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Studies of the adsorbed water layers on solid surfaces by means of the thermal analysis special technique[1]

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Abstract

The paper presents the thermogravimetric studies of water film properties on the solid surfaces using the programmed desorption under the quasi-isothermal conditions. The samples wetted in a different way before the measurements were heated under the suitable quasi-isothermal conditions of temperature increase in the derivatograph using a platinum labyrinth crucible in order to evaporate water films from the surface. During the measurements, the mass loss Q-TG and the differential Q-DTG curves were registered as a function of temperature and/or time which are characterized by the inflections showing individual stages of water desorption from the samples. On the basis of experimental data, the surface wetting mechanism and kinetics of the thermodesorption of water films, discontinuous properties of adsorbed water layers on porous surfaces, adsorption capacity of samples and nature of active sites (e.g. hydroxyl groups) have been presented. It was stated that this method could be successfully applied in the studies of adsorbed water films and surface wetting phenomena. © 1998 Elsevier Science B.V.

Keywords: Special thermal analysis; Thermodesorption of water; Properties of vicinal water; Water/solid interactions; Heterogeneity properties of adsorbents

1. Introduction

As a result of the interaction between water molecules and surface, a wetting process which is considered as the water adsorption on the solid surfaces takes place. The wetting of solids is a phenomenon of great natural and industrial importance. The water/solid interface is important in natural systems, above all in geochemistry, in natural waters, soils and sediments and in the systems possessing interesting properties and various applications [1,2].

Grains of the materials fully immersed in the water are covered with the layers of bonded or so-called vicinal water in which molecules are suitably oriented. Thickness of this layer, according to Derjaguin and Churaiev, can correspond to 0.1 μm, i.e. 1000 or even more diameters of water molecules depending on the kind of the structure [3–6]. The molecules situated closest to the solid surface are most strongly bonded and ordered. The strength of the water–solid interaction decreases with the distance from the surface and in some regions the properties of water layers do not differ from those of liquid water [7]. Good wettability

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of solids useful in some systems (e.g. lubrication protective covers, herbicides) is undesirable in the separation processes (e.g. chromatography, enrichment of minerals). Water molecules adsorbed on the surfaces have different properties compared with volume water and make an energetic barrier in the interface separation processes. For that reason, in the enrichment processes of minerals by the floatation method, there is a tendency to eliminate this phenomenon [8,9].

Typical adsorbents (such as silica gel, active carbon, aluminum oxides) and some porous minerals and materials are characterized by high specific surface area and pore volume. Wetting process of the surface depends on the kind and size of intermolecular water–solid interactions. Depending on the kind of solids, atoms or ions can be connected by covalent (atomic), ionic or intermolecular bonds. In the case of disruption of these bonds due to the grinding process, the newly created surface is characterized by high surface free energy and strong electrostatic field. The surfaces of such materials as silica gel and other adsorbents act in a very active way with water molecules and are defined as polar or hydrophilic surfaces. They are highly energetic solids and possess great adsorption capacity [10].

The properties of vicinal water such as viscosity, density, freezing temperature, dielectric constant and the role of bonded water films in the dispersed are well known and documented in many papers [3–7,9,11,12]. The recent studies by various thermal analysis techniques [13–16] showed that the properties of aqueous films present on the solid surfaces change with the distance not in a monotonical way but stepwise and depends on physicochemical properties of the surface, including the porous structure of the studied materials. However, the structure of vicinal water is not well known. Literature [17–24] reports on the schemes of linear and cyclic structures which can be formed by the water molecules bonded with solid surfaces together with calculations of the interaction energy for one molecule. A few models and theories obtained on the basis of neutron scattering and total internal reflection Raman spectrometry have also been reported. Papers [25,26] present the calculations of activation energy of water molecules on the surface of pure minerals and on those covered with chemicals. The presence of individual water structures on the pure surfaces and the mechanism of possible transitions of water structure close to the interface after the collector adsorption were suggested. The difficulties in determination of water film structure are due to possibilities of formation of various vast structures both in the bulk water and that close to the surface. As it is known, one water molecule can simultaneously form 0–4 hydrogen bonds with the neighbors whose lifetime is of the order of 10^{-12} s. The regeneration of such structures depends on the conditions e.g. the type of interactions.

Vicinal water seems to be very interesting though its properties are little known. Vicinal water shows transitions in the structure. So far, the molecular mechanism of these transitions has not been determined. The papers [27–32] that presented the studies on heat capacity of the vicinal and heavy water in the silica gel pores and porous glasses, stated that the heat capacity of water present in the micropores was by 25% greater than that of the bulk water. Notable heat capacity 'spikes' were observed at temperatures which could be related to structural transitions in the vicinal water. A few papers [33–39] show the results of calorimetric and dielectric studies of the glassy state of water obtained by rapid cooling or by hyperquenching. They demonstrate the reversibility of water glass–liquid transitions. So far, there have not been any calorimetric data confirming the above hypothesis. It was only found [40] that energies of transitions were probably of the order from 1 to 20 cal/mol. In the papers [41,42] water molecules in hydrogels were classified into three categories according to the phase transition behavior: non-freezing, freezing bound and free water. The freezing bound water formed metastable ice by slow cooling and formed amorphous ice by quenching. The paper [43] presents the cyclic changes of heat flow which were associated with the changes in the properties of water due to changing temperature. It was stated that depending on the process course (cooling or heating sample), water structure either undergoes cyclic reproduction (during the cooling process) or decay (during heating) in the studied systems that include water. The lack of data about the water structural transitions is due to experimental difficulties. The experimental conditions like heating rate, apparatus sensitivity, water purity, sample-pan setting should be properly and carefully chosen. These experimental difficulties are also due to anomalous properties of the water molecule (small size and slight asymmetry) and its specific structure.

For this reason, the liquid structural transitions are immediate and low energetic but extensive in its bulk and very difficult to record.

The adsorption and calorimetric methods were very often adopted to study adsorbed water layers [44,45]. Over the past decade, there has been much theoretical and experimental progress reported in a number of papers [46–48], e.g. chromatographic [49], thin wicking technique [50], automatic adsorption apparatus [51], INS study [52], modern neutron scattering and internal reflection Raman spectrometry methods [18–24]. However, they are time consuming, apparatus are often very expensive and the obtained results are not sufficient to explain all of the adsorbed water properties, wetting phenomenon occurring on the solid surface and its role in the interface processes.

Thermogravimetry has rarely been used to study properties of adsorbed water layers. A derivatograph was used to determine thermal stability of industrial adsorbents and cements as well as to study the kinetics of structural relaxation of amorphous silica gel and to investigate the content of water in chemical compounds and materials [53,54]. For that reason, the thermal analysis special technique was adopted to investigate the properties of adsorbed water layers, mechanism and kinetics of water film destruction and wetting processes of solid surfaces.

2. Experimental

Measurements of programmed thermodesorption of water from the solid surfaces under the classical and quasi-isothermal conditions were started at the beginning of eighties [55,56] by means of the simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary). The quasi-isothermal technique was patented in eight countries by F. and J. Paulik [57–60], improved and installed in the Derivatograph Q-1500 D and computerized to be Derivatograph-C (MOM, Budapest, Hungary). In this technique, the type of a specially shaped sample holder (labyrinth crucible) was introduced [57]. Recently, the Derivatograph Q-1500 D was connected with the computer via the interface equipped with a suitable program Derivat to register the sample mass as a function of temperature and/or time and to determine the differential curves Q-DTG with respect to temperature and/or time as well as to integrate corresponding areas on the differential thermal analysis DTA curves during the classical measurements. The sample mass loss TG and Q-TG and the differential DTG and Q-DTG curves in relation to temperature and time and DTA and T curves under the classical and quasi-isothermal conditions were registered and printed using the open and platinum labyrinth crucible and computer system.

The studies were made using various solid samples with respect to their heterogeneous properties. This paper presents the results of water thermodesorption from the porous adsorbents of commercial pure silica gel (Kieselgel of Si-40, Si-60 and Si-100 types, Merck, Darmstadt Germany) of mesopore radii 40, 60 and 100 Å as well as from the samples of active carbon of Merck (Germany) and Norit (The Netherlands) types. In the studies of water thermodesorption the samples were prepared as follows. To obtain different thickness of liquid adsorption films on the solid surfaces, the samples were wetted with distilled water till complete saturation and/or saturated with water vapor in the vacuum desiccator at $p/p_0=1$.

2.1. Classical (dynamic) measurements of water thermodesorption from the adsorbent surfaces

The 1300–1400 mg of fully immersed tested adsorbents with water were placed in a open platinum crucible and thermodesorption measurements were carried out in the temperature range 20–200°C [55,56]. The furnace heating rate was 1.25 K/min. The following curves were plotted: sample mass loss TG, curve, differential sample mass loss DTG curve, temperature dependence between the sample investigated and standard sample DTA curve as well as temperature increase T curve.

2.2. Quasi-isothermal measurements of water thermodesorption from the adsorbent surfaces

The ca. 800 mg fully immersed with water and ca. 150–650 mg saturated with water vapor tested adsorbents were transferred into a platinum labyrinth crucible [57] and thermodesorption measurements under the quasi-isothermal conditions were carried out in the temperature range 20–250°C [56], with the furnace heating rate of 6 K/min. The relationships Q-TG=$f(T,t)$ and Q-DTG=$f(T,t)$ were plotted.

3. Results and discussion

3.1. *Studies of discontinuous properties of water layers on adsorbents*

Fig. 1 shows the results of water thermodesorption measurement from the Si-60 silica gel sample fully immersed in water under the classical conditions using an open crucible. This figure presents the following curves: thermogravimetric sample mass loss TG, differential DTG and DTA curves and temperature *T* curve [55,56]. The characteristic minima I, II and III exist on the obtained DTG and DTA curves. Fig. 2 presents the similar TG, DTG and T curves of water thermodesorption from the active carbon Merck sample fully wetted in water. The similar three low temperature inflections (I, II and III) on the DTG and DTA curves were observed.

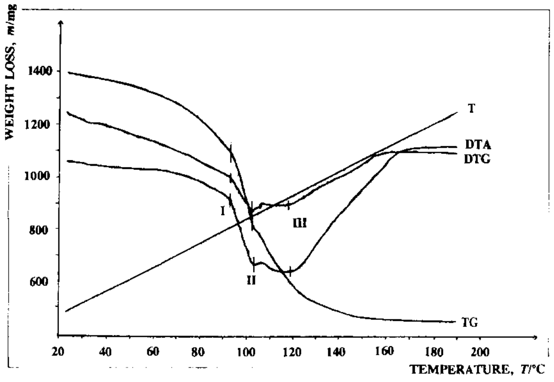

Fig. 1. The thermogravimetric TG, the differential DTG and DTG curves and temperature T curve of water thermodesorption from fully immersed silica gel Si-60 sample under classical conditions.

The existence of low temperature, I, II and III peaks on the DTG and DTA curves may be ascribed to the differences in bonding energy of water molecules in the adsorbed films on the silica gel and active carbon surfaces. The experimental results presented in Figs. 1 and 2 suggest that the desorption of water from the studied surfaces occurs in few steps. The region to the minima I in Figs. 1 and 2 corresponds to the desorption of bulk water from the tested samples fully immersed in water. The water desorbed in the regions from inflection I to the end of the thermodesorption process remains in the surface forces range of the pores (peaks II) and active sites (peaks III). This water has modified the properties due to the water-surface interactions and porous silica gel structure.

The selectivity of the inflections on the thermogravimetric curves was increased by using the thermodesorption technique under the quasi-isothermal conditions. Fig. 3 presents the thermogravimetric mass loss Q-TG and differential Q-DTG curves in relation to the temperature obtained during thermodesorption of water from the sample of completely wetted silica gel Si-60 under the quasi-isothermal conditions. From the data in this figure it follows that 3 steps of the thermodesorption process (i.e. evaporation of the bulk water, water from mesopores and from active sites of surface) were obtained. The segment

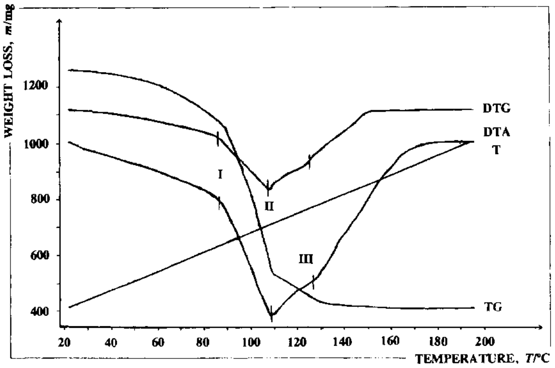

Fig. 2. The TG, DTG, DTA and T curves of water thermodesorption from fully immersed active carbon Merck sample under classical conditions.

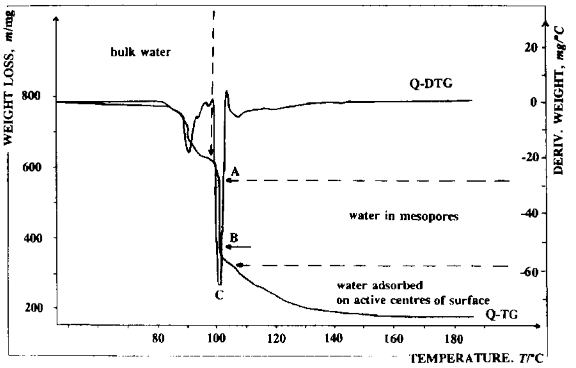

Fig. 3. The mass loss Q-TG curve and differential Q-DTG curve with respect to temperature of water thermodesorption from completely immersed silica gel Si-60 sample.

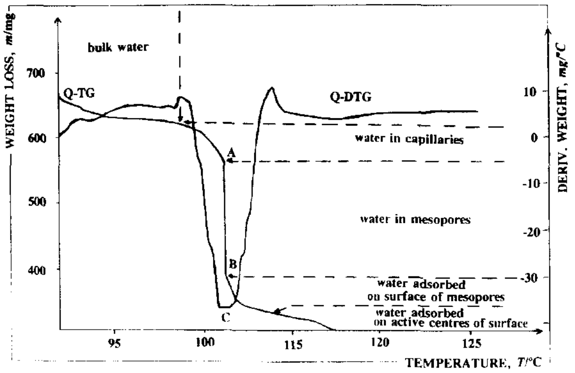

Fig. 4. The mass loss Q-TG curve and differential Q-DTG curve with respect to temperature of water thermodesorption from mesopores of completely immersed silica gel Si-60 sample (the enlargement part of Q-TG and Q-DTG curves on Fig. 3).

AB of Q-TG curve parallel to the axis of ordinates corresponding to the evaporation process of water from the mesopores has been recorded. Due to the fact that the difference of segment AB is mathematically infinite, the Q-DTG curve in point C was numerically shortened ("cut") by the computation program for practical reasons. That is clearly seen in Fig. 4 in which an enlarged fragment of the Q-TG and Q-DTG curves in the temperature range corresponding to the water thermodesorption from mesopores is presented. From Fig. 4 it appears that evaporation of water from mesopores is preceded by desorption of water present in the intergranular spaces of silica gel as well as in capillary tubes of its surface. Next, the water is desorbed from mesopores (Q-DTG curve, segment AB). The Q-TG curve presented in Fig. 3 make it possible to determine adsorption capacity of the studied silica, volume of mesopores present on the surface and amount of water bonded with the surface. As follows from the data presented, accurate determination of the inflection points on Q-TG curves related to a certain part of desorbed water is a very difficult and important problem. The first derivatives of weight-loss DTG curves with respect to temperature and time are very interesting and useful. The above parameters are calculated from the value of sample mass loss from the Q-TG curves. For precise determination of inflection points in the Q-TG curves the differential curves Q-DTG in relation to temperature and time are used [14]. The amount of water present in mesopores equals 7.95 statistical monolayers and corresponds to 0.79 cm^3/g 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 and is in very good agreement with above obtained from thermogravimetric special technique. Finally, water adsorbed on mesopore surface (3.18 statistical 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 monolayer n was calculated as follows. The amounts of water desorbed were expressed in millimoles per gram. These data were converted to the thickness of water on the surface (i.e., the number n of statistical adsorbed monolayers) on the basis of silica gel specific surface area knowledge and that a molecule of water occupies 12.5 Å^2, assuming uniform coverage and using equation:

$$n = aNS/A \qquad (1)$$

where: a is the amount of water desorbed, N is Avogadro number, A is specific surface area and S=12.5 Å^2.

The original "step" shape of the Q-TG curves presented in Figs. 3 and 4 results, first of all, from the peculiarity of the thermodesorption process steering [57] as well as from the application of a special, platinum labyrinth crucible [58] which enables step evaporation of the water from the sample under the quasi-isothermal conditions [59,60].

Interpretation of the surface wetting mechanism processes and water thermodesorption of differently wetted samples can be explained as follows [56,61,62]. The kinetics of the controlled thermodesorption of water from solid surfaces is influenced by the interactions between molecules in the adsorption layers (due to so-called lateral interactions) and water molecules on the solid surface [14]. The energy of interactions depends on the properties of adsorbate molecules (e.g. water polarity) as well as heterogeneous properties of the surface (kind and number of active sites and porosity). The above parameters affect the properties of water adsorption films (mainly their thickness and structure) but the programmed thermodesorption process shows the state of the layers on the studied surface in the form and type (course) of the obtained mass loss curves. It follows from the experimental data that many factors influence the shape of the thermogravimetric Q-TG and Q-DTG curves obtained during thermodesorption of liquids from the solid surfaces under the quasi-isothermal conditions. The most important are a kind of solid and wetting liquid, amount of the liquid present in the sample (thickness of the surface adsorbed layer and a way of surface immersing), apparatus parameters steering the kinetics of desorption (e.g. heating and evaporation rates), kind of program used in the apparatus enabling the quasi-isothermal conditions, type of crucible, way of data registration, kind of the program for calculation of derivatives Q-DTG in relation to temperature and time. To obtain correct and useful results of the programmed thermodesorption it is necessary to prepare suitable samples before measurements (depositing water films of a proper thickness) and to determine the exact experimental quasi-isothermal conditions in a measuring apparatus.

The total immersing process causes filling up of the surface, pores, capillary and intergranular spaces of silica gel samples. It is well known that the properties of water layers depend on the surface distance and the properties of vicinal water adsorbed on the surface are much different from those of bulk water. It is the reason for the existence of the steps in the thermodesorption process of water films from active sites, pores, capillaries and intergranular spaces as well as bulk water. At least 3 inflections are found on the water thermodesorption curves Q-TG from the heterogeneity surface of the completely immersed studied samples [14]. Figs. 3 and 4 show the inflection B related to the differences in water properties adsorbed on the surface and in the pores of the silica gel samples. On the other hand, the immersing of silica gel with water vapor in a desiccator where $p/p_0=1$ blocks all adsorption active centers and the surface forces of the sample studied, only. Under this condition the surface and capillary forces are compensated as in the McBain balance adsorption method.

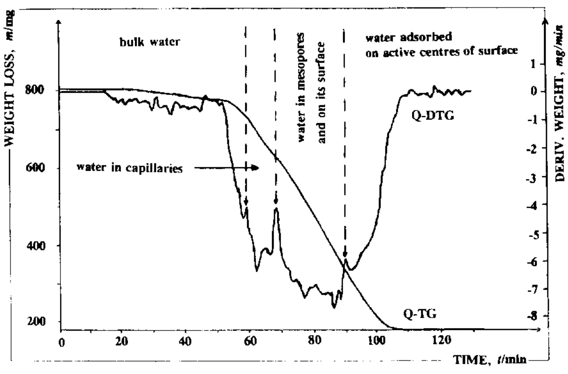

Fig. 5. The mass loss Q-TG curve and differential Q-DTG curve with respect to time of water thermodesorption process presented in Fig. 3.

The studies carried out so far show that the differential curves Q-DTG in relation to time are more useful because they permit to study the liquid desorption kinetics and the mechanism of thermodesorption [14]. Moreover, the dependence of Q-DTG curve is due to a distribution function of activation energy of water desorption according to the Polanyi-Wigner equation [63–65]. Very interesting first derivative DTG curves in respect to time were obtained for the silica gel samples fully immersed and saturated in the water vapor in a desiccator. Fig. 5 presents the mass loss Q-TG and the differential Q-DTG curves in relation to time obtained during the same process of water evaporation from the silica gel sample given in Fig. 3. As follows from Fig. 5, evaporation of water from the mesopores of 60 Å radii is preceded by the desorption of molecules from the intergranular space of silica gel grains as well as from some capillary tubes present on its surface. Next, the water from the mesopore inside is evaporated, then that adsorbed on its surface and finally the molecules most strongly bonded with the active sites of silica gel surface. As follows from the comparison of the data in Figs. 3 and 5, the shape of Q-DTG curve obtained during registration of the sample mass loss in time (Fig. 5) is quite different from the analogous one obtained during registration of the sample mass loss with the change of temperature (Fig. 3). The Q-TG curve in Fig. 5 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 (among others it does not possess the "cut" segments). It is worth noting that the Q-DTG curve presented in Fig. 5 is characterized by high selectivity and resolving power distribution. It can be considered as a certain type of "spectrum" of thermodesorption process describing an energetic state of water molecules

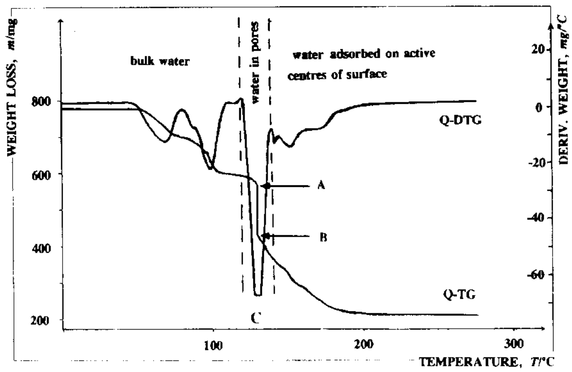

Fig. 6. The mass loss Q-TG and differential Q-DTG curves with respect to temperature of water thermodesorption from completely immersed sample of active carbon (Merck type).

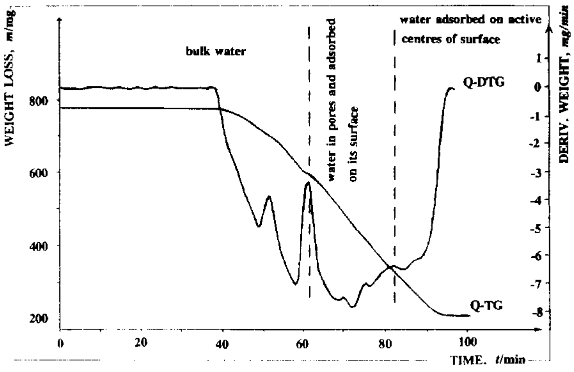

Fig. 7. The mass loss Q-TG and differential Q-DTG curves with respect to time of water thermodesorption process presented in Fig. 6.

on the silica gel sample and reflecting the distribution function of desorption energy of liquid on the studied surface.

With the increase in porosity and specific surface area of high porosity adsorbents a number of inflections increase during thermodesorption on the Q-TG curves and selectivity and the resolving power distribution of the method improves (more distinct inflections are obtained). In case of active carbon, there are various active sites as well as pores (macro-, meso-, micro- and even submicropores) which decide both about the extent of surface forces (i.e. a number of adsorbed layers) and the extent of structuring. Fig. 6 shows the thermogravimetric mass loss Q-TG and the differential Q-DTG curves in relation to temperature of water thermodesorption from the sample of completely wetted active carbon Merck type under the quasi-isothermal conditions. As follows from the data in this figure, the similar AB segment exists on the Q-TG curve parallel to the axis of ordinates which corresponds to the process of water evaporation from the surface pores. For this reason, the differential of the AB segment in point C was also numerically shortened. Fig. 7 presents the mass loss Q-TG curve and the difference Q-DTG curve with respect to time of the same evaporation process of water from the active carbon sample which was presented in Fig. 6. As follows from the comparison, the shape of Q-TG curve obtained during the registration of the sample mass loss with respect to time is completely different from the analogous one obtained during the registration of the sample mass loss in relation to temperature. The Q-TG curve in Fig. 7 does not possess characteristic "steps" and the corresponding segment parallel to the axis of ordinates but it is inclined to it at an angle, too. Therefore, the differential Q-DTG curve does not possess the numerically "cut" segments and is characterized by high selectivity and resolving power similar to those in Fig. 5. For that reason, it was applied to the studies of mechanism and kinetics of solid surface wetting phenomenon [15].

4. Studies of the silica gel and active carbon surfaces by means of the programmed thermodesorption of water under the quasi-isothermal conditions

Applications of adsorbents or catalysts requires knowledge of many surface physicochemical parameters, mainly their adsorption properties and porosity as well as selectivity, catalytic activity and properties of the surface active sites. For estimation of their nature, quantity, localization and energy of active centers (Lewis or Brønsted acid type) adsorption and microcalorimetric methods are most frequently used. The experimental studies showed that the programmed thermodesorption of water could be successfully applied to estimate a kind and number of active centers, particularly of hydroxyl groups on the silica gel surface [15]. As mentioned above, the shape of Q-TG and Q-DTG curves shows the character of interactions between the water molecules and the energetically differentiated active sites localized on the adsorbent surface. Surface wetting phenomena depends on the nature of surface active sites and porosity. As follows from the studies carried out so far, the presence of a great number of liquid molecules on the sample surface diminishes 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 water layers on the surfaces can be controlled by the immersion mode of solid samples. For that reason, in the studies of water films adsorbed on active centers, the samples of adsorbents were saturated with liquid vapors in the vacuum desiccator ($p/p_0 = 1$). In the course of the above preparations all the surface forces of the tested solids have been blocked. The samples prepared in this way did not include the excess of bulk liquid whose presence influenced the thermodesorption kinetics and mechanism ("screening" of the surface).

Fig. 8 presents the Q-TG and Q-DTG curves with respect to time of water thermodesorption from the heterogeneous surfaces of Si-40, Si-60 and Si-100 silica gel samples saturated in water vapor in the desiccator. From the figure it appears that Q-TG curves do not possess the segments parallel to the axis of ordinates. They correspond to the bottom part of the Q-TG curve presented in Fig. 3 which is a result of different ways of sample wetting. It is very interesting that apart from different methods of sample wetting processes, some steps of the water thermodesorption may be correlated [25,26]. From Fig. 8, it appears that two or three small (discrete) stages can be distinguished on the thermogravimetric differential Q-DTG curves. The first stage is evaporation of the water film from low-energetic sites of silica gel surface. During the next stages thermodesorption of molecules from high-energetic active centers of the surface takes place. Individual peaks on the Q-DTG curves result from the presence of different energetic types of hydroxyl groups OH^- on the silica gel surface (e.g. bonded, free and active). Fig. 8 shows that thermodesorption of water from the silica gel Si-40 sample is the slowest which is due to a large bonding energy in the ice-like structures formed in the range of surface forces (a higher degree of water structuring in smaller pores of 40 Å radii). Thus, on the basis of the above thermogravimetric technique data it is possible to calculate a number of individual hydroxyl groups present on the surface of various heterogeneous type of the silica gel surface and compare their hydrophilicity. From the data obtained by the use of the thermogravimetric method, a number of hydroxyl groups were calculated and good agreement with the analogous ones obtained by reduction of the complex $(CH_3)_2Zn$–THF from the silica gel active centers was reached [15].

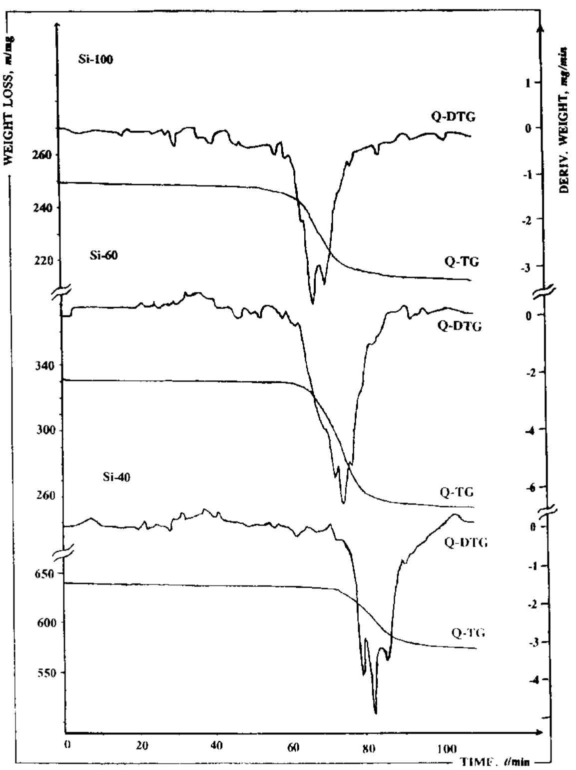

Fig. 8. The mass loss Q-TG curves and differential Q-DTG curves with respect to time of water thermodesorption from heterogeneous Si-40, Si-60 and Si-100 silica gel samples saturated with water vapor in desiccator.

Fig. 9 presents the Q-TG and Q-DTG curves in relation to the temperature obtained during evaporation of water from the different active carbon (Merck and Norit) samples saturated with water in the desiccator. As follows from Fig. 8, the Q-DTG curves possess the peaks and inflections resulting from the presence of various active sites on the sample surfaces. It reflects two or three steps of desorption process of water molecules from low and high energetical active centers presented on the studied surfaces.

As mentioned above, the differential Q-DTG curve in relation to time (so-called "spectrum") of the thermodesorption process reflects an energetic state of water molecules on the studied surfaces of various heterogeneous properties. On the other hand, the water thermodesorption process under the quasi-isothermal conditions describes evaporation of molecules from various pores, surfaces and finally active sites of different energy. The distribution function of desorption energy $f(E)$ can be determined on the basis of water thermodesorption measurements. For energetically heterogeneous surface of solids and according to the Tronconi and Forzatti model of liquid thermodesorption, the rate of desorption r_d (i.e. differential mass loss Q-DTG data) is calculated from the equation [65]:

$$r_d = -(d\Theta/dt)_n = A/\alpha \int_{E_{min}}^{E_{max}} \Theta(E,T)^n \exp(-E/RT) f(E) dE \quad (2)$$

where Θ is the average degree of coverage, α is the heating rate, A is the pre-exponential coefficient, n is the reaction order, t is the time of desorption, T is the temperature and R is the gas constant.

A few examples of practical application of Eq. (2) in estimation of energetic heterogeneity of solid surfaces are reported in the literature, only [65]. The differential Q-DTG curves presented in Figs. 8 and 9 show the course of the distribution functions of water desorption energy on the silica gel and active carbon surfaces. They can be applied to estimate water film properties, energetic heterogeneity of the studied surfaces and correlate the tested materials.

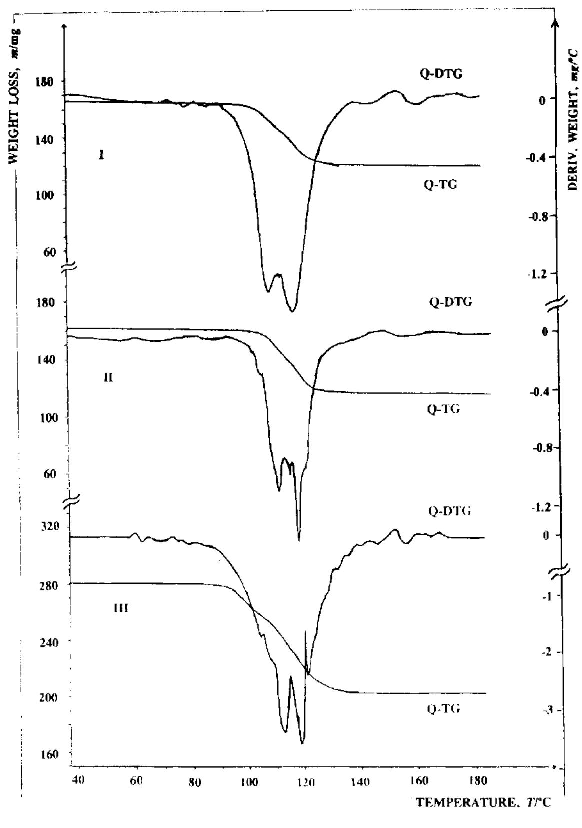

Fig. 9. The mass loss Q-TG curves and differential Q-DTG curves with respect to temperature of water thermodesorption from active carbon (I – Merck, II and III – Norit types) samples saturated with water vapor in desiccator.

5. Conclusions

The properties of adsorbed water layers on the solid surfaces have been studied using the thermogravimetry method under the quasi-isothermal conditions. The nature of active sites and surface porosity influence on the surface wetting phenomena. The shapes of the thermogravimetric Q-TG and Q-DTG curves depend on the thickness of adsorbed water layers on the studied surface. Thus, the water film thickness on solid surfaces was controlled by the immersion mode of samples. The bulk water evaporation process differs significantly from thermodesorption of bonded water from the pores and molecules adsorbed on the surface active sites. It is manifested by the inflection points on Q-TG and Q-DTG curves for the fully immersed samples. The correlation between the amounts of desorbed water and type of immersion sample processes has been found. On the basis of the obtained data it is possible to characterize properties of the adsorbed water layers and the mechanism of surface wetting phenomenon (determination of adsorption capacity, adsorbed film thickness, range of surface forces, discontinuous properties of adsorbed water layers), water-surface interfaces (changes in the mechanism of the wetting process due to the nature of active sites and surface porosity) and energetic heterogeneity of surface samples (distribution function of desorption energy as well as determination of the type and value of active sites, hydrophilicity and hydrophobicity of the surface) and structural heterogeneity of solids (estimation of pore volume).

The above examples illustrate great applicability of the methods described above, among others, due to the fact that it is possible to obtain many parameters characterizing the properties of water/solid systems in one experimental run. From the above studies it can be stated that the programmed thermodesorption method of water from the sample surfaces under the quasi-isothermal conditions can be successfully applied to estimate the adsorbed water films. This technique is convenient, useful and effective especially in characterization of the water/solid systems and can be competitive with the traditional one because of the speed and accuracy of the obtained data and the simplicity of experimental operations.

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