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APPLICATION OF PROGRAMMED THERMODESORPTION OF THE LIQUID UNDER QUASI-ISOTHERMAL CONDITIONS TO INVESTIGATE PHYSICOCHEMICAL PROPERTIES OF LIQUID LAYERS AND SOLID SURFACES

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This paper presents the results of measurements of the programmed thermodesorption of polar and nonpolar liquids from the surface of different types of solids. The course of thermodesoption was found to depend on the properties of the solid and the wetting liquid. Thermodesorption occurred not exponentially but in steps, which reflects the noncontinuous changes in the properties of the surface layer with the distance from the solid surface. This effect intensified with the increase in polarity of the wetting liquid and the heterogeneity of the solid surface. The earlier investigations showed that application of the method of differential thermal analysis allowed determination of the distribution of the adsorption potential of the liquid on the solid surface.

Keywords: liquid layers and solid surfaces, programmed thermodesorption, surface heterogeneity

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Introduction

Differential thermal analysis under quasi-isothermal conditions has been widely applied to investigate the decomposition of chemical compounds and the kinetics and mechanisms of the reactions [1–10]. The great interest in this type of investigation stems from the specific control and the course of the heating process, and also from the specific transformations of the sample in the derivatograph furnace. One of the characteristic features of this programme is the fact that the apparatus causes rapid heating of the sample until its transformation takes place. The apparatus permits the maintenance of isothermal conditions, and thus different processes (e.g. decomposition) occur at constant temperature. The temperature of decomposition does not depend on the measuring conditions, but only on the chemical properties of the sample. In comparison with investigations performed under dynamic conditions, the quasi-isothermal method has many advantages, such as a wider range of practical applications and significantly higher selectivity. This method is more reliable during investigations of the changes taking place in the 'coinciding process'. The quasi-isothermal method allows a precise determination of the amount of crystallization water, the temperature of release of this water from the sample, and the mechanism of the process.

In this connection, efforts have been made to apply the programmed thermodesorption of water from the solid surface under quasi-isothermal conditions [11] to investigate the properties of liquid-solid systems. The main aim of these investigations was to determine the physicochemical properties of water layers (these properties change as a result of the interaction of water molecules and the solid surface [12]) and to establish the physicochemical characteristics of the solid surface. On the basis of investigations of programmed thermodesorption under quasi-isothermal conditions, it was found [11, 13–21] that the properties of water present on the surface of different solids changed step by step with the distance from the surface, but not exponentially as was suggested in the literature [22]. From the plotted $\Delta m = f(T)$ curves, the thickness of a vicinal water film with different properties and the statistical number of layers of the 'bonded water' were calculated. Such a characteristic 'step' course of the thermodesorption of water from the solid surface was explained by the change in mechanism of the wetting process, the change in the structure of water due to the interactions with the solid surface, the presence of macro- and micropores on this surface, and the action of capillary forces. Reference [20] showed the existence of a relationship between the thickness of the water layer adsorbed on the solid (this water has different properties from those of the bulk water) and the volume of the micropores of active carbon. This problem has been discussed so far only in a paper [23] describing investigations of the thermodesorption of water from a zeolite surface.

Since the available scientific literature contains few data as far as this problem is concerned, the paper also presents the hitherto published results on the thermodesorption of polar and nonpolar liquids from energetically, geometrically and structurally heterogeneous solid samples.

Experimental

Apparatus

Measurements on the programmed thermodesorption of liquid from the surface of the tested solids under quasi-isothermal conditions were made with a Q-1500 D derivatograph (MOM, Hungary). The samples were wetted with the tested liquid to the saturation state and then transferred to a suitable platinum crucible. The thermodesorption measurements were then performed in the temperature range 20°–200°C. The $\Delta m = f(T)$ curves were recorded.

The sepcific surface areas of the tested samples were determined by a chromatographic method of thermal desorption of nitrogen, using a suitable apparatus.

Materials

The investigations were made for different natural materials such as Brazil quartz (rock crystal containing ca. 10 ppm of impurities, size fraction 0.15–0.25 mm), crystalline sulphur (99.98% of S, size fraction 0.25–0.3 mm), pit-coal (originating from the Lublin Coal Basin and containing ca. 1% of sulphur, size fraction 0.15–0.25 mm), hematite (Krzywy Róg, USSR containing 65% of iron, size fraction 0.25–0.3 mm), brown coal (Konin Coal Basin, size fraction

Table 1 Specific surface areas of the tested samples

Sample	Specific surface area $m^2 \cdot g^{-1}$
Quartz	0.04
Sulphur	0.57
Coal	1.5
Hematite	2.59
Copper ore	4.07
Brown coal	5.21
Alumina	86.5
Silica gel	150
Activated carbon	980

0.15–0.25 mm) and activated carbon from the Military Technical Academy (Warsaw). Measurements were also made of the thermodesorption of liquid from the surfaces of alumina and silica gel. The specific surface areas of the samples are listed in Table 1.

Results and discussion

The results of the measurements are presented in Figs 1–4, in the form of $\Delta m = f(T)$ curves obtained during the programmed thermodesorption under quasi-isothermal conditions. The measurements were made for:

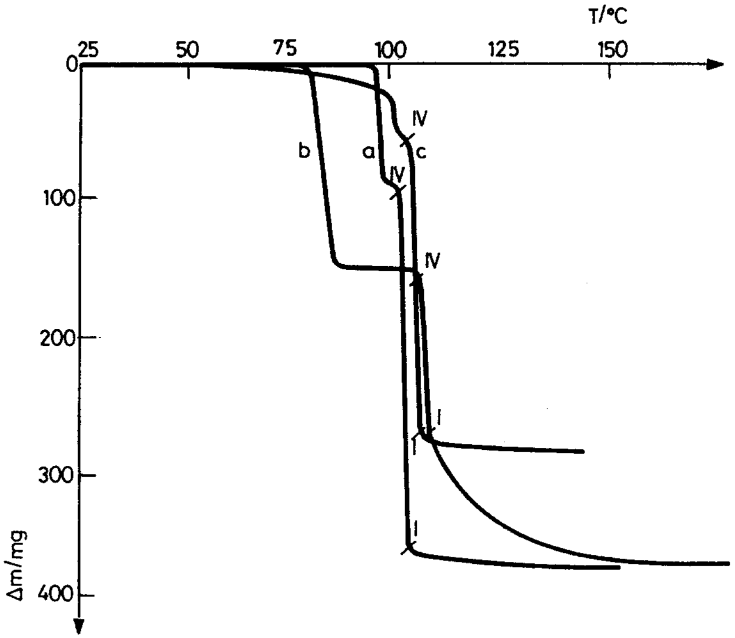

Fig. 1 Quasi-isothermal curves of desorption of water from quartz (*a*), sulphur (*b*) and coal (*c*) surfaces

a/ Water contained in powdered solids characterized by very low specific surface areas {Fig. 1 – quartz (a), sulphur (b) and pit-coal (c)}, a moderate specific surface area {Fig. 2 – hematite (a), copper ore (b) and brown coal (c)} and a very high specific surface area {Fig. 3 – alumina (a), silica gel (b) and activated carbon (c)}.

b/ Propanol (a), octane (b) and benzene (c) desorbed from samples of activated carbon characterized by a very high specific area (Fig. 4).

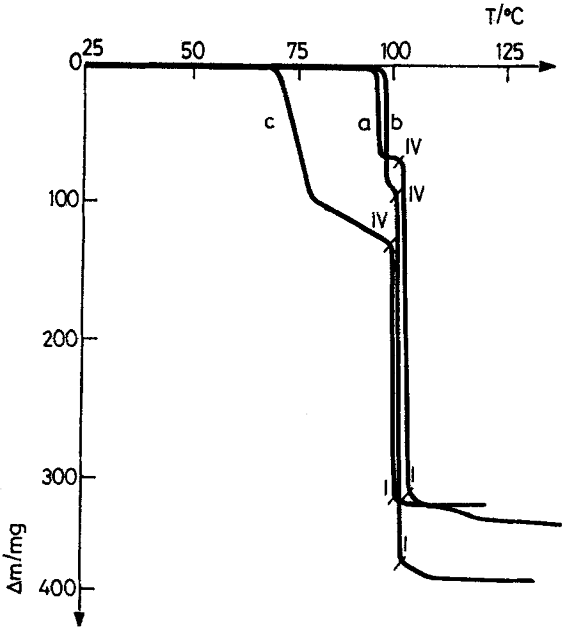

Fig. 2 Quasi-isothermal curves of desorption of water from hematite (*a*), copper ore (*b*) and brown coal (*c*) surfaces

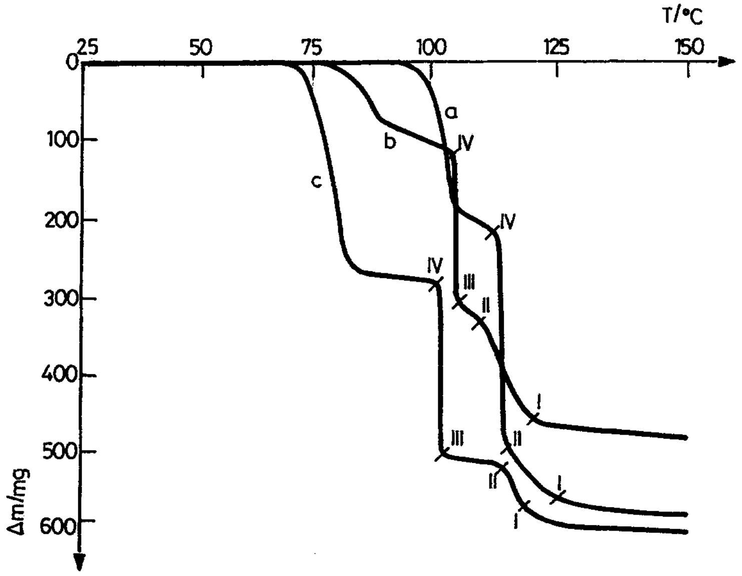

Fig. 3 Quasi-isothermal curves of desorption of water from alumina (*a*), silica gel (*b*) and activated carbon (*c*) surfaces

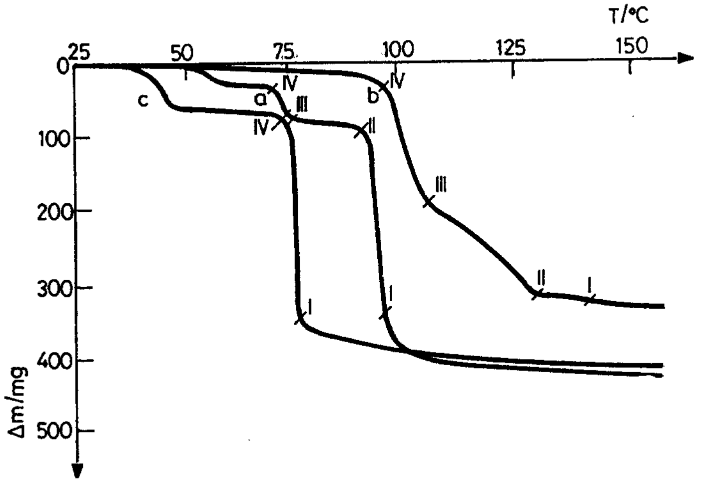

Fig. 4 Quasi-isothermal curves of desorption of propanol (*a*), octane (*b*) and benzene (*c*) from activated carbon surfaces

From the experimental data presented in these Figures, it appears that each curve of thermodesorption of liquid from the surface of the tested solid exhibits at least three inflection points. These result from the differences in bond energy of the liquid molecules bonded with the surface of the tested samples and in adsorption layers. In the process of thermodesorption of water from the surface of hydrophobic samples (sulphur) or crystallic and nonporous samples (e.g. quartz, hematite and copper ore), in general two steps can be distinguished: the evaporation of bulk water added in excess to the sample (the region before inflection point IV), and the desorption of interparticle and capillary water, together with a small amount of water adsorbed in the micropores and on the solid surface (bonded or vicinal water from inflection point I to the end of the process) (Figs 1 and 2).

With increase in porosity and consequently in specific surface area, and also with increase in the heterogeneity of the surface of the tested solids, such as alumina, silica gel and active carbon, the number of steps in the thermodesorption process increases in the presented curves (Fig. 3). These steps become more distinct. The surface of active carbon contains either different active centres or macro-, meso-, micro- and even submicropores, which determine the properties of both the surface and the adsorbed layers of the liquid [23]. In this case the mechanism of the process can be interpreted as follows. The first step consists in the evaporation of bulk water added in excess to the sample (the region up to inflection IV). The successive steps of evaporation (the region between inflections IV and I) consist in desorption of water contained in the capillaries and in the macro- and mesopores of the tested samples. The last step (from inflection I to the end of the process) consists in the thermodesorption of water strongly bonded in micro- and submicropores, and of water adsorbed on the surface of the tested sample. For cognitive reasons, this is the most interesting step of the thermodesorption process, which yields information about the nature of the interactions and about the physicochemical properties of the tested surface (e.g. the nature and type of the interactions, the distribution of the adsorption potential, etc.). Removal of this type of water takes place at the highest temperature (usually above 120°C) because it requires a great amount of energy. This type of water is characterized by modified ice-like structures. In such a structure each molecule of water is bonded with neighbouring molecules via four hydrogen-bonds, the energy of the bonds between the molecules ranging from 40 to 45 kJ/mol [24].

The thickness of the layers of water is not established exactly because the changes in the structure of this water take place in a very short time, i.e. 10^{-12} s [22, 25], and because of the dispersion and nondispersion interactions of water with the active centres of the surface characterized by different energies. It should also be noted that, as regards the magnitude of adsorption of water from the gas phase at 20°C and the amount of water corresponding to inflection I, these quantities are comparable in spite of the fact that they were determined by different methods and under different measuring conditions [13–19]. Such similarity of the results is probably due to the range of action of surface forces on the water molecules, as well as to the existence of the region of formation of ice-like structures in the vicinal layers of the liquid. The greatest effect of the surface was observed during investigations of the active carbon – water system (Fig. 3, curve *c*– the very significant 'stepwise' course of the thermodesorption process) because of the changes in the properties of the water layers (mainly the structure of these layers). This results from the dipole structure of the water and from the interactions of the water molecules with the walls of different pores and active centres characterized by different energies, which is connected with the heterogeneity of the surface of active carbon. For propanol (Fig. 4, curve *a*), octane (curve *b*) and benzene (curve *c*), this effect is less significant. For this reason, the results of measurements of the programmed thermodesorption of benzene from samples of active carbon under quasi-isothermal conditions were utilized [21, 26] in calculations of the adsorption potential A from the equation

$$A = RT \ln (p/p_o) \tag{1}$$

where p is the equilibrium pressure of the adsorbate, p_o is the saturated vapour pressure of the adsorbate at temperature T and R is the gas constant.

The magnitude of the interactions between the liquid molecules and the solid surface is determined either by the properties of these molecules (e.g. their polarity) or by the nature of the surface, e.g. its adsorption properties and porosity [27]. In general, the majority of solid surfaces are energetically, geometrically and structurally heterogeneous and moreover porous. The above parameters determine the properties of liquid films (mainly their thickness and structure), and the course of the thermodesorption process reflects the properties of these films on the tested surface.

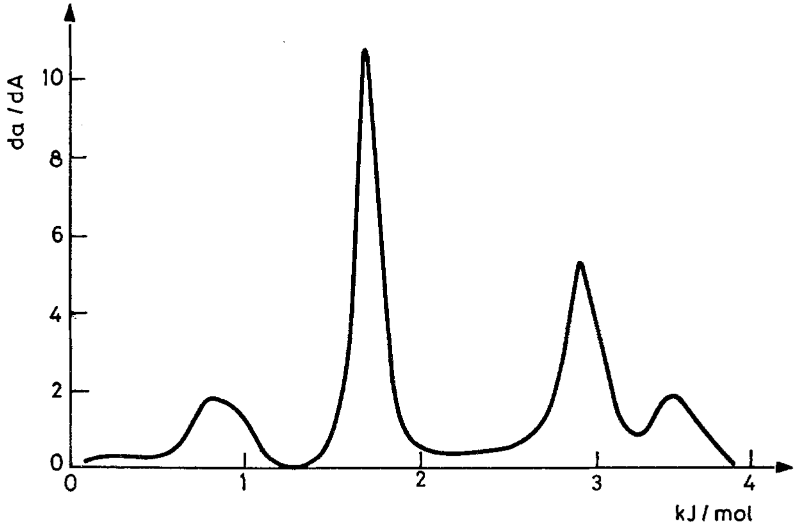

Fig. 5 Adsorption potential distribution of benzene on activated carbon surface

From the data relating to benzene thermodesorption from activated carbon, the change in adsorption potential A connected with the change in relative pressure p/p_0 was calculated from Eq. (1) for a given coverage of the surface a. The relationship $da/dA = f(A)$ was plotted and is presented in Fig. 5. The curves display several characteristic peaks connected with the physicochemical properties of the solids. On the basis of these properties, one can estimate the nature of the solid surface by means of differential thermal analysis and computer methods.

Conclusions

On the basis of investigations of the programmed thermodesorption of liquid from a solid surface under quasi-isothermal conditions, it can be concluded that this method may be successfully used to evaluate the adsorbent – adsorbate interactions and the physicochemical properties of the surface (especially the energetic state and porosity). Depending on the properties of the wetting liquid and the physicochemical properties of the surface, $\Delta m = f(T)$ curves of different shapes can be obtained reflecting the state of the solid-liquid system. The results show that the solid surface changes some properties of water, mainly the structure and the thickness of the vicinal layers. The investigations have confirmed the earlier observations that these changes are stepwise, but not exponential, as the distance from the surface varies. This process becomes more intensive with increase in polarity of the molecules of the wetting liquid and in the heterogeneity and specific surface area of the solid.

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Zusammenfassung — Diese Arbeit legt die Meßergebnisse von gesteuerter Thermodesorption polarer und unpolarer Flüssigkeiten an verschiedenartigen Feststoffen dar. Man fand, daß der Weg der Thermodesorption von Feststoff und Benetzungsflüssigkeit abhängt. Die Thermodesorption erfolgt nicht exponentiell, jedoch in Schritten, welche unkontinuierliche Veränderungen in den Eigenschaften der Oberflächenschicht in Abhängigkeit vom Abstand von der Feststoffoberfläche zeigen. Dieser Effekt nimmt mit steigender Polarität der Benetzungsflüssigkeit und mit steigender Heterogenität der Feststoffoberfläche zu. Frühere Untersuchungen zeigten, daß die Anwendung von DTA die Bestimmung der Verteilung der Adsorptionspotentiale der Flüssigkeit auf der Feststoffoberfläche ermöglicht.