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Inorganic substances

APPLICATION OF PROGRAMMABLE LIQUID THERMODESORPTION UNDER QUASI-ISOTHERMAL CONDITIONS TO STUDY PHYSICOCHEMICAL PROPERTIES OF LIQUID FILMS AND SOLID SURFACES

P. Staszczuk and M. Jaroniec

FACULTY OF CHEMISTRY, MARIA CURIE-SKLODOWSKA UNIVERSITY,
M.CURIE-SKLODOWSKA SQ.3, 20-031 LUBLIN, POLAND

The paper presents possible applications of differential thermal analysis for study of the physicochemical properties of liquid/solid systems, mainly through programmable liquid thermodesorption from the sample under quasi-isothermal conditions. The results prove its applicability in the determination of solid physicochemical properties, and particularly in calculations of adsorption potential distribution, the activation energy of molecules adsorbed on the surface and the surface heterogeneity by means of computer techniques.

Keywords: liquid films, programmable liquid thermodesorption, quasi-isothermal conditions, solid surface

Introduction

The methods of differential thermal analysis are seldom used to describe solid surface properties (e.g. adsorption capacity or porous structure) [1–3]. The results of measurements of liquid adsorption and desorption from the gaseous phase and the heats of processes taking place on silica gel surfaces with a derivatograph are presented in [4–7].

Differential thermal analysis under quasi-isothermal conditions has been widely applied for the study of chemical compound distribution, and the kinetics and mechanisms of reactions [8–10]. The interest in these studies stems from the control of the specific character, the heating process course and the sample trans-

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formation in the derivatograph oven. The characteristics of the programme carried out under quasi-isothermal conditions is that the instrument causes quick heating of the sample before its transformation starts. However, during transformation, the instrument permits thermal conditions which allow processes such as decomposition to take place at constant temperature. Therefore, the decomposition temperature depends not on the study conditions, but on the chemical properties of the sample. As compared with studies under dynamic conditions, the quasi-isothermal method has some advantages, e.g. a larger range of applicability and a greater selectivity. It is more reliable during transformation studies in "self-covering" processes. The quasi-isothermal method permits precise determination, for example, of the quantity and temperature of crystal water dissociation from a compound and its mechanism.

These observations led to attempts to apply programmable liquid thermodesorption from a solid surface in studies of liquid/solid system properties [11]. The main aim was to devise a method of determining the physicochemical properties of both surface and liquid films which change as a result of interaction with a solid [12].

Data on this subject are very scanty in the literature. A similar problem has been discussed in [13] in connection with water thermodesorption from a zeolite surface. The present paper reports results on polar and non-polar liquid thermodesorption from solid samples which are heterogeneous with regard to energetic, geometric and structural aspects [14–23].

Experimental

Apparatus

Programmable liquid thermodesorption from solid surfaces under quasi-isothermal conditions was measured with a Q-1500 D derivatograph (MOM Hungary). The samples were wetted with the studied liquid to reach complete saturation, then moved to a platinum crucible, and thermodesorption measurements were made in the temperature range 20°–200°C. The $\Delta m=f(T)$ curves were registered. Specific surface area was determined by a chromatographic method of nitrogen thermal desorption, using a special apparatus. Table 1 gives values of the specific surface areas of the various samples.

Material

The studies were carried out on samples of natural solids: quartz (Brazilian rock crystal containing impurities of the order of 10 ppm, 0.15–0.25 mm fraction) crystalline sulphur (99.98% S, 0.25–0.3 mm fraction), coal (Lublin Coal Basin, with low sulphur content of 1% 0.15–0.25 mm fraction), hematite (from USSR, 65% of Fe, 0.25–0.3 mm fraction), copper ore (Lublin Basin, 0.25–0.3 mm fraction) and brown coal (Konin, 0.15–0.25 mm fraction). Determinations were also made of the liquid thermodesorption from the surfaces of alumina, silica gel and active carbon (Merck and Norit).

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

Results and discussion

The results of the determinations are given in Figs 1–10 in the form of curves obtained from programmable thermodesorption under quasi-isothermal conditions.

Figure 1 presents the thermal distribution of hydrated copper sulphate under quasi-isothermal conditions. Crystal water is seen to be evolved from the sample in a manner dependent on temperature [1–10].

Liquid thermodesorption from the surfaces of various solids is presented in Figs 2–7. As follows from the experimental data presented there, at least three inflection points are observed in each curve of liquid thermodesorption from the surfaces. They result from differences in energy of liquid molecule bonding with the sample surface and adsorption layers. The thermodesorption of water from the surface of a sample of hydrophobic character (e.g. sulphur) or minerals with a crystalline structure and low porosity (quartz, hematite and copper ore), presented in Figs 2 and 3, can be divided into two stages: the evaporation of volume water added in excess to the sample (the process course to inflection IV) and the desorption of intergrain and capillary water with a small quantity of water adsorbed in micropores and solid surfaces, i.e. vicinal water (from inflection I to the end of the process).

With a porosity increase, as shown by increases in specific surface size and the heterogeneous properties of the surfaces of such solids as alumina, silica gel and active carbon, the number of inflections also increases in the curves (Fig. 4), which become more distinct. On the surface of active carbon there are various active centres and pore types (macro-, meso-, micro- and even submicropores). These determine the properties of specific surface area and adsorbed liquid layers [13]. As follows from the studies presented in the above Figures, it can be stated

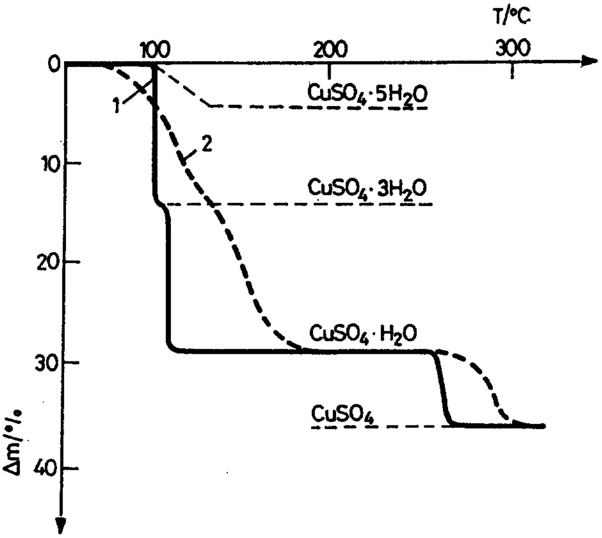

Fig. 1 Thermal decomposition of $CuSO_4\cdot5H_2O$ under quasi-isothermal conditions

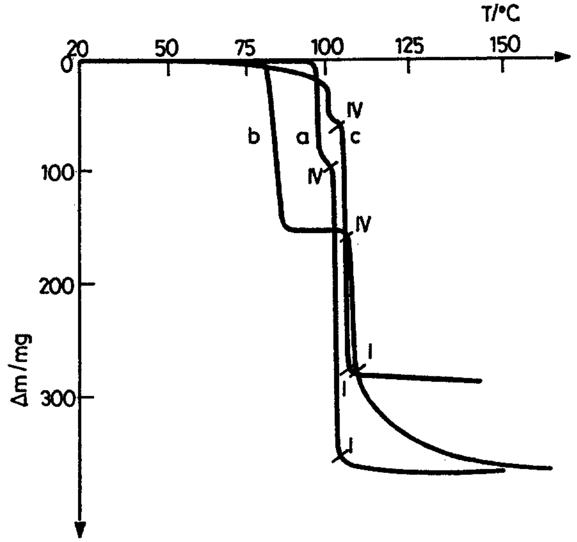

Fig. 2 Water thermodesorption under quasi-isothermal conditions from quartz (curve *a*), sulphur (curve *b*), and coal (curve *c*) surfaces [18, 19]

that the properties of the liquid, and particularly of water, present on the surface of various solids change stepwise with the distance to the surface [11, 14–24], but not exponentially as suggested in the literature [24, 25]. This characteristic stepwise water thermodesorption process from solid surfaces results from liquid/solid

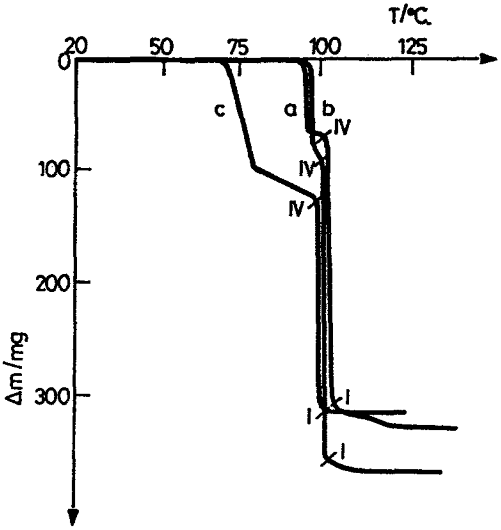

Fig. 3 Water thermodesorption under quasi-isothermal conditions from hematite (curve *a*), copper ore (curve *b*) and brown coal (curve *c*) surfaces [16]

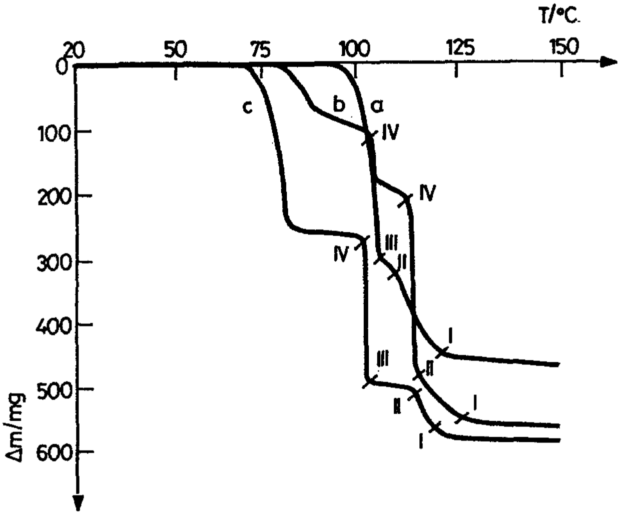

Fig. 4 Water thermodesorption under quasi-isothermal conditions from alumina (curve *a*), silica gel (curve *b*) and active carbon (curve *c*) surfaces [11, 20, 21]

and liquid/liquid interactions and their changes in the individual adsorption layers causing the liquid structure change. The energetic state and porous structure of the solid affect the above phenomena.

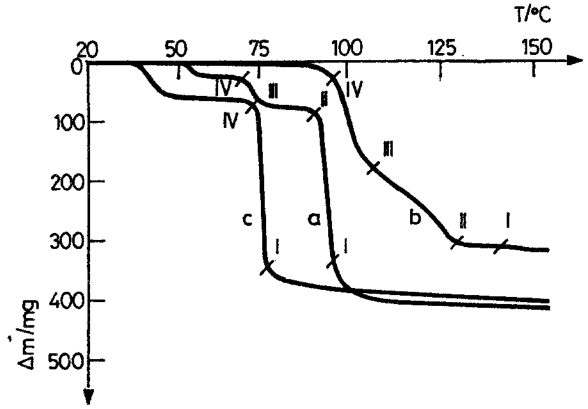

Fig. 5 Thermodesorption of propanol (curve *a*), octane (curve *b*) and benzene (curve *c*) under quasi-isothermal conditions from activated carbon surfaces [22, 23]

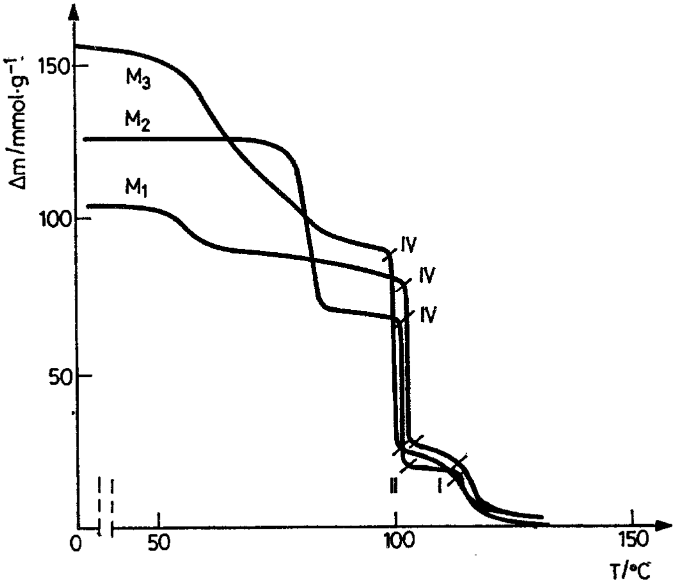

Fig. 6 Water thermodesorption under quasi-isothermal conditions from active carbon (Merck) [21]

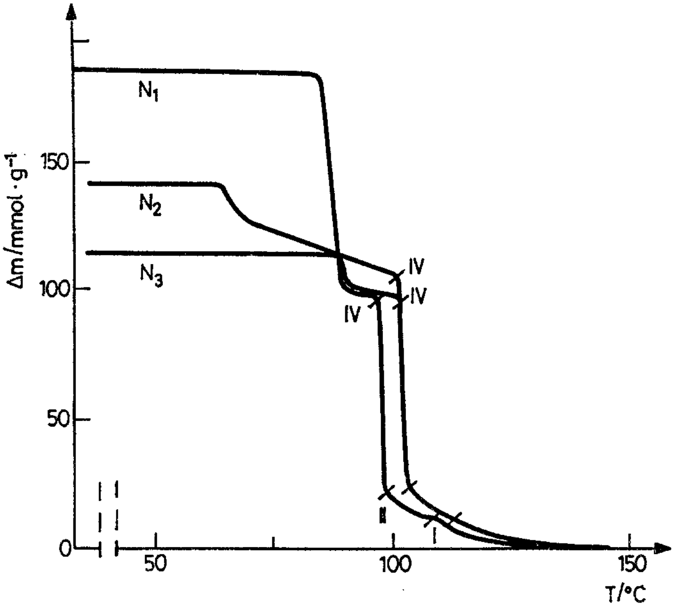

Fig. 7 Water thermodesorption under quasi-isothermal conditions from active carbon (Norit) [21]

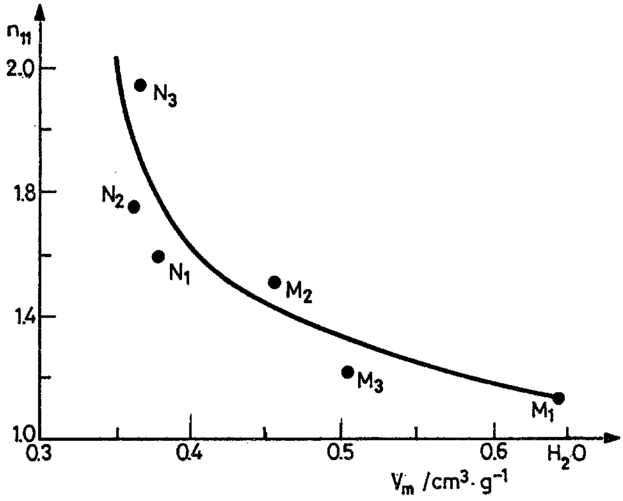

Fig. 8 The number of statistical monolayers of desorbed water corresponding to inflection point II as a function of the adsorbed water volume on active carbon (Merck and Norit) [21]

From a cognitive and practical point of view, the last stages of the thermodesorption process (inflections I and II) are the most interesting. These provide information about the interactions, the energetic state of the surface and its physicochemical properties (among others, the nature of the interactions, the energy of molecular activation, the adsorption potential distribution and the pore type). Removal of the liquid, e.g. water, from the surface takes place at the highest temperature of the process (usually above 120°C) because much energy is required as a result of the modified liquid structures formed (in the case of water: ice-like clusters [26]). The greatest influence of the surface was observed in the

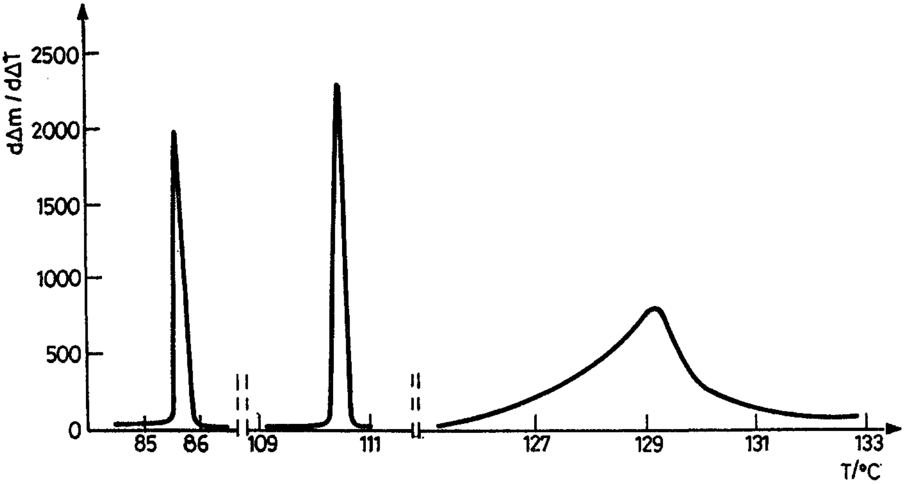

Fig. 9 Derivative of the mass loss of benzene from an active carbon surface with respect to temperature

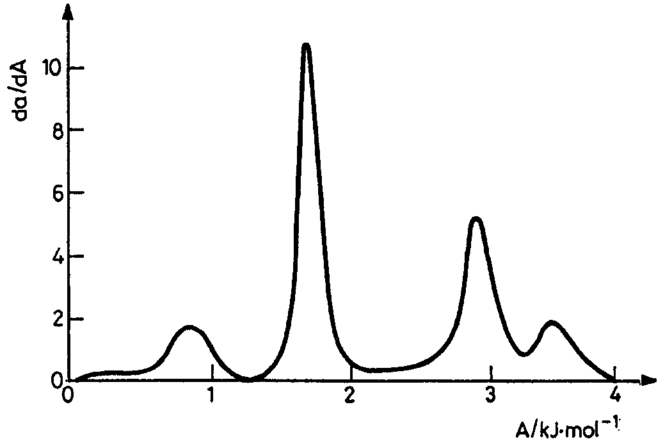

Fig. 10 Adsorption potential distribution of benzene on an active carbon surface [22, 23]

studies on the active water/carbon system (Fig. 4, curve *c* – distinct stepwise character of the thermodesorption process). This influence is smaller in the cases of propanol (Fig. 5, curve *a*), octane (curve *b*) and benzene (curve *c*).

To calculate a derivative of liquid mass loss in relation to temperature and adsorption potential distribution, measurements were made of the programmable thermodesorption of benzene from active carbon samples under quasi-isothermal conditions [22, 23]. The obtained data are given in Figs 9 and 10. The relations presented in the Figures result from the distribution function of the desorption activation energy. The functions show the heterogeneity of the sorbent arising from the micropores, i.e. structural heterogeneity, and heterogeneity arising from different adsorption centres, i.e. surface heterogeneity.

Conclusions

From the studies to date on liquid programmable thermodesorption from solid surfaces under quasi-isothermal conditions, it can be stated that the method can be applied for the determination of adsorbate/adsorbent interactions. It allows the determination of liquid films and the physicochemical properties of a solid surface (especially its energetic state and porosity). Depending on the properties of the wetting liquid and the physicochemical properties of the studied surface, various courses of the curves $\Delta m=f(T)$ showing the state of the liquid/solid system can be observed. The obtained results showed that the solid surface causes changes in the molecular interactions in the individual adsorption layers, which in turn causes changes in its thickness and structure. The studies confirmed the earlier observations that the adsorption layer properties change with the distance from the surface in a stepwise manner, but not exponentially. The process increases with increase in the polarity on the wetting liquid molecules, the heterogeneous properties and the developed specific surface of the solid.

The obtained curves show the properties of the liquid on the surface (e.g. macro-, meso- and micropores). This is a very quick and convenient method, which permits studies on surface heterogeneity in relation to different adsorbates. Liquids of different natures (polar and non-polar) can be used, and studies can be made on surface heterogeneity in relation to these liquids. It is also possible to study the effects of the surface heterogeneity (controlled by chemical and physical modification of the sorbents) on the solid wettability, liquid film formation, and their structural and thermal stability. These problems are significant in many scientific and technical fields. The method is useful in studies of the effects of surface water on its surface properties, compared with other liquids and their interactions. It allows determination of the properties of the films formed at different humidities, and the extents of the hydrophobic and hydrophilic character. Investigations on the effects of small quantities of substances (modifiers) on the film stability on the surface can be carried out by this method. The method of differential thermal analysis is convenient for determination of the properties of the thermally treated adsorbent (changes in structure and heterogeneity), e.g. after sorbent heating, then cooling and spreading of the liquid, the change in its properties can be determined. It should be taken into account that this type of measurement can be carried out in an atmosphere of various gases.

The above examples show the wide applicability of the method for study of the surface properties of liquid films and solid surfaces, their heterogeneity and its effects on the thermal stability of liquid films.

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Zusammenfassung — Es werden mögliche Anwendungen von DTA zur Untersuchung von physikochemischen Eigenschaften von Flüssig/Fest-Systemen dargestellt – hauptsächlich über die programmierbare Thermodesorption aus der Probe unter quasi-isothermen Bedingungen. Die Resultate zeigen die Anwendbarkeit bei der Bestimmung von festphysikochemischen Eigenschaften, insbesondere der Berechnung der Verteilung des Adsorptionspotentiales, der Aktivierungsenergie der an der Oberfläche adsorbierten Moleküle und der Heterogenität der Oberfläche mittels computerisierter Methoden.