

Special applications of thermal analysis in the investigation of liquid/solid systems

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Abstract

The thermal analysis method was successfully applied to study of the heterogeneity properties of solid surfaces and adsorbed liquid films. The method utilized the thermogravimetric mass loss Q -TG and differential Q -DTG curves with respect to temperature and time obtained during thermodesorption process of liquids from solid surfaces under quasi-isothermal conditions. On the basis of the experimental data, using an analyzer equipped with an automatic ultra-slow heating device and a labyrinthine conical crucible, the discontinuous properties of adsorbed layers, changes in the mechanism of the wetting process due to the liquid/surface interactions, adsorption capacity of the tested samples and nature of surface-active sites have been presented. It appears that the special thermogravimetry technique is very useful in studying the liquid/solid systems and competes well with the traditional ones because of the speed and accuracy of the obtained data and the simplicity of experimental operations.

Keywords: Liquid/solid interactions ; Properties of liquid films; Special thermal analysis; Surface properties of solids; Thermodesorption of liquids

1. Introduction

The solid surfaces are energetically and geometrically heterogeneous. The above parameters depend on the properties of adsorbed liquid films, mainly their thickness and structure. Methods of characterization of liquid/solid systems (adsorption layers, adsorbate-adsorbent interactions and heterogeneity properties of solid surfaces) are usually based on adsorption, calorimetric and porosimetric studies [1]. They consist in the estimation of: adsorption abilities for various substances and adsorption capacities (determination of adsorption isotherm and extent of adsorption at $p/p_0 = 1$, where p is the equilibrium pressure and p_0 the saturated vapor pressure of the adsorbate), energy

effects accompanying the adsorption process (heats of adsorption and desorption, heats of immersion, adsorption-potential distribution functions, adsorption- and desorption-energy distribution functions) and the porosity of solids (specific surface area, radii and volume of pores as well as pore-distribution functions). The aforementioned methods are time consuming, the calculations involved arduous, it is therefore necessary to develop other more simple and rapid methods of characterizing liquid/solid system properties.

Thermal analysis has been adopted to investigate liquid/solid interfaces [2–5]. The principal idea of these investigations was to register the changes taking place in the process contrary to adsorption, i.e. in the thermodesorption of liquids from the solid surfaces under quasi-isothermal conditions. The amount and kinetics of liquid thermodesorption are influenced by

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the extent of interactions between a liquid molecule and solid surface, properties of the adsorbate (e.g. its polarity), character and type of surface, its adsorption properties (concentration and nature of active sites) and porosity (pore volume and size, specific surface area). The method consists mainly in measuring the liquid mass loss from the sample during the thermodesorption process carried out under suitable conditions.

The paper presents the results of a special application of thermal analysis in the study of liquid/solid systems. During the measurements, the Q -TG curves of mass loss and differential Q -DTG curves were registered as a function of temperature and/or time and are characterized by the inflections showing individual stages of liquid desorption from the samples.

2. Experimental

2.1. Apparatus

Measurements of programmed liquid thermodesorption under quasi-isothermal conditions from the surface of solids, under investigation were made by means of the simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary). The apparatus is connected with a computer at the interface and equipped with the Derivat program for calculation of the first derivatives of mass loss Q -DTG curves with respect to temperature and time as well as to integrate corresponding areas on the DTA curves during classical measurements. The weight-loss-TG and Q -TG curves were measured under classical and quasi-isothermal conditions over a (20–300)°C temperature range, using an analyzer equipped with an automatic ultra-slow heating device, a labyrinthine conical crucible and capable of maintaining quasi-isothermal conditions to increase the resolution of thermal analysis. The TG, Q -TG, DTG, Q -DTG, DTA and T curves were registered and printed with the help of the computer system. Compared with the studies carried out under the classical 'dynamic' conditions, the quasi-isothermal method has some advantages, among which are a broader applicability and much greater selectivity. This method is more reliable in the investigations of transformations of overlapping processes [5].

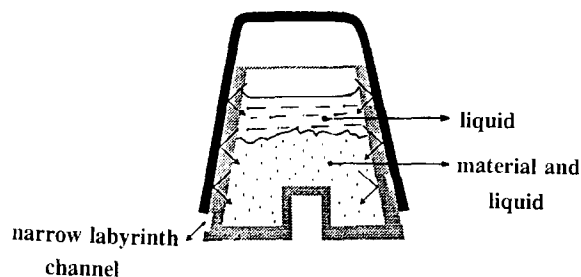


Fig. 1. Paulik's conical crucible for the attainment of a self-generated atmosphere [9].

2.2. Application of the quasi-isothermal technique for studying liquid/solid systems

The thermogravimetry carried out under the quasi-equilibrium (quasi-isothermal and quasi-isobaric) conditions have been developed by Paulik et al. [6,7] and Rouquerol [8] at the beginning of the sixties. Fig. 1 presents the labyrinthine conical crucible for carrying out reactions in a self-generated atmosphere [9]. The quasi-isothermal technique enables precise determination of, for example, the amount of crystalline water released from the chemical compound under investigation at a given temperature and the mechanism of the decomposition process. Fig. 2 presents the thermal distribution of hydrated copper sulphate under classical, or so-called, 'dynamic' (Fig. 2A) and quasi-isothermal (Fig. 2B) conditions. The sample mass loss (in mg) is denoted along the ordinate. Water of crystallization is seen to evaporate from the sample in a manner dependent on temperature. The Q -TG curves describing chemical compounds decomposition are characterized by inflection and the so-called 'steps' (parts of curve parallel either to the ordinates or abscissae) resulting from chemical bonds disruption and evaporation of a specific kind and amount of crystalline water from the sample at the temperature of transformation. The original 'step' shape of the Q -TG curves results, first of all, from the peculiarity of the thermodesorption process steering as well as from the application of a special, platinum labyrinthine conical crucible [10].

These observations led to attempts to apply programmable liquid thermodesorption from solid surfaces under quasi-isothermal conditions in studies of liquid/solid system properties [3]. The method

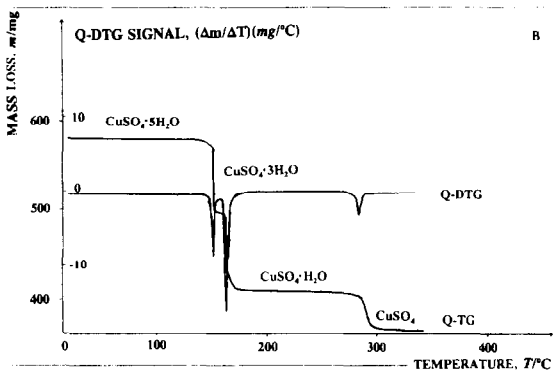
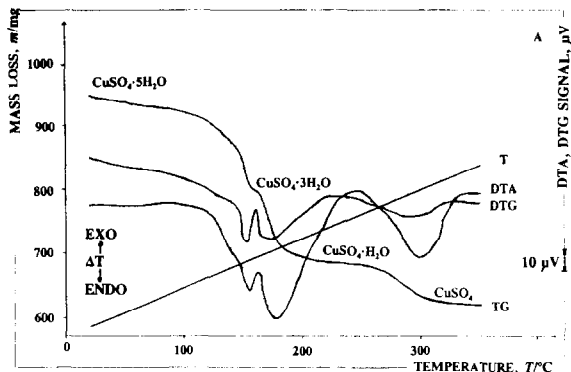


Fig. 2. Thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ under: (Fig. 2A) classical, and (Fig. 2B) quasi-isothermal conditions.

enables step evaporation of the liquid from the sample studied as a result of physical bonds disruption. The main aim was to devise a method for determining the physico-chemical properties of both surface and liquid films which change as a result of interaction with a solid. The Q symbol means the mass loss in the TG curve and differential mass loss in the DTG curve obtained during quasi-isothermal conditions [10].

2.3. Samples

The studies were carried out on silica gel surfaces of various heterogeneous properties of Si-40, Si-60 and Si-100 types of mesopore radii 20, 30 and 50 Å (Merck, Darmstadt, Germany), respectively. The samples studied were exposed to the adsorptive substance (benzene, octane butanol) by different methods in order to prepare surface films of different thickness:

by immersing them in the pure liquid and by exposing them to vapors in the vacuum desiccator, where the relative vapor pressure was $p/p_0 = 1$.

3. Results and discussion

Figs. 3–5 present classical thermal analysis curves of benzene, octane and butanol from silica gel Si-60 sample using open crucible. The samples mass loss (in mg) of liquids along the ordinates are denoted. Three low-temperature endothermic peaks (I, II and III) are

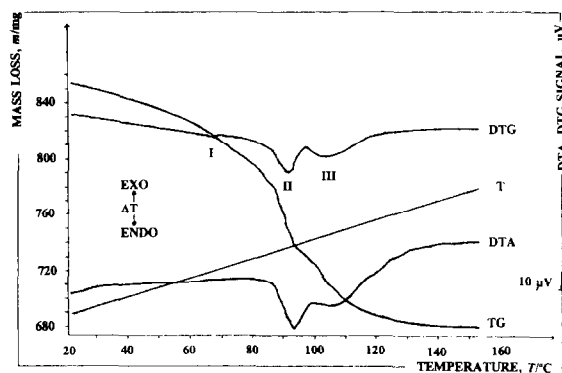


Fig. 3. The TG, DTG, DTA and T curves of benzene thermodesorption from fully immersed silica gel Si-60 sample under classical conditions (peak I – desorption of bulk benzene, peak II – desorption of benzene from mesopores, peak III – desorption of benzene more strongly bonded to the silica gel surface).

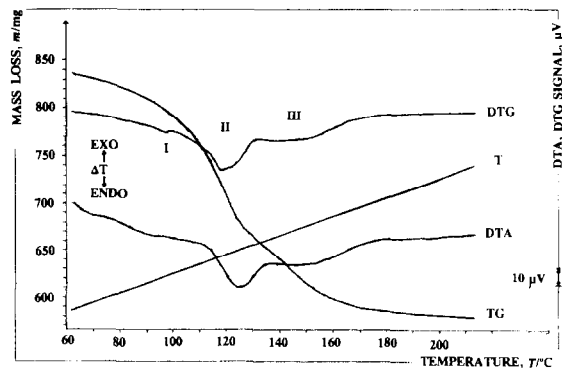


Fig. 4. The TG, DTG, DTA and T curves of octane thermodesorption from fully immersed silica gel Si-60 sample under classical conditions (peak I – desorption of bulk octane, peak II – desorption of octane from mesopores, peak III – desorption of octane more strongly bonded to the silica gel surface).

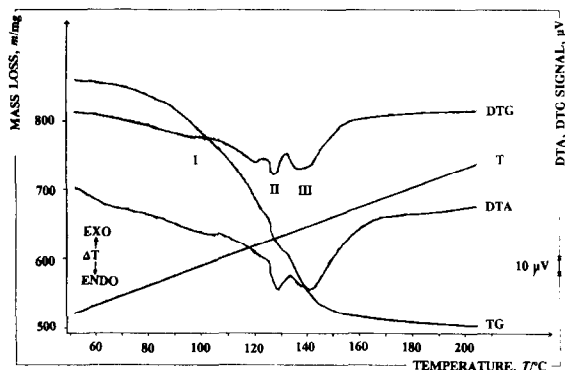


Fig. 5. The TG, DTG, DTA and T curves of butanol thermodesorption from fully immersed silica gel Si-60 sample under classical conditions (peak I – desorption of bulk butanol, peak II – desorption of butanol from mesopores, peak III – desorption of butanol more strongly bonded to the silica gel surface).

seen in the DTG curves. These peaks correspond to analogous peaks in the DTA curves, which account for stepwise liquid removal from the silica surface as the temperature increases. The existence of low-temperature peaks on DTG and DTA curves may be ascribed to differences in bonding energy of liquid molecules in adsorption region near silica surface. In the first stage, mainly bulk liquids are desorbed (peaks I); next, molecules present in mesopores (peaks II); and then, the molecules more strongly bonded to the silica gel surface (peaks III) [2,3].

During evaporation of liquids from the silica gel samples in quasi-isothermal conditions using a labyrinthine conical crucible on Q -TG curves, similar inflections and the segments parallel to the axes ('steps') to those in Fig. 2 are observed because of the existence of various kinds of liquids adsorbed on the surface by means of different physical bonds.

Fig. 6 presents the Q -TG and Q -DTG curves with respect to temperature of benzene thermodesorption from completely immersed silica gel Si-60 sample under quasi-isothermal condition. The sample mass loss (in mg) of benzene is denoted along the ordinate. The Q -TG curve is characterized by numerous inflections, segments parallel to the ordinates (e.g. AB) and abscissae forming 'steps', which result from evaporation of bulk benzene, intergranular and capillary benzene, benzene present in the mesopores as well as of that adsorbed on the active sites of the silica surface. At least three inflections are found on the liquid

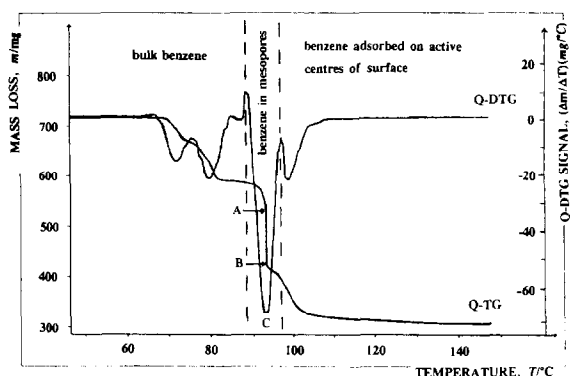


Fig. 6. The mass loss Q -TG and differential Q -DTG curves with respect to temperature of benzene thermodesorption from completely immersed silica gel Si-60 sample under quasi-isothermal condition (part of the Q -TG curve (AB) parallel to the ordinate – desorption of benzene from mesopores).

thermodesorption Q -TG curves from the surface of the completely immersed samples under investigation. They result from the discontinuous properties of adsorbed layers and disruption of the adsorbate–adsorbate and adsorbate–adsorbent bonds and stage process of benzene desorption being in the different energetic states in the sample. The AB section of the Q -TG curve (Fig. 6) is parallel to the ordinate, and the calculation of the first derivative of weight-loss Q -DTG curve with respect to temperature is practically impossible (because it is infinite) and the Q -DTG curve is cut for practical reasons at the point C.

The mechanism and kinetics of the controlled thermodesorption of liquids from solid surfaces is influenced by the interactions between adsorbate molecules in the adsorption layers (due to so-called lateral interactions) and liquid molecules with the solid surface [5]. The energy of the interactions depends on the properties of adsorbate molecules polarity as well as the nature of the active sites and surface porosity. The above-mentioned parameters affect the properties of liquid adsorption films (their thickness and structure), but the programmed thermodesorption process shows the state of the layers on the studied surface in the form of obtained Q -TG mass loss curves. The Q -TG curves presented in Fig. 6 make it possible to determine adsorption capacity of the studied sample, volume of mesopores present on the surface and the amount of benzene bonded to the surface. The accurate determination of the inflec-

tion points on the Q -TG curves, related to a certain part of desorbed liquid, is a very difficult though important problem. The first derivatives of weight loss Q -DTG curves with respect to temperature and time are very interesting and useful. Thus, for precise determination of inflection points in the Q -TG curves, the differential curves Q -DTG in relation to temperature and time are used [5]. The studies carried out so far proved that the differential curves Q -DTG in relation to time are more useful because they allow the study of the kinetics and mechanism of the liquid thermodesorption process and energy heterogeneity of the solid surfaces according to the method developed by Staszczuk et al. [11].

Fig. 7 presents the mass loss Q -TG and the differential Q -DTG curves in relation to time obtained during the same process of benzene evaporation from the silica gel sample given in Fig. 6. As follows from Fig. 7, the evaporation of benzene from mesopores of 30 Å radii is preceded by the desorption of molecules from the intergranular space of silica gel grains as well as from one capillary tube present on its surface. Benzene from the inside mesopore is evaporated first, then that adsorbed on the mesopores surface and, finally, the molecules most strongly bonded with the active sites of silica gel surface. As follows from the comparison of the data, the shape of Q -DTG curve obtained during registration of the sample mass loss in time (Fig. 7) is quite different from the analogous one obtained during registration of the sample mass loss with the change of temperature (Fig. 6). The Q -TG

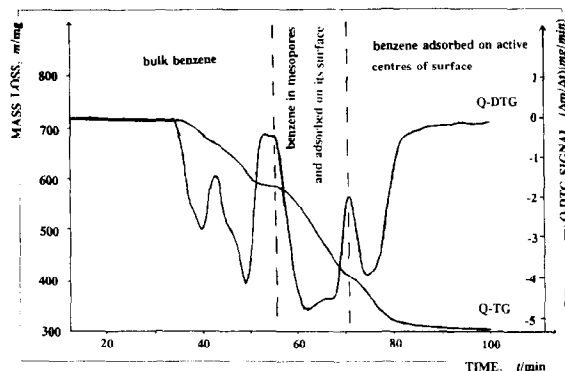


Fig. 7. The mass loss Q -TG and differential Q -DTG curves with respect to time of benzene thermodesorption process presented in Fig. 6 (kinetic curves).

curve in Fig. 7 does not possess characteristic 'steps' and the corresponding segment AB, parallel to the ordinate, but is inclined to it at an angle because kinetic curve of sample mass loss. Therefore, the differential Q -DTG curve in relation to time is different from the analogous Q -DTG curve in relation to temperature, among other difference does not possess 'cut' segments such as point C in Fig. 6. It is worth noting that the Q -DTG curve presented in Fig. 7 is characterized by a high selectivity and resolving power distribution. It can be considered as a certain type of 'spectrum' of thermodesorption process describing an energy state of benzene molecules on the silica gel sample because it reflects the desorption energy distribution function of liquid on the studied surface.

As was mentioned above, the thermodesorption process under the quasi-isothermal conditions reflects the energy state of the adsorbed liquid films on the studied surface. A lot of parameters influence the shape of the Q -TG and Q -DTG curves, particularly the kind of liquid and surface studied, heating rate and decomposition, type of apparatus and crucible, registration program of the experimental data used, some parameters of desorption kinetic process, etc. [12,13].

Figs. 8 and 9 show the mass loss thermogravimetric Q -TG and the differential Q -DTG curves in relation to temperature of octane and butanol thermodesorption of octane and butanol thermodesorption processes

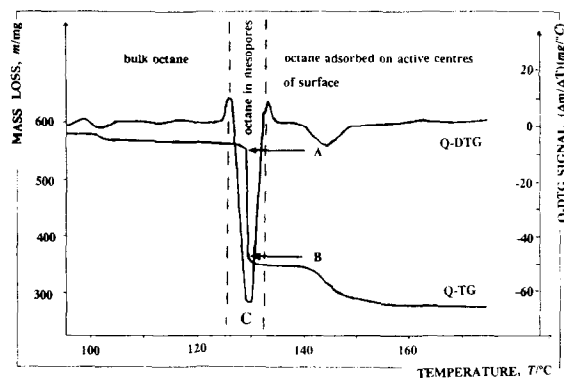


Fig. 8. The mass loss Q -TG and differential Q -DTG curves with respect to temperature of octane thermodesorption from completely immersed silica gel Si-60 sample under quasi-isothermal condition (AB – part of Q -TG curve parallel to the ordinate represents desorption of octane from mesopores).

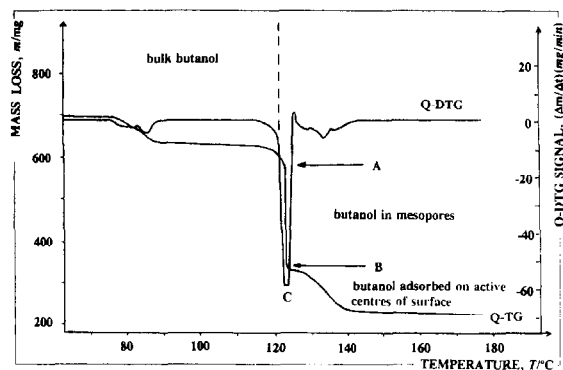


Fig. 9. The mass loss Q -TG and differential Q -DTG curves with respect to temperature of butanol thermodesorption from completely immersed silica gel Si-60 sample under quasi-isothermal condition (AB – part of Q -TG curve parallel to the ordinate represents desorption of butanol from mesopores).

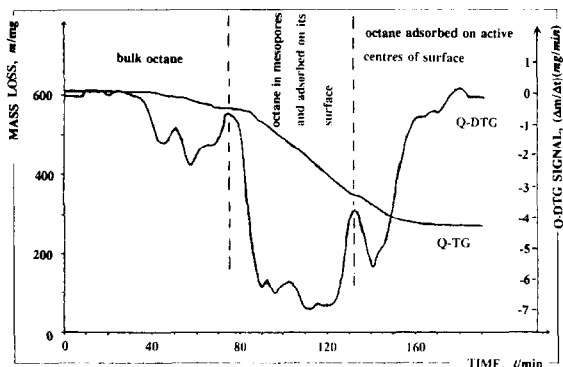


Fig. 10. The mass loss Q -TG and differential Q -DTG curves with respect to time of octane thermodesorption process presented in Fig. 8 (kinetic curves).

from the samples of completely immersed silica gel Si-60 sample under quasi-isothermal conditions. As in the case of Fig. 6, three stages are found on the liquids-desorption curves. Figs. 10 and 11 present the mass loss Q -TG and the differential Q -DTG curves with respect to time (kinetic curves) of the same evaporation processes of octane and butanol from the silica gel samples which were presented in Figs. 8 and 9, respectively. They can be applied in the studies of mechanism and kinetics of solid surface wetting phenomenon [14] and energy heterogeneity of solid surfaces [5,15,16].

Comparative thermoanalytical studies of the silica gel samples saturated with vapor in a desiccator and

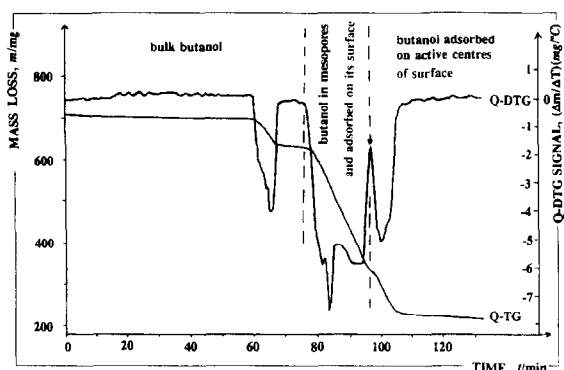


Fig. 11. The mass loss Q -TG and differential Q -DTG curves with respect to time of butanol thermodesorption process presented in Fig. 9 (kinetic curves).

fully immersed in liquid provided information about the mechanism of wettability of surface (discontinuous properties of adsorbed layers) and permitted the characterization of the sample studied in terms of the adsorption capacity, the specific surface area and porosity (pore volume) [5]. It is very interesting that apart from different saturated methods of tested samples, some 'steps' of the liquid thermodesorption process may be correlated with the parameters of liquid adsorbed from the gaseous phase obtained by classical adsorption (e.g. McBain balance) and other methods (e.g. porosimetry, modified derivatography) [17,18].

The shape of Q -TG and Q -DTG curves show the character of interactions between molecules and energy-wise differentiate active sites localized on the adsorbent surface. Surface wetting phenomena depend on the amount and kind of surface active sites and porosity. As follows from the studies carried out so far [14], the presence of a great number of liquid molecules on the sample surface decreases the resolving-power distribution and selectivity of thermodesorption process. It results from lateral interactions of liquid molecules which decrease the bonding energy of the molecules adsorbed with the surface active sites. The thickness of adsorbed layers on surfaces can be controlled by the immersion mode of solid samples. For that reason, in the studies of liquid films adsorbed on active sites, the samples of silica gel were saturated with liquid vapors in the vacuum desiccator, where $p/p_0 = 1$. During these preparations, all surface forces of the tested solids have been blocked. The samples

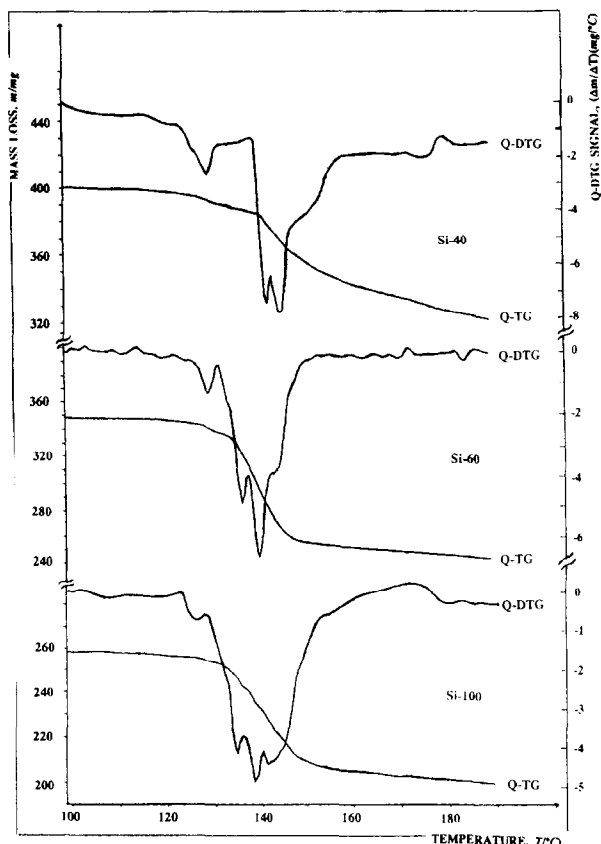


Fig. 12. The mass loss Q -TG and differential Q -DTG curves with respect to temperature of butanol thermodesorption under quasi-isothermal conditions from Si-40, Si-60 and Si-100 silica gel samples saturated with vapor in desiccator.

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. 12 presents the Q -TG and Q -DTG curves in relation to temperature obtained during evaporation of butanol from the silica gel Si-40, Si-60 and Si-100 samples saturated in the desiccator. From this figure it appears that Q -DTG curves do not possess the segments parallel to the ordinate. They correspond to the bottom part of the Q -TG curve presented in Fig. 9, which is a result of different ways of sample wetting. It follows from the figure, that the Q -DTG curve possesses peaks and inflections resulting from the presence of various active sites on the sample surfaces. It reflects a two-to-three steps of butanol

thermodesorption process from low and high energy-active sites. Fig. 12 shows that thermodesorption of butanol from the silica gel Si-40 sample occurs at a higher temperature, which is due to a large bonding energy in butanol structures formed in the range of surface forces (a higher degree of butanol structuring in smaller pores of 20 Å radii). As already mentioned, the differential Q -DTG, so-called 'spectrum' curve of thermodesorption process reflects an energy state of butanol molecules on the surface of silica gel. From the Q -DTG curves, energy distribution function of desorption (energy heterogeneity) can be determined and correlated. The investigation on the nature of active sites of silica gel surface and other solids on the basis of liquid thermodesorption measurements under quasi-isothermal conditions can be successfully carried out.

4. Conclusions

On the basis of the investigations, it can be stated that thermodesorption process of liquids under quasi-isothermal conditions (Q -TG and Q -DTG courses) depend on the adsorbate-adsorbate and adsorbate-adsorbent interactions. The solid surface causes significant changes of properties (particularly, in structure and thickness) of the adsorbed liquid layers. For that reasons, three stages of liquid thermodesorption process from the completely immersed silica gel have been obtained. On the basis of simple and rapid experiments of liquid thermodesorption process under quasi-isothermal conditions, from the sample studied it is possible to obtain important information concerning:

1. *Liquid films* (discontinuous properties and thickness of adsorbed layers, type of liquid energy states, mechanism of surface film destruction, kinetic thermodesorption and thermal stability).
2. *Liquid/solid interactions* (thermodynamic functions: activation energy, adsorption potential distribution function, desorption energy distribution function).
3. *Surface properties of solids* (adsorption capacity, surface wetting phenomena, surface heterogeneity: type and amount of active sites; structural heterogeneity: specific surface area, total pore volume).

It can be concluded that the described special thermogravimetric technique is a precise, useful, rapid and effective method, apart from its classical applications, in characterizing of the liquid/solid systems. The outlines of the method shows a great potential for application in the study of different systems because of the speed and accuracy of obtaining data and the simplicity of experimental operations.

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