curves.

New applications of the TA techniques in above studies were possible by simultaneous techniques called derivatograph Q-1500 D (MOM Budapest) which was created by Paulik and Paulik [4–6].

Studies on the application of TA method in investigations of physicochemical properties of liquid-solid systems (properties of the adsorption layers, adsorbate-adsorbent interactions and heterogeneous properties of solid surfaces) were begun by author of this paper 20 years ago [7]. The first measurements were carried out using a classical ‘dynamic’ program [8, 9]. Next, the changes of mass loss of a suitable saturated material samples heated under quasi-isothermal [9] and isothermal [10, 11] heating programs were studied. On the basis of the obtained results discontinuous changes of adsorbed layer properties (especially vicinal water) and its role in enrichment process of minerals were confirmed [12]. Recently, the quasi-isothermal technique has been successfully applied to characterization of the heterogeneous properties of solid surfaces.

Results and discussion

Classical ‘dynamic’ measuring technique in studies of the liquid/solid systems

The liquid thermodesorption from completely immersed of solid surfaces under classical ‘dynamic’ conditions has been made [7–9, 12–15]. The thermodynamic functions (e.g. surface free energy and its components, activation energy, heat of evaporation, film pressure), adsorbed film thickness, and studies of the discontinuous properties and thermal stability of adsorbed layers were studied.

Paper [9] presents investigations of water thermodesorption from a silica gel surface under ‘dynamic’ conditions (Fig. 1). Three low-temperature peaks are seen in the DTA (endothermic) and DTG curves, which account for stepwise water removal from the silica gel surface as the temperature increases. It reflects the discontinuous properties of adsorbed water film on silica gel surface. From the obtained experimental results the activation energy, heat of dehydratation, surface free energy and water film pressure were calculated on the basis of a modified Gibbs-Duhem equation:

$$\pi_n = -\gamma_{Tn} + \Delta T_n \Delta S_m \tag{1}$$

and

$$\gamma_{Tn} = -RT_n \int_{p_n}^{p} a^s \mathrm{d}(\ln p_n) \tag{2}$$

where a^s is the amount of desorbed water, ΔS_m is the entropy change corresponding to the transfer of water liquid phase to vapor, γ_{Tn} is the interfacial tension in the silica gel-water system corresponding to film pressure π_n on the surface at temperature T_n and water pressure p_n, p_o is the saturated water vapor pressure and R is the gas constant.

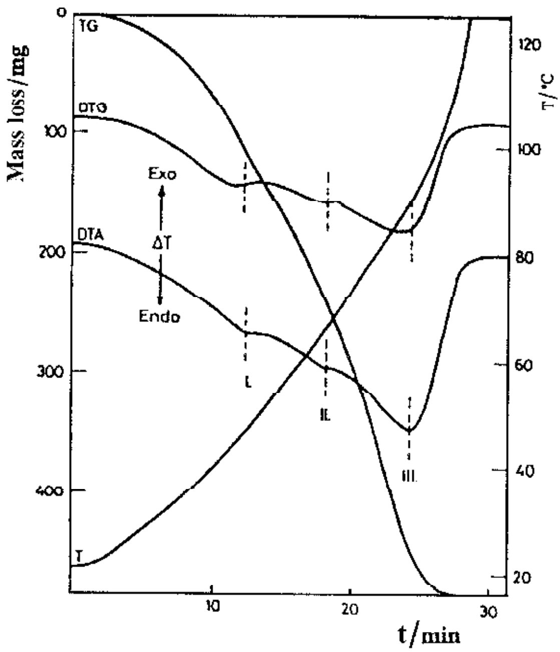

Fig. 1 Classical 'dynamic' thermal curves of water thermodesorption from silica gel

Correlations of changes in water film pressure π_n and the values of work of spreading, immersion and adhesion are presented in Fig. 2. The value of surface free energy on the studied silica gel was calculated from Fowkes's equation [9]. Using this method, the properties of water films on marble and barite surfaces covered with tetradecylammonium chloride (TDAHCl) were studied before and after the process of enrichment by the flotation method [13, 14]. The influence of the amount of above flotation collector on the water film thickness, activation energy, enthalpy, entropy and vicinal water molecules was determined (Fig. 3). From the obtained data, the possible structures of water, their changes depending on the amount of TDAHCl preadsorbed on the studied surface, as well as influence on the mechanism and effectiveness of the enrichment mineral process were discussed [12].

The latest papers describe the possibilities of application of TA in characterizing porosity and number of hydroxyl groups on the silica gels and other

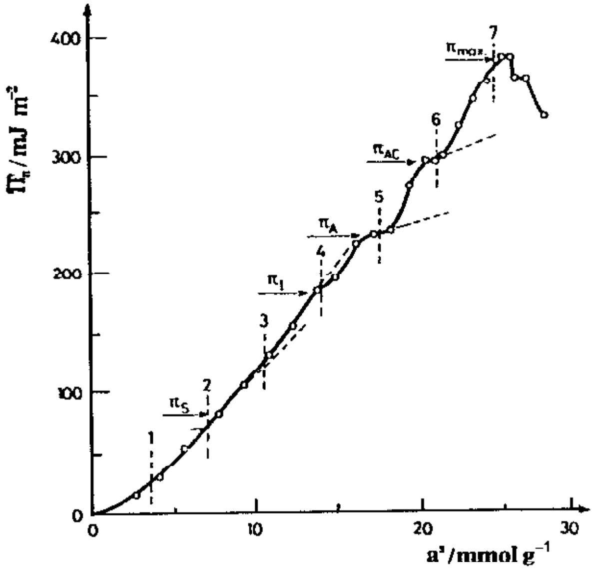

Fig. 2 Dependence of water film pressure on the amount of desorbed water

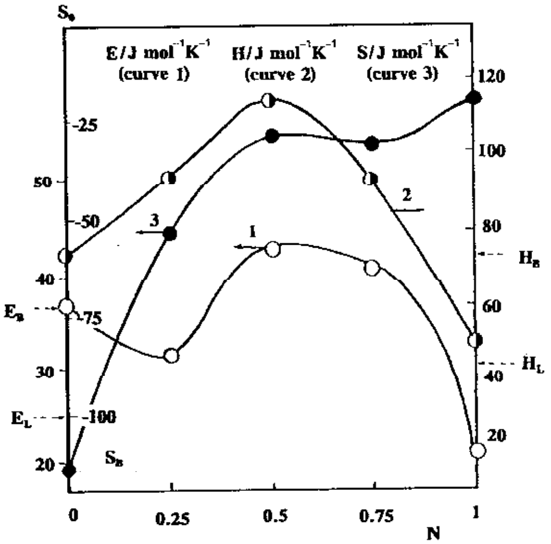

Fig. 3 Activation energy E (curve 1), enthalpy H (curve 2) and entropy (curve 3) changes of water evaporation from the surface as a function of the statistical TDAHC1 monolayer N coverage deposited on barite (subscript B – bonded water, subscript L – volume water)

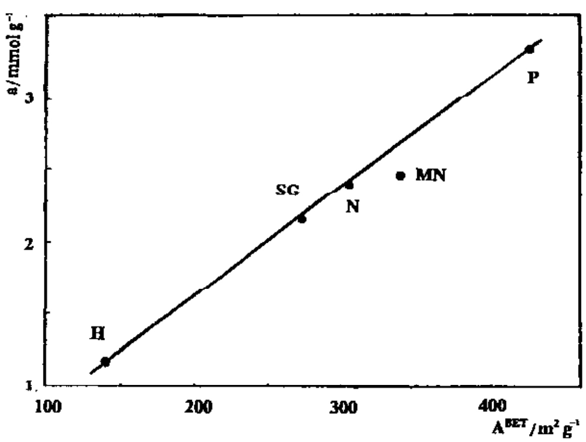

Fig. 4 Amounts of water desorbed from silica gel surfaces as a function of specific surface areas (samples: H-Hypersil, SG-Schuchardt, N-Nucleosil, MN-Kieselgel MN, P-Partisil)

studied sample surfaces (e.g. chemically bonded phase for use in HPLC) [15, 16] as well as energetic effects accompanying phase and structural changes of the adsorbed films [17, 18]. The measured mass loss TG curves included steps which reflected the evaporation of the liquid from different pores and desorption of molecules from solid surface. The heights of these steps could be directly correlated to the adsorption values and capacity, total porosity and specific surface area of the samples. The above mentioned parameters obtained by TA method were correlated with the corresponding measurements, such as those made by means of the McBain balance, sorptomatic method, porosimetry, chromatography and other sorption techniques, and good agreement was found. Figure 4 presents amounts of water desorbed from silica gel surfaces in so-called 'adsorption regions' recorded by derivatograph on TG curves as a function of specific surface areas made by sorptomatic method. The specific surface area of unknown silica gel samples can be determined on the basis of above calibration curve. The current studies of solid surface completely immersed in liquids have demonstrated the big usefulness of TG and DTG curves for obtaining many information about liquid/solid systems.

Studies of adsorption and desorption of liquids from gaseous phase under isothermal conditions by means of the modified derivatograph

The derivatograph Q-1500 D was modified to permit adsorption and desorption processes and calorimetric measurements under isothermal conditions (in constant temperature) [10]. An adapter to saturate the indifferent carrier gas with the vapor of the liquid studied and to conduct it to the solid sample has been con-

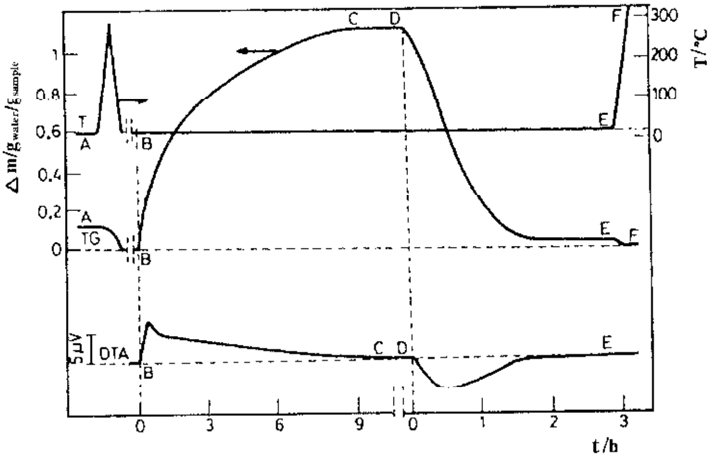

Fig. 5 The T, TG and DTA curves corresponding to adsorption and desorption of water vapor onto and from silica gel at 20°C. The T curve: peak AB – sample heating to 300°C and cooling to 20°C, sector BE – constant temperature (20°C) during measurement, sector EF – sample heating to 300°C after the desorption process. The TG curve: sector AB – evaporation of hygroscopic and vicinal water, BC – adsorption of water, CD – plateau, DE – desorption of water, EF – thermal desorption of water. The DTA curve: sector BC – corresponds to the heat of water adsorption on silica gel, CD – plateau, sector DE – heat of desorption of water from the silica gel surface

structed and place the tubing of an ultrathermostat within the furnace space [11]. Changes in sample weight take place as a result of adsorption and desorption processes of the vapor of liquids (e.g. water) flowing in an inert gas (e.g. nitrogen) through a measuring chamber at constant temperature (Fig. 5). From the obtained experimental data, the adsorption capacity as well as adsorption and immersion heats of water on silica gel were determined. The dependence of the calculated heats of adsorption on the values of water adsorption have been made [10]. Estimation of these parameters is an important problem in the characterization of sorption properties of materials. It was stated that the greatest amount of heat is evolved during the stage of forming the first adsorption water layers on the silica gel surface. Adsorption measurements of various materials were carried out and surface free energy and its components were calculated [19–21].

Programmed thermodesorption of liquids from solid surfaces under quasi-isothermal conditions

Measurements of programmed water thermodesorption under quasi-isothermal conditions from the completely wetted silica gel sample were started using derivatograph Q-1500 D. The Q-TG curves in relation to temperature were registered using an analyzer equipped with an automatic ultraslow heating device [4], commercial recorder, a special platinum labyrinth crucible (Fig. 6 A) [5] and capable of maintaining quasi-isothermal and quasi-isobaric conditions to increase the resolution of TA. A few years ago, the apparatus was connected with a computer by the interface (Fig. 6 B) and provided with the Derivat program. This extended apparatus enable the collection of the experimental Q TG data in relation to temperature and time and calculation of the first derivatives of mass loss Q-DTG curves with respect to temperature and time. Moreover, the Derivat program possible to increase the suitable parts of the Q-TG and Q-DTG curves.

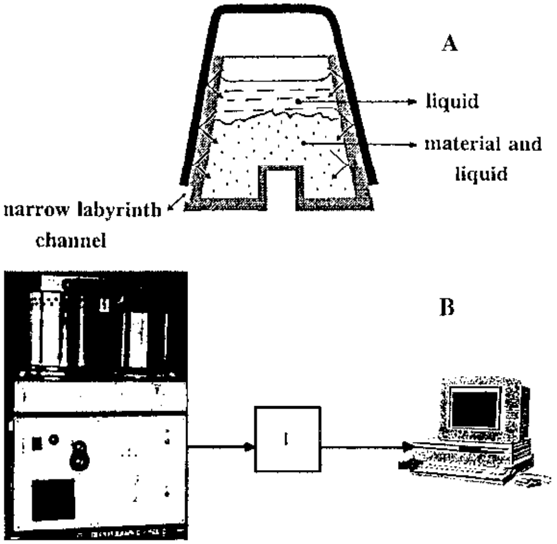

Fig. 6 Paulik's special platinum labyrinth crucible (A) with sample of fully immersed material and derivatograph Q-1500 D (B) connected by interface (I) with computer

The studies were made using various solid samples with respect to their heterogeneity properties. This paper presents the results of polar and nonpolar liquids (water, butanol and benzene) thermodesorption from porous adsorbents of commercial silica gel (Kieselgel Si-60 type, Merck Darmstadt, Germany), aluminum oxide (Aluminum Co. of America, AL-COA Center, PA, USA) as well as active carbon Ambersorb (Rohm and Haas Co., USA) samples. In the studies of liquids thermodesorption the samples were prepared as follows. To obtain different thickness of liquid adsorption films on the solid surfaces, the samples were wetted with pure liquids till complete immersion [9] and/or saturated with liquid vapor in the vacuum desiccator at $p/p_0=1$ [18].

Before thermodesorption process of liquids from solid surfaces the mass loss and temperature calibrations of apparatus have been made. Figure 7 presents the Q-TG and Q-DTG curves in relation to temperature (A) and time (B) of the evaporation process of pure water in quasi-isothermal conditions.

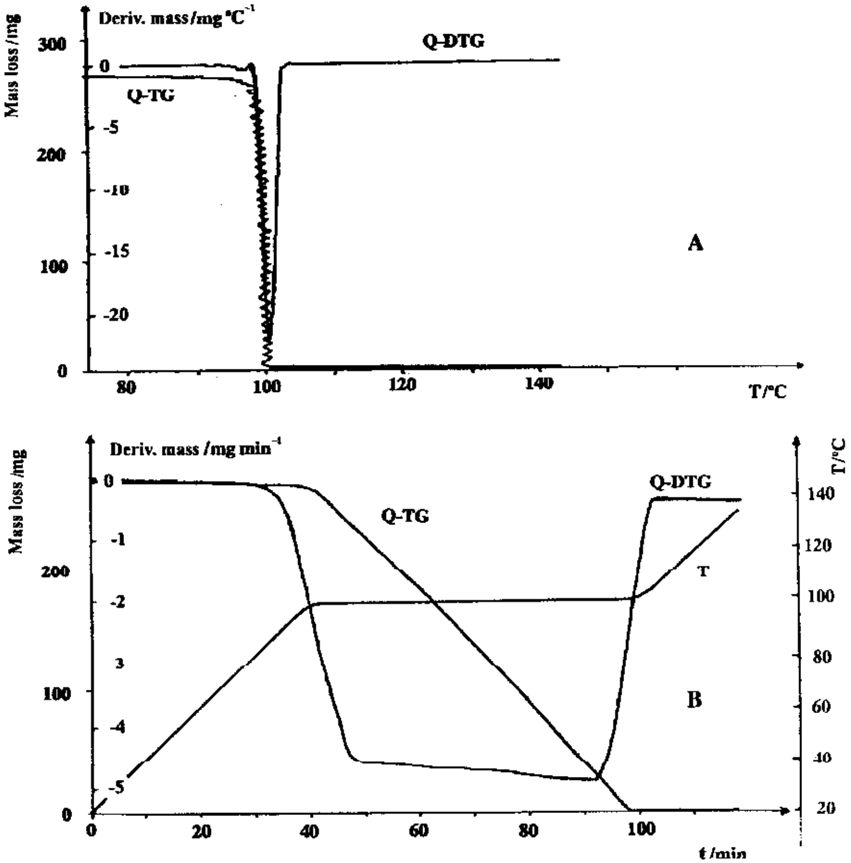

Fig. 7 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of pure water thermodesorption from labyrinth crucible

Figure 8A presents the thermogravimetric mass loss Q-TG and differential Q-DTG curves in relation to temperature obtained during thermodesorption of benzene from the sample of completely wetted of Si-60 silica gel under quasi-isothermal conditions. From this Figure it follows that 3 steps of the thermodesorption process, i.e. evaporation of the bulk benzene, benzene from capillary tubes, pores and from active centers of surface were obtained. The original 'step' shape of Q-TG curve presented in Fig. 8A results from the peculiarity of the thermodesorption process steering as well as from the application of a special crucible which enables step evaporation of the liquid from the sample under quasi-isothermal and quasi-isobaric conditions. The segment AB of Q-TG curve parallel to the axis of ordinates corresponding to the evaporation process of benzene from the mesopores radii 60 Å has been recorded. The evaporation process of benzene from mesopores is preceded by desorption of benzene present in capillary tubes

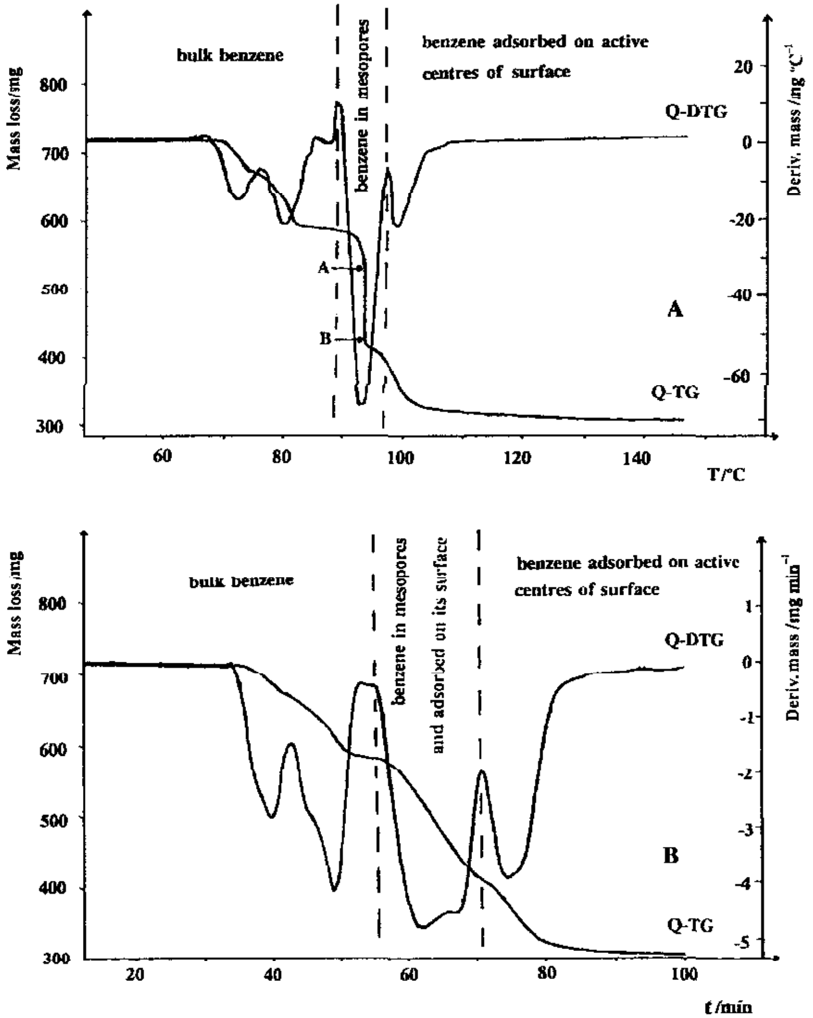

Fig. 8 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of benzene thermodesorption from completely immersed Si-60 silica gel sample

of its surface as well as from intergranular spaces of silica gel grains. The Q-TG curve presented in Fig. 8A make possible to determine adsorption capacity of the studied sample surface, volume of mesopores present on the surface and amount of benzene 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 the inflection points on Q-TG curves related to a certain part of desorbed liquid. Moreover, the dependence of Q-DTG in relation to time is due to a distribution function of activation energy of liquid desorption according to the Polanyi-Wigner equation [22, 23]. Figure 8B presents the mass loss Q-TG and differential Q-DTG curves in relation to time obtained during the same process of benzene evaporation from silica gel sample given in Fig. 8A. As follows from the comparison of the data in Figs 8A and 8B, the shape of Q-TG and Q-DTG curves obtained during registration of the sample mass loss in time (Fig. 8B) are quite different from the analogous one obtained during registration of the sample mass loss with the change of temperature (Fig. 8A). The Q-TG curve in Fig. 8B does not possess characteristic 'steps' and the corresponding segment AB parallel to the axis of ordinates but it is inclined to it at an angle. Therefore, the differential Q-DTG curve in relation to time is different (because kinetic desorption curve) from the analogous Q-DTG curve in relation to temperature. It is worth noting that the Q-DTG curve presented in Fig. 8B is characterized by high selectivity and resolving power distribution. It can be considered as a certain type of 'spectrum' of thermodesorption process describing and energetic state of benzene molecules on the silica gel sample and reflecting the distribution function of desorption energy of liquid on the studied surface.

Interpretation of the surface wetting mechanism processes and benzene thermodesorption can be explained as follows. The kinetics of the controlled thermodesorption of benzene from silica gel surface is influenced by the interactions between molecules in the adsorption layers (due to so-called lateral interactions) and benzene molecules with the solid surface. The energy of interactions depends on the properties of adsorbate molecules (e.g. liquid polarity) as well as heterogeneous properties of the surface (kind and number of active centers and pores). The above parameters affect the properties of benzene adsorption films (mainly their thickness and structure) but the programmed thermodesorption process shows the energetical state of the adsorbed layers on the studied surface in the form and type (course) of the obtained mass loss curves. The total immersing process causes filling up of the surface, pores, capillary and intergranular spaces of the silica gel sample. It is well known that the properties of benzene layers depend on the surface distance and the properties of bonded benzene adsorbed on the surface are different from those of bulk ones. It is the reason for the existence of the steps in the thermodesorption process of benzene films from active sites, pores, capillaries and intergranular spaces as well as bulk phase.

The adsorption of benzene on silica gel Si-40, Si-60 and Si-100 samples were measured by means of McBain balance [24]. The adsorption isotherms were made and adsorption capacities were correlated with thermogravimetric benzene desorption Q-TG data from fully immersed silica gel samples. It was stated that adsorption capacity amounts of silica gel surfaces from balance method correspond to benzene desorption value from so-called 'adsorption regions' (bottom parts) of the Q-TG curves.

As in Fig. 8, similar course of Q-TG and Q-DTG curves during water thermodesorption from Si-60 silica gel sample was obtained (Fig. 9). On the basis of the obtained thermogravimetric data the thickness of the adsorbed water layers and mesopore volume of silica gel have been calculated. It appears that the amount of water present in mesopore (AB sector of Q-TG curve) equals 7.95 statistical monolayers and corresponds to 0.79 $cm^3 g^{-1}$ of water volume. The mesopore volume of Si-60 sample determined by means of the sorptomatic measurements (low temperature adsorption-desorption of nitrogen) equals 0.75 $cm^3 g^{-1}$ and is in very good agreement with above from thermal analysis special technique. Finally, water adsorbed on mesopore surface (3.18 statistical

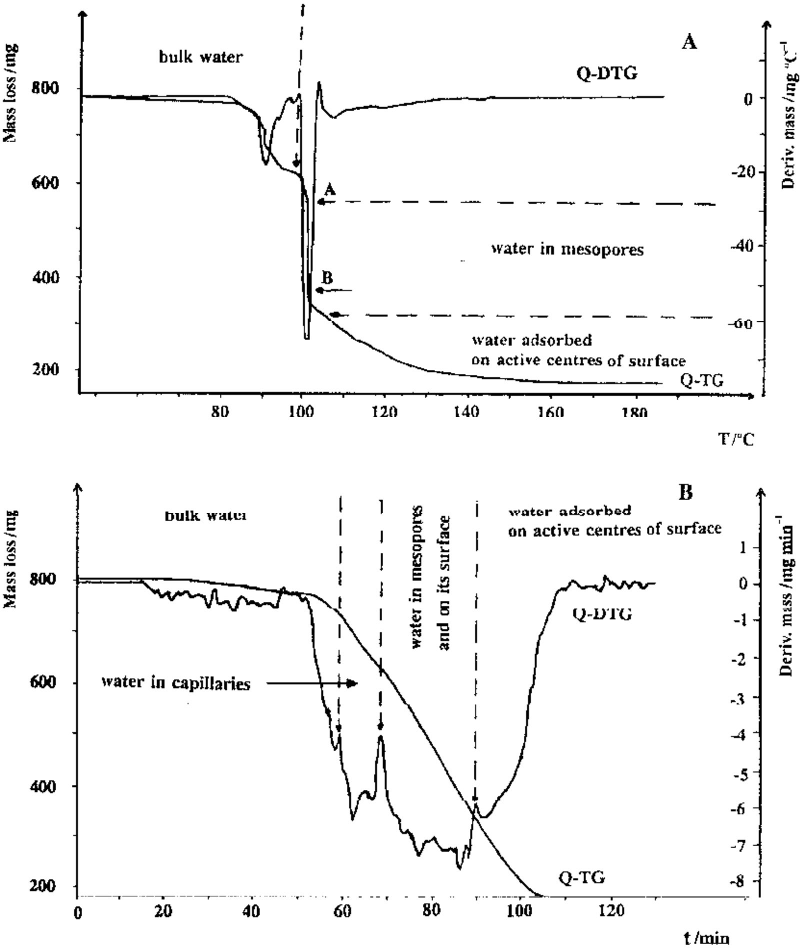

Fig. 9 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of water thermodesorption from completely immersed Si-60 silica gel sample

monolayers) and that most strongly bonded with the active sites of silica gel surface (4.62 statistical monolayers) have been evaporated. The number of statistical water monolayers were calculated on the basis of water mass loss from Q-TG curve, silica gel specific surface area knowledge and that a molecule of water occupies 12.5 Å^2, assuming uniform coverage [25].

Application of quasi-isothermal system to characterization of the energetical and geometrical heterogeneities of solid surfaces

Energetical and geometrical heterogeneities are characteristic features of solid surfaces. The above properties causes differences in adsorption energy and capacity of the materials studied [26, 27]. In order to control the separation, ad sorption and catalytic processes, and to optimize the surface (e.g. adhesive and hydrophobic/hydrophilic) properties of solid materials, it is necessary to determine their porosity and surface energies and estimate possible contributions of non-specific and specific interactions in forming the liquid surface films. Over the past decade, there has been much theoretical and experimental progress reported in a number papers using automatic sorption apparatus and calorimetry, chromatography, spectrometry and other methods [28, 29]. However, they are time consuming, apparatus are often very expensive and the obtained results are not sufficient to explain all of solid surface heterogeneity, the liquid-solid interactions, the adsorbed film properties and wetting phenomenon and its role in the interface processes.

Recent theoretical and experimental studies showed that the programmed liquid thermodesorption under quasi-isothermal conditions could be applied to estimate heterogeneous properties of the solid surfaces [30, 31]. The kind and number of active centers, particularly of hydroxyl groups on the silica gel surface using thermogravimetry water desorption data was calculated and good correlation with independent method have been obtained [16]. As was mentioned above, the shape of Q-TG and Q-DTG curves show the character of interactions between liquid molecules and the energetically differentiated active sites localized on the adsorbent surface. According to the Polanyi-Wigner equation and the Tronconi-Forzatti model of liquid thermodesorption the rate of desorption r_d is described by equation [22]:

$$r_d/\alpha = -\mathrm{d}\Theta/\mathrm{d}T = k_n\Theta_n/\alpha = \pi^2 D_n k_d \Theta/\alpha r_g^2 c_m k_a \tag{3}$$

where Θ is coverage degree, α is heating rate, r_s is the radius of the studied material grain, D_n is the effective diffusion coefficient, k_d is the constant of desorption rate, k_a is the constant of adsorption rate, k_n is the effective desorption rate constant, c_m is the initial concentration of the molecule adsorbed, n is the reaction order and T is the temperature.

The dependence of thermodesorption rate r_d on activation energy E_d is given by the Arrhenius equation:

$$r_d = -d\Theta/dt = A(\Theta)\exp[E_d(\Theta)/RT]\Theta^n \qquad (4)$$

where A is the pre-exponential coefficient, t is time of desorption and R is gas constant.

The desorption activation energy distribution function can be determined on the basis of liquid thermodesorption data from the equation [23]:

$$r_d = -d\Theta/dt = A/\alpha\int\{\Theta(E_d,T)^n\exp[-E_d/RT]\}\ dE_d \qquad (5)$$

On the basis of the energy activation desorption data the mesopore radius was evaluated from equation:

$$E_d = Q_{vp} = Q^o_{vp} + a/r_k \qquad (6)$$

where Q_{vp} is vaporization heat in mesopores, Q^o_{vp} is vaporization heat of pure liquid, 'a' is constant for liquid studied and r_k is mesopore radius, and presented in paper [31].

As was mentioned above, the surface wetting phenomenon of solids depends on the nature of surface active centers and its porosity. As follows from the studies carried so far, the presence of a great number of liquid molecules on the sample surface decreases resolving power distribution and selectivity of thermodesorption process. It results from the lateral interactions of liquid molecules which diminish the bonding energy of the molecules adsorbed with the surface active centers. The thickness of adsorbed liquid layers on the surface can be controlled by the immersion mode of solid samples. For that reason, in the studies of liquid films adsorbed on solid surfaces, the samples of adsorbents were saturated with liquid vapors in the vacuum desiccator, where p/p_o–1. In the course of the above preparations all the surface forces of the tested solids have been blocked. Under this condition the active centers and capillary forces are compensated as in the McBain balance and other sorption methods, when p/p_o=1. The samples prepared in this way did not include the excess of bulk liquid whose presence influenced the thermodesorption kinetics and mechanism (so-called 'screening' of the surface) [3].

Figures 10 and 11 present the Q-TG and Q-DTG curves with respect to temperature and time of water and benzene thermodesorption from the alumina oxide samples saturated with vapor in desiccator, respectively. From Figures it appears that Q-TG curves in relation to temperature do not possesses the segments parallel to the axis of ordinates and corresponds to the bottom parts of the Q-TG curves presented in Figs 8A and 9A. It is result of different ways of sample wetting. The Q-DTG curves in Figs 10 and 11 possess peaks and inflections resulting from presence of various energetical kind of water and benzene molecules filling up of the surfaces and pores of the aluminium oxide samples. It reflects three steps of liquids thermodesorption processes from low (desorption of liquids con-

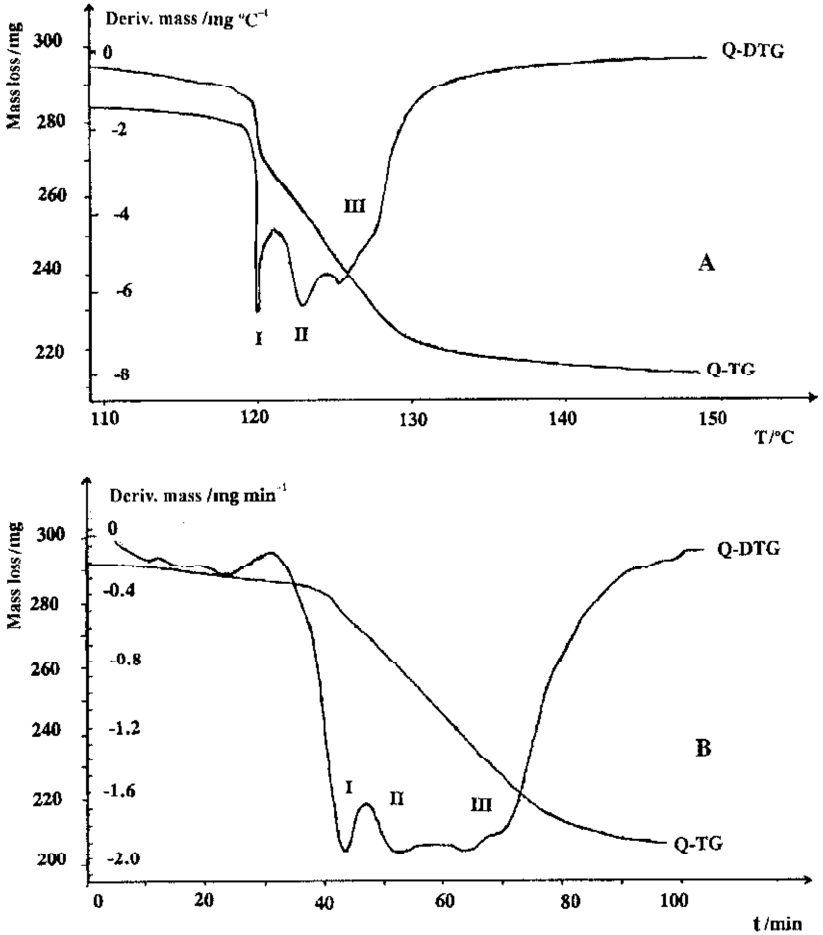

Fig. 10 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of water thermodesorption from aluminum oxide sample saturated with vapor in desiccator

densation layers – peaks I and from mesopores – peaks II) and high energy active sites (inflections III). Figures 10 and 11 show that thermodesorption of water and benzene from active sites of aluminum oxide surfaces (inflections III) occur at a high temperature, which is due to a large bonding energy in liquids structures formed in the range of surface forces (a high degree of water and benzene film structuring).

As in the case of Figs 10 and 11, three stages are found on the liquid-desorption Q-DTG curves presented in Figs 12 and 13. The Figures present the Q-TG and Q-DTG curves in relation to temperature and time of water (Fig. 12) and ben-

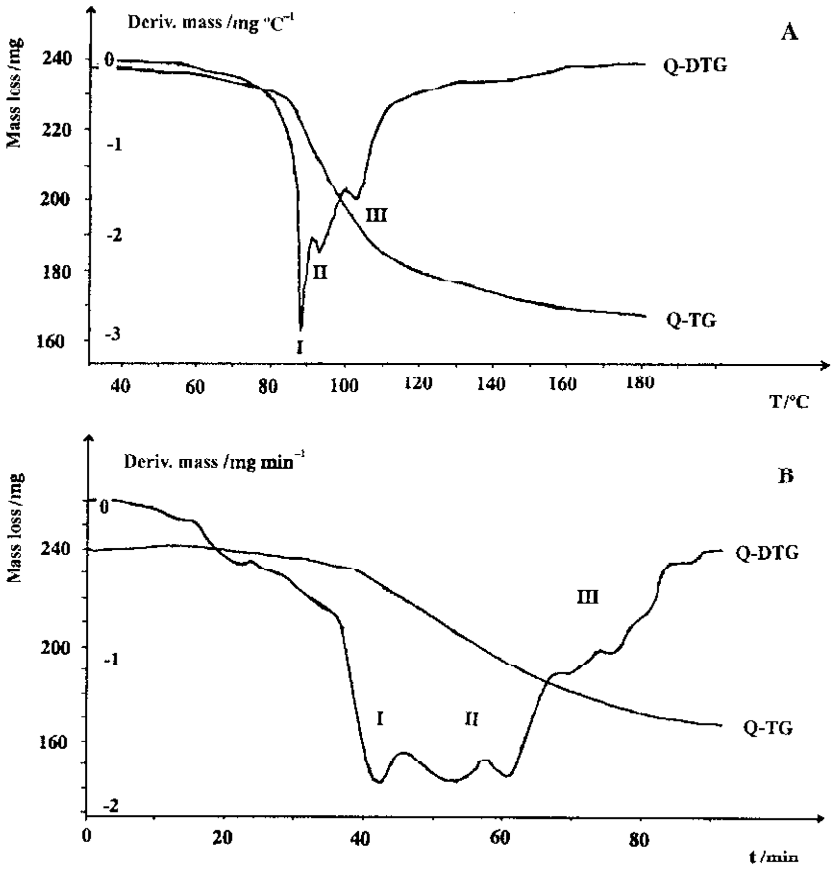

Fig. 11 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of benzene thermodesorption from aluminum oxide sample saturated with vapor in desiccator

zene (Fig. 13) evaporation from active carbon samples saturated with vapors in desiccator. During the last stages (inflections III) thermodesorption of liquid molecules from high-energetic active centers of surface takes place. Individual peaks and inflections on above Q-DTG curves result from the presence of different energetic types of active centers of materials studied. Figures 12 and 13 show that last parts thermodesorption of water and benzene from active carbon surfaces occur at a high temperature range of 140–160°C. It is due a large bonding energy in structures (especially ice-like water) formed in the range of surface forces near interfaces. It is very interesting that some steps related to liquids thermodesorption values from different solid surfaces presented in Figs 10–13 are similar and may be correlated with other sorption methods [24].

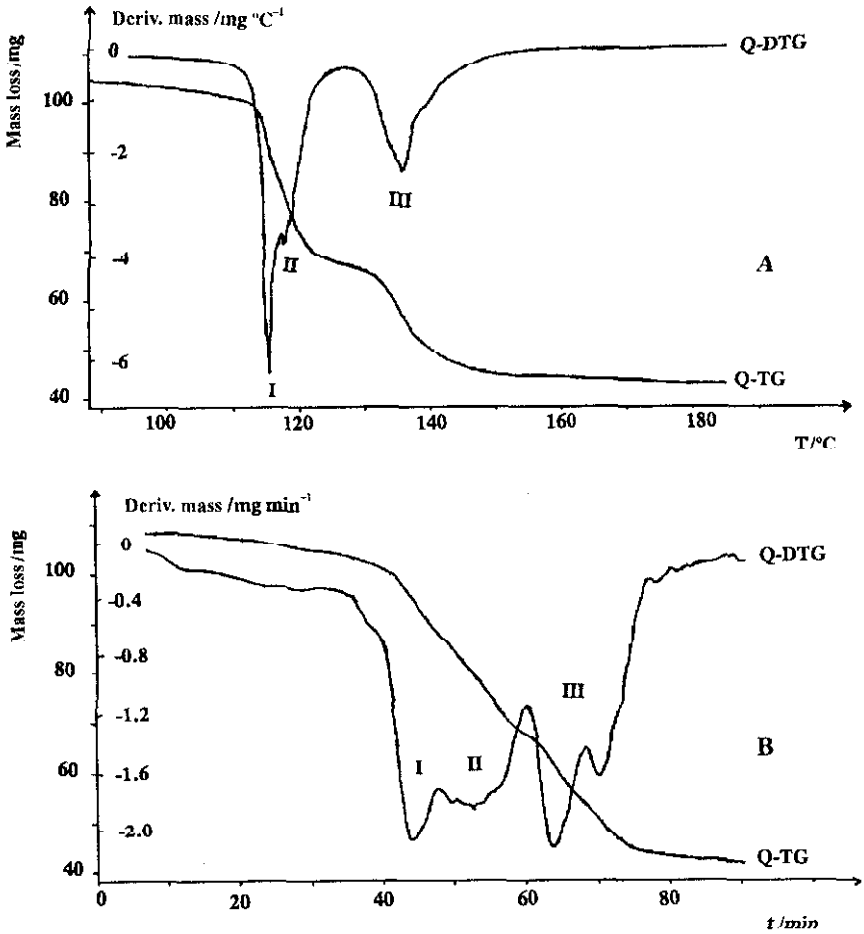

Fig. 12 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of water thermodesorption from active carbon sample saturated with vapor in desiccator

Lately, the numerical procedure for evaluation of energy distribution and mesopore-size distribution functions of preadsorbed liquids on the mesoporous surfaces using quasi-isothermal method was developed [30–32]. It is based on the condensation approximation to treat the thermodesorption kinetics of liquid from solid surfaces. The energy distribution function of *n*-butanol adsorbed on silica gel surface (Fig. 14) and pore-size distribution function (Fig. 15) on the basis of the Eq. (6) and one quasi-isothermal experiment of butanol thermodesorption process have been made. The theory and example of application of above approach to quantitative description of energetical and geometrical heterogeneities

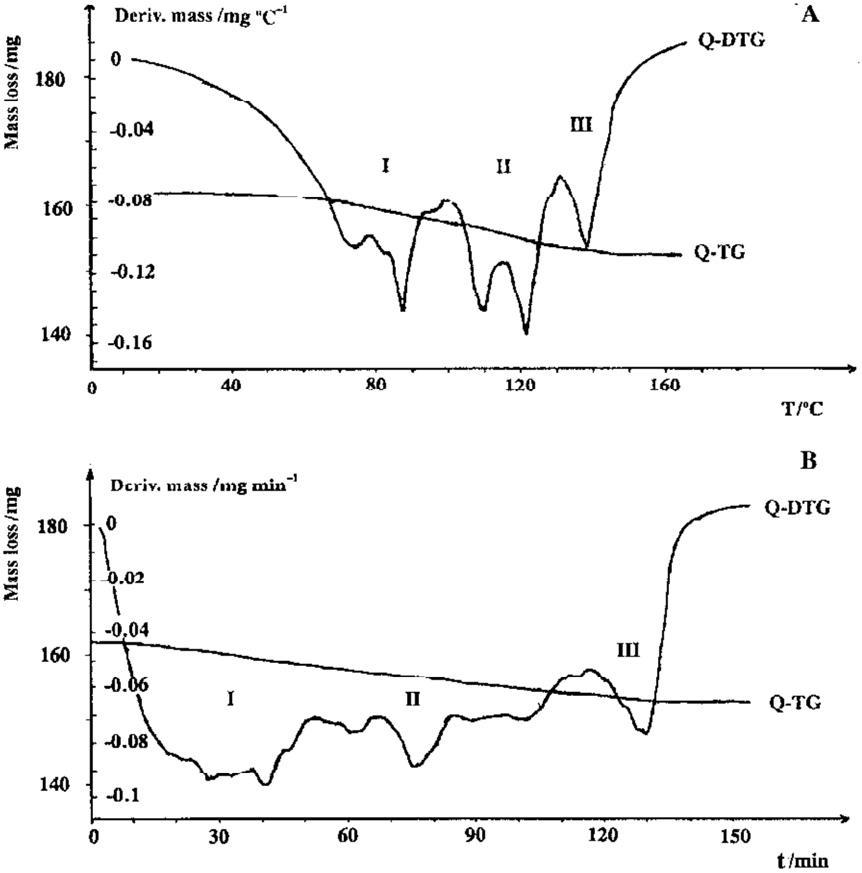

Fig. 13 The mass loss Q-TG and differential Q-DTG curves with respect to temperature (A) and time (B) of benzene thermodesorption from active carbon sample saturated with vapor in desiccator

of silica gel surface on the basis of the single *n*-butanol thermodesorption Q-TG and Q-DTG curves are given in the papers [31, 32]. The evaluated distribution functions satisfactory agree with parameters of the porous silica gel structure and with known characteristics of the *n*-butanol adsorption on its surface.

Summary

The results obtained so far show the extensive applicability of the simultaneous techniques called derivatograph Q-1500 D. It can be stated that presented method is simple, useful and effective in characterizing the physicochemical properties of both a heterogeneity of solid surfaces, adsorbed liquid films and in evaluation of the liquid-solid interactions. It is additional application of the

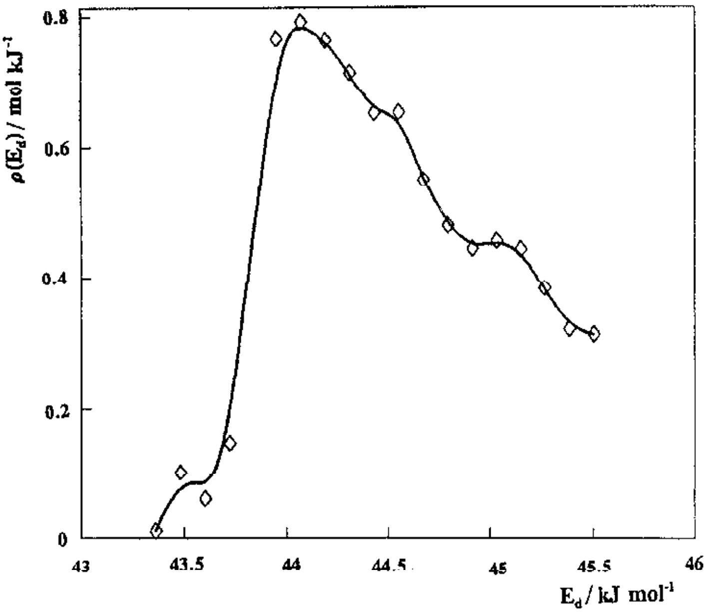

Fig. 14 Desorption energy distribution function of *n*-butanol from silica gel surface

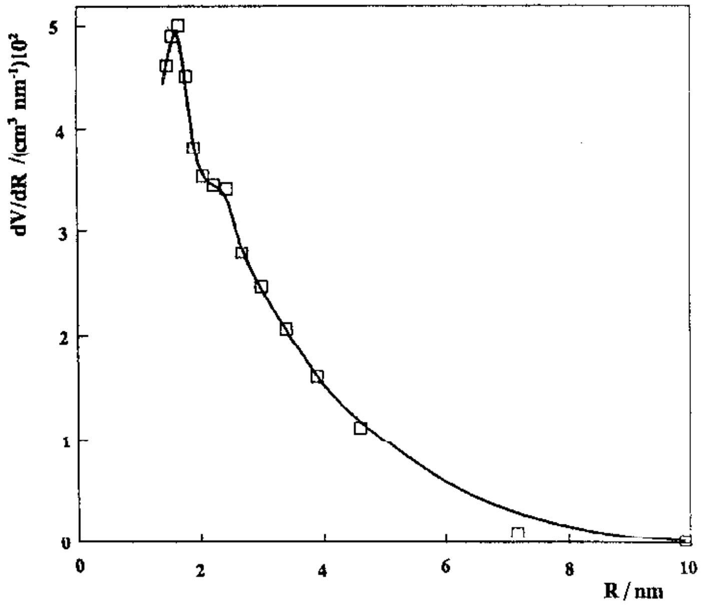

Fig. 15 Differential mesopore-size distribution function of the silica gel surface

above system to it conventional one. The Q-TG and Q-DTG curves are very important because on the basis of the one thermodesorption experiment it is possible to receive many parameters concerning liquid/solid interfaces. The above curves consist of steps and inflections which are associated with the liquid-liquid and liquid-solid interactions. The heights of these steps and inflections depend on the nature and number of the active centers of the surface studied and are related to the energy interactions. They contain information about the adsorption capacity (e.g. thickness of adsorbed films), the pore volume (i.e. geometrical heterogeneity), discontinuous change of adsorbed layer properties, mechanism of wetting process and interactions between liquid molecules and solid surfaces (i.e. energetical heterogeneity).

The extension of the silica gels number and other adsorbents with different pore-size (e.g. using the new carbon sorbents [33]), number of the liquids possessing various acid/base properties and wettability, and use independent special, adsorption and calorimetric data for characterization of these adsorption processes, makes the possibility to create on the basis of the above method the quantitative characterization of the heterogeneity properties of solid surface and adsorbed liquid films by means of the above described special technique.

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Thanks are due to Prof. Ferenc Paulik, creator of the simultaneous techniques called derivatogaph Q-1500 D, and Dr. Vladimir I. Bogillo for fruitful discussion and cooperation and to Aluminum Co. of America (USA) and Rohm and Haas Co. (USA) for sullying the alumina oxide and active carbon samples.

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