

APPLICATION OF THERMAL ANALYSIS IN STUDIES OF ENERGETIC HETEROGENEITY OF SOLID SURFACES

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Abstract

The paper reports a study of the programmed thermodesorption of benzene, octane, methanol and propanol from the silica gel surface under quasi-isothermal conditions. The experimental data revealed the gradual desorption of the liquid, due to the heterogeneous nature of the silica gel surface. This phenomenon was used in calculations of adsorption potential distribution. It was concluded that this method can be successfully applied in studies of the heterogeneity of solid surfaces, and is more convenient than traditional adsorption methods.

Keywords: heterogeneity of solid surface

Introduction

Almost all solid surfaces possess heterogeneous properties. For example, typical adsorbents such as active carbon, aluminium oxides and silica gels are characterized by surface heterogeneity. These properties are due to the differences in the size of the pores on the surface (structural heterogeneity), and also to various surface groups, active centres, contamination and irregularities of the crystal lattice. This surface heterogeneity may be divided into chemical heterogeneity (different active centres) and geometrical heterogeneity (irregularities of the crystal lattice). Structural and surface heterogeneity are characteristic features of solids and depend on the adsorbate type and molecules responsible for the adsorption extent. The above heterogeneous properties cause differences in adsorption energy (energetic heterogeneity) and hence in the adsorption capacity [1-3]. The causes of the heterogeneous properties of solids differ. For minerals found in nature, the causes are the geological origin and the situation in the rock deposit (a process of material formation), together with the preliminary treatment and preparation for studies (e.g. grinding). The cause of the heterogeneity of synthetic adsorbents such as active carbon is the heterogeneity

of the substrate for production (e.g. coal) and the heterogeneity of the process of activation of carbon grains or granules by gaseous substances [4].

Methods of solid porous structure (structural heterogeneity) analysis are based on adsorption studies. The parameters characteristic for a studied sample are determined numerically or graphically from the adsorption isotherms. For the quantitative characteristics of the adsorbent energetic surface, the differential distribution of adsorption energy E in the adsorption theory is accepted. This distribution is usually denoted by $\chi(E)$ and defined as [5]

$$\chi(E) = dw/dE \quad (1)$$

where w is the number of active centres on the surface.

When the pressure, volume and temperature related to the adsorbate are not changed by the adsorption strength field, the adsorption potential E can be identified with the change in adsorption potential ($E=A$). Statistical methods can then be applied in the analysis of the energetic and structural heterogeneity of the solid surface. From studies of adsorption isotherms, 'characteristic' curves in the form of mathematical functions are obtained. The 'characteristic' curves describe the dependence of the differential molar work of adsorption A on the volume adsorption space:

$$A = a \nu \quad (2)$$

where a is the amount adsorbed and ν is the molar volume of a in the adsorbed state.

The differential molar work of adsorption A represents the change in the Gibbs function in the adsorption, taken with a negative sign with respect to the standard state [5]:

$$A = -RT_i \ln (p_o/p_i) \quad (3)$$

where T_i is the temperature in the equilibrium saturated vapour p_o at the equilibrium pressure p_i .

Despite their drawbacks, adsorption methods are often used for the determination of solid surface heterogeneous properties. As they are time-consuming and the calculations are arduous, it is necessary to develop other simple and quick methods of obtaining heterogeneity parameters. Thermal analysis has recently been applied in studies of solid surface heterogeneous properties. This consists in the utilization of the phase changes of liquids adsorbed on solid surfaces during the cooling (freezing, melting) or heating of samples (evaporation). The temperature of freezing, e.g. of water, in capillaries is known to

depend on their radius. Thus, the process of water freezing in a sample possessing various pores in a DSC chamber will take place gradually, depending on the pore diameter, up to freezing in the micropores 3 Å in diameter, i.e. the diameter of the water molecule [6], and the data obtained reflect the distribution of the pore radii in the studied sample [7].

The process that is the reverse of the adsorption of substance on the sample surface, i.e. the programmed thermodesorption of liquid from the studied surface under appropriately chosen conditions, is dependent on the energy of the interactions between the adsorbed molecules and the solid surface. Samples of solids adequately wetted with the studied liquid (saturated, fully wetted) are heated in a TGA apparatus by means of dynamic [8], quasi-isothermal [9] or high-resolution [7] methods. The differential curves of mass loss obtained display inflections relating to the parameters describing the heterogeneous properties of the studied sample [10].

This paper reports studies of the programmed thermodesorption of some chosen liquids from the silica gel surface. The adsorption potential was calculated, its distribution was determined the adsorption properties of the studied surface were estimated.

Materials and methods

The 0.1–0.2 mm fraction of silica gel Si-60 (Merck, Germany) for column chromatography was used in the investigations. The specific surface areas of the silica gel samples were determined by the chromatographic method of nitrogen thermal desorption using a suitable apparatus: Sorptomatic-1800 (Carlo Erba, Italy). The porous structure parameters obtained were: specific surface area $S_{\text{BET}}=460 \text{ m}^2/\text{g}$, pore volume $V_p=0.7 \text{ cm}^3/\text{g}$ and average pore size $R_p=35 \text{ \AA}$. Such surfaces of wide-pore gels include more free OH groups than active or bonded ones.

Measurements of programmed liquid thermodesorption from the silica gel surfaces under quasi-isothermal conditions were made with a Q-1500 D derivatograph (MOM Hungary). The silica gel was dried before measurements to remove hygroscopic water from its surface. The samples were then wetted to reach complete saturation with the studied liquid (benzene, octane, methanol or propanol), left for a few hours for adsorption equilibrium to be established and transferred to the platinum crucible. Programmed thermodesorption in the temperature range 20–250°C was measured at a heating rate of 3°C min^{-1} in the measuring chamber. The curves of temperature increase (T) and loss of sample mass (Q-TG) were recorded. The details concerning the methods, apparatus and technique used are given in [9].

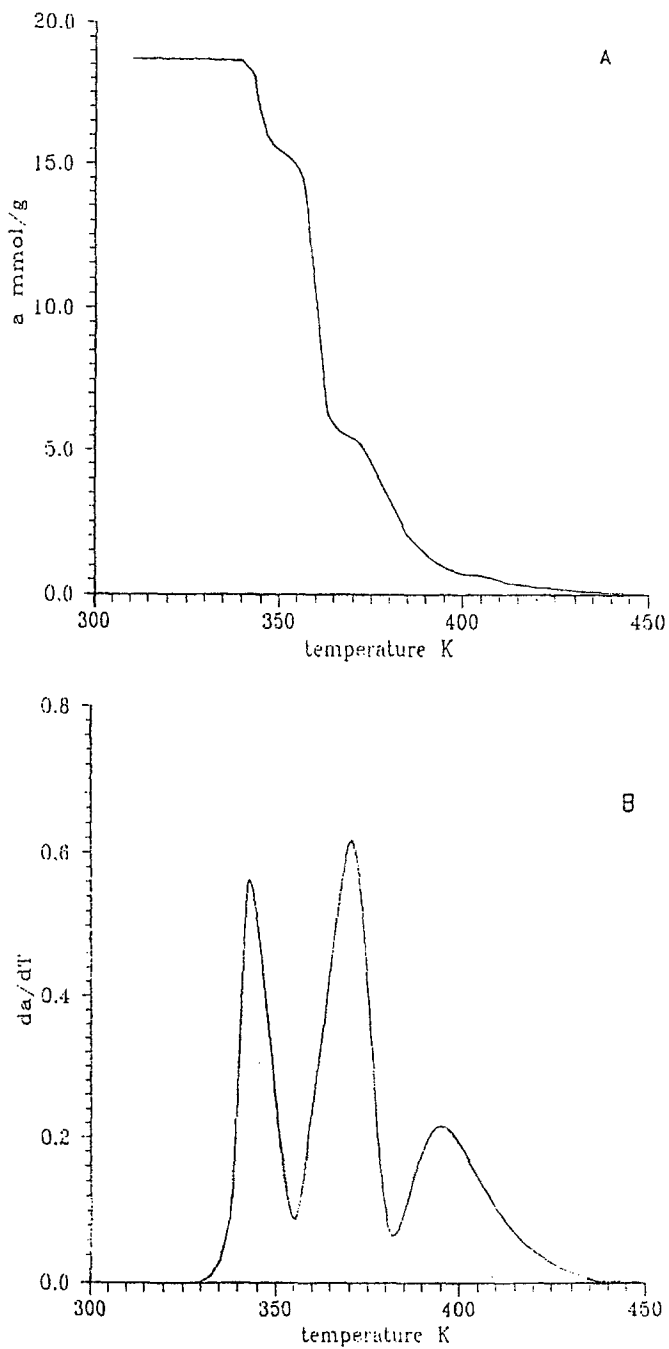


Fig. 1 Quasi-isothermal curve of benzene desorption from silica gel surface (A) and derivative of the mass loss with respect to temperature (B)

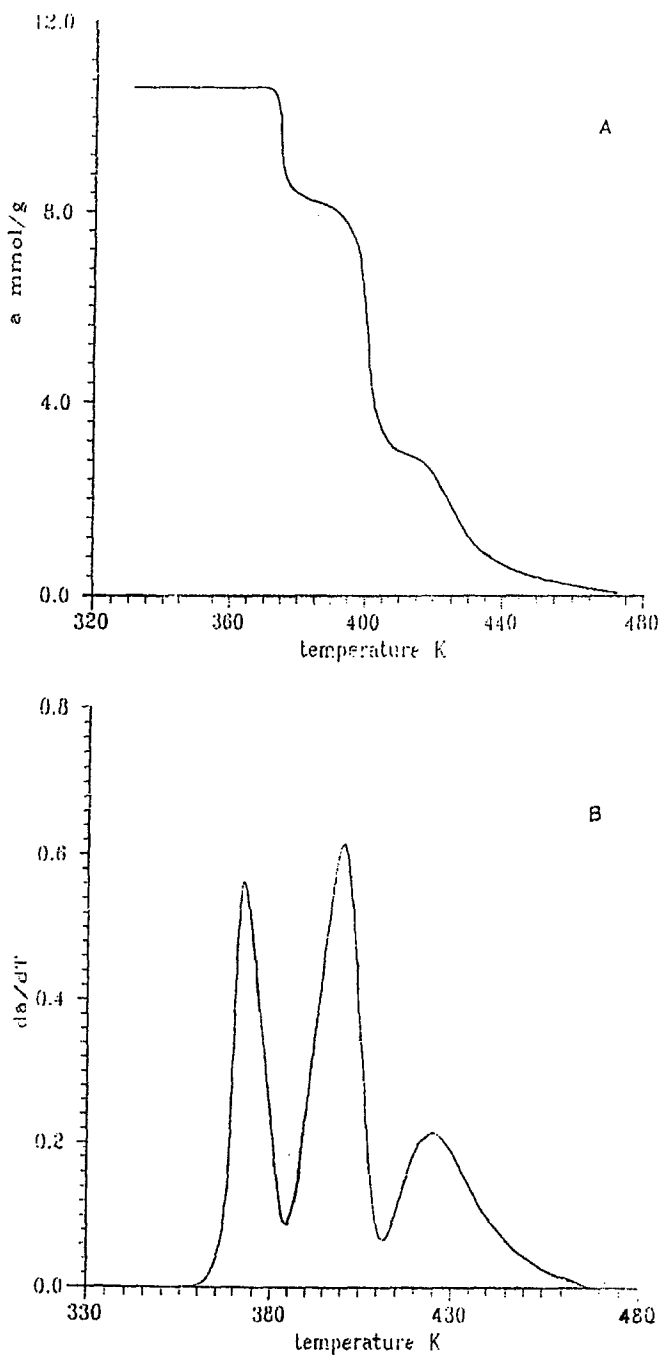


Fig. 2 Quasi-isothermal curve of octane desorption from silica gel surface (A) and derivative of the mass loss with respect to temperature (B)

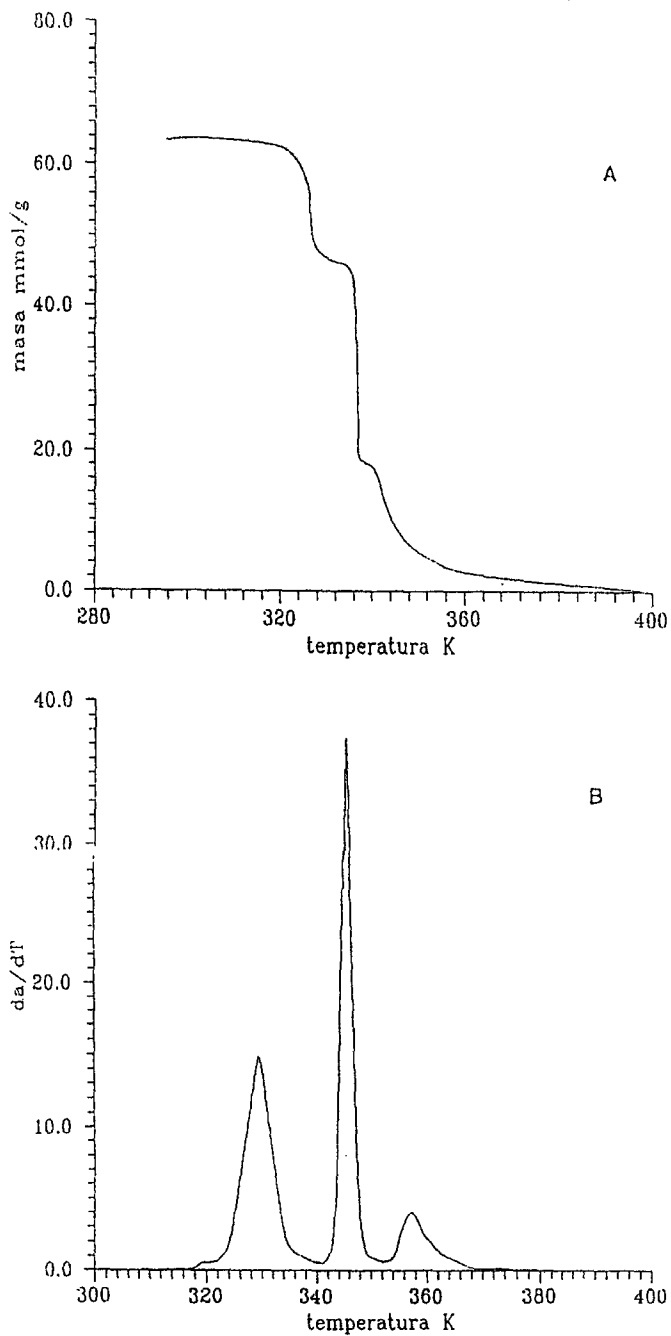


Fig. 3 Quasi-isothermal curve of methanol desorption from silica gel surface (A) and derivative of the mass loss with respect to temperature (B)

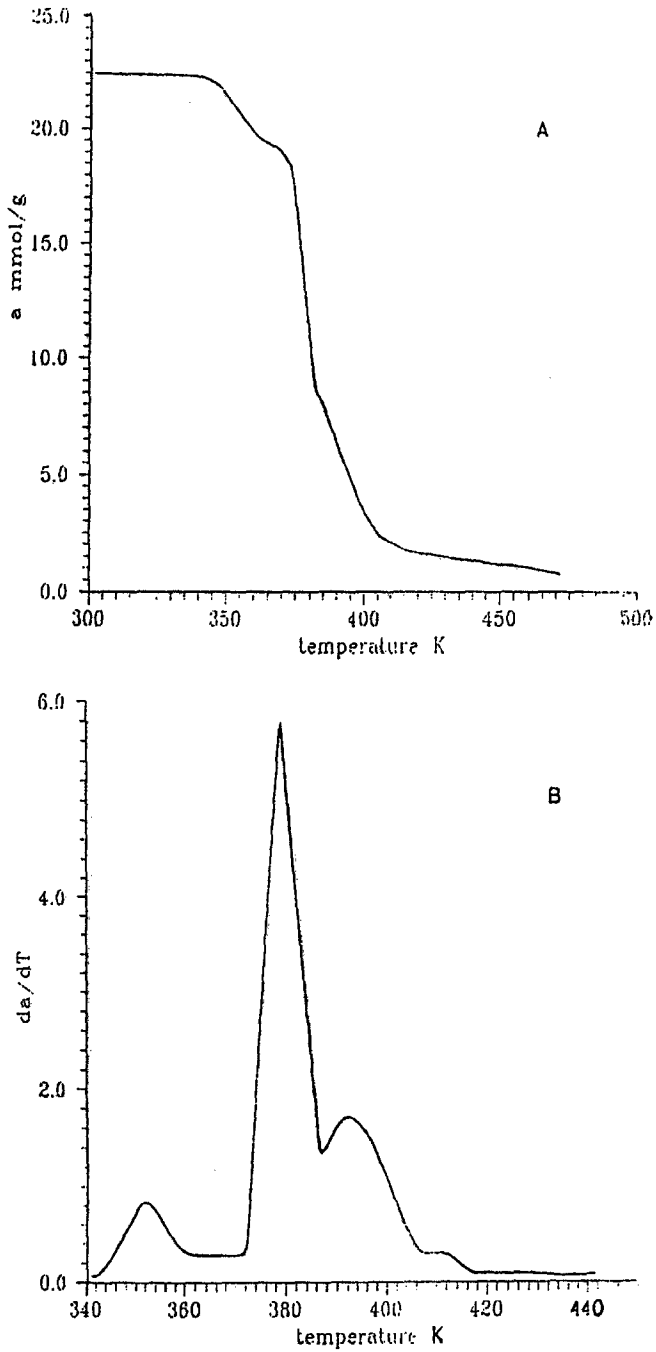


Fig. 4 Quasi-isothermal curve of propanol desorption from silica gel surface (A) and derivative of the mass loss with respect to temperature (B)

Results and discussion

Figures 1A, 2A, 3A and 4A present the Q-TG curves of thermodesorption of benzene, octane, methanol and propanol from the silica gel surface. They reveal the dependence of the mass loss on the temperature increment of the sample under the quasi-isothermal conditions, and also the adsorption affinity of the gel sample for the studied liquids. The curves obtained are characterized by the fact that at suitable temperatures inflection points are observed, which is evidence of the gradual thermodesorption of the liquids from the surface. A number of inflections in the curves are due to differences in the mechanism of the adsorption process for the individual molecules, the differences in the structure of the adsorption layers adsorbed on the various active centres of the gel surface, and the differences in energy of the binding of the molecules on the surface. The gel samples show affinity for the liquids used in the surface wetting process.

This is more clearly seen in the differential curves $da/dT=f(T)$ presented in Figs 1B, 2B, 3B and 4B. These Figures display the dependence of the derivatives of mass loss with respect to temperature on the heating temperature. These values were obtained from the experimental $a=f(T)$ curves by using an N Tablet Modes ND-03A digitizer (Japan). As can be seen in Figs 1-4B, curves with 3-4 peaks were thus obtained. The first results from bulk liquid thermodesorption, whereas the following ones result from different active centres on the silica surface. The curves correspond to the function of the desorption activation energy E_a for the distribution of liquid molecules [11-13] on the surface, but the differences in the peak shapes relate to the specific structure of the adsorption layers and also to the energy of interaction with the porous structure of the gel surface. The curves show that the decomposition functions E_a are characteristic for individual liquid/silica gel systems and depend on the energy of adsorbent/adsorbate interactions.

It should be noted that the peaks in Figs 1B (benzene), 2B (octane) and 4B (propanol) are broadened and shifted towards higher temperatures (400, 430 and 400 K, respectively) as compared with the analogous ones in Fig. 3B (methanol), which indicates the stronger interactions of benzene, octane and propanol with the silica surface than those in the methanol/silica system. The first peaks in Figs 1-4B correspond to the thermodesorption of liquid added in excess to the studied gel sample. The properties of the liquid then change due to the reaction of capillary forces and the active centres of the gel surface, and the liquid undergoes thermodesorption. The two last peaks corresponding to the thermodesorption process relate to the distribution of the desorption activation energy. This function, in turn, characterizes the heterogeneity of the solid resulting from micropores, i.e. the structural heterogeneity and the heterogeneity relating to the existence of various adsorption centres on the surface. These results point to the existence of two types of active centres on the surface sample.

On this basis, the values of molar free energy (of adsorption potential) A from Eq. (3) were calculated by using the dependence of the saturated vapour pressure on temperature [14]:

$$\log p = D - B/(T + C) \quad (4)$$

where D , B and C are constants and T is the temperature of the measurement.

The above suggestion was confirmed by calculations of the adsorption potential A from the data of the thermal analysis and from Eq (3). From the data (Figs 1–4) on liquid thermodesorption from the silica surfaces under quasi-isothermal conditions, transformed as $a = f(T)$, the adsorption potentials A (i.e. the change in molar free energy related to change in liquid vapour pressure p_i/p_o for a given packing of the surface layer) were calculated. The adsorption potential distribution was then calculated in the form of the dependence $da/dA = f(A)$ by means of a computer program [15], and is presented in Figs 5–8. The results obtained by means of the numerical method are given in Figs 5 (benzene), 6 (octane), 7 (methanol) and 8 (propanol) as a function of the adsorption potential distribution $da/dA = f(A)$. It follows from the presented Figures that benzene, octane and methanol exhibit two peaks each, whereas propanol gives three peaks, which indicates the energetic heterogeneity of the silica gel surface. The

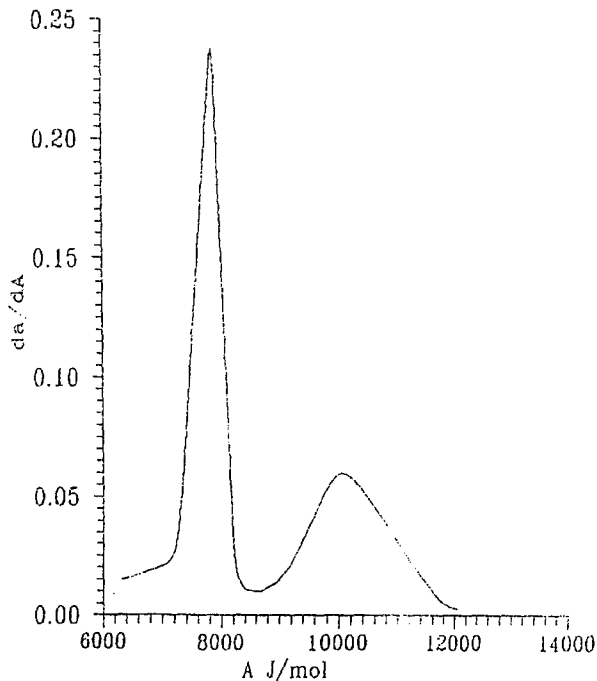


Fig. 5 Adsorption potential distribution of benzene on silica gel surface

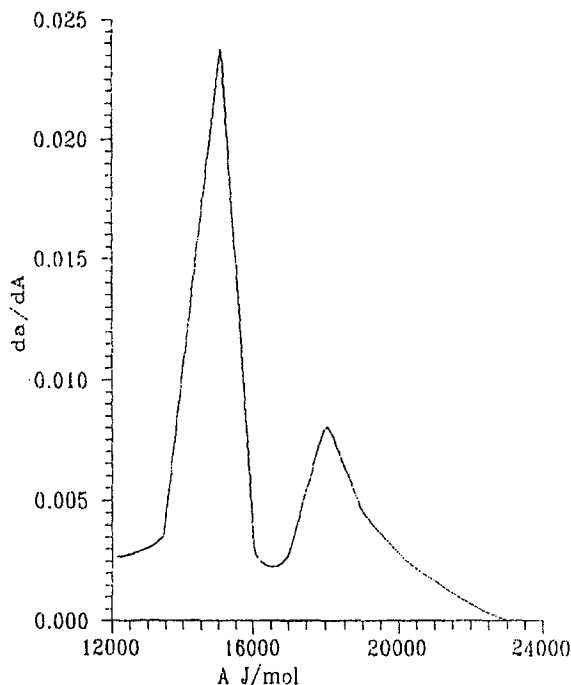


Fig. 6 Adsorption potential distribution of octane on silica gel surface

peaks corresponding to the highest values of adsorption potential A for a given curve result from the chemical heterogeneity of the gel surface due to the presence of various adsorption centres. The shapes and sizes of the peaks are governed by many factors, including the adsorption centre energy, the gel porosity and the liquid molecule/gel surface interactions.

The relations presented in Figs 5–8 result from the distribution function of the adsorption potential. The functions show the heterogeneity of the silica arising from the micropores, i.e. structural heterogeneity, and the heterogeneity arising from different adsorption centres, i.e. surface heterogeneity. As the curves show, the functions of the adsorption potential distribution on the silica gel surface are of Gaussian bimodal form, with the presence of two different adsorption centres. One centre corresponds to the low-energy active centres (free OH groups) and the other to the high-energy active centres (active OH groups). The curve of adsorption potential distribution corresponding to the octane/silica sample (Fig. 6) is broadened and shifted towards higher values of adsorption potential relative to that for the methanol/silica system (Fig. 7). This is due to the stronger octane interactions with the silica surface. However, the smaller width of the analogous peaks is a result of weaker molecular interactions of sol-

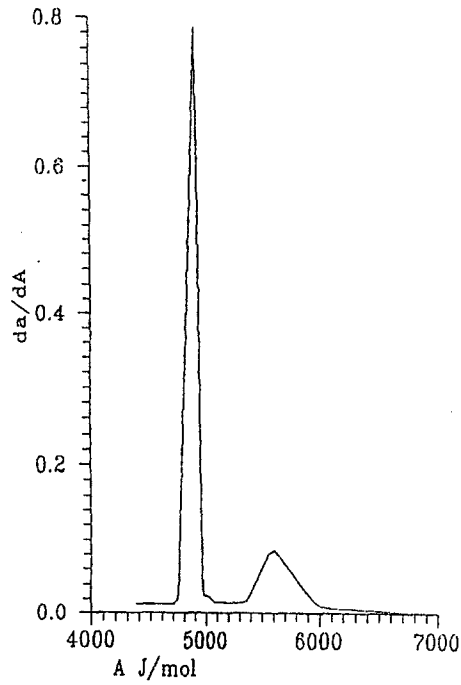


Fig. 7 Adsorption potential distribution of methanol on silica gel surface

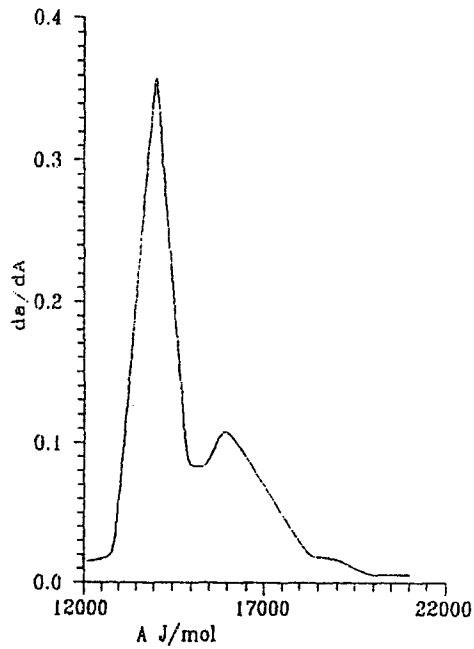


Fig. 8 Adsorption potential distribution of propanol on silica gel surface

vents such as methanol and propanol with the heterogeneous sample surface. The number and the type of the active centres on the surface are responsible for the shape of the distribution curves. It can be stated that the adsorption energy of the surface OH groups increases in the following sequence: bonded < free < active. Removal of liquid adsorbed on highly active centres takes place at the highest temperature of the process as it requires the greatest amount of energy under the measurement conditions. The temperatures of the liquid adsorption process and the calculated values of the adsorption potential show that the octane film is bonded most strongly with the gel surface, followed by benzene, propanol and methanol.

To summarize, it can be stated that the programmed thermodesorption of the studied liquids from the silica gel surface is a gradual process, depending on the energy of interactions between molecules and active centres. The calculated adsorption potential distribution shows the energetic state of the studied surface. From the data obtained, it can be said that the quasi-isothermal method of thermal analysis can be applied for estimation of the heterogeneous properties of solid surfaces, for it is quick, simple and precise as compared with the traditional adsorption methods.

References

- 1 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York 1982.
- 2 M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam 1988.
- 3 W. Rudziński and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, New York 1992.
- 4 J. Choma, *Przem. Chem.*, 62 (1983) 203.
- 5 M. Jaroniec and J. Choma, *Mater. Chem. Phys.*, 15 (1986) 521.
- 6 M. Sasthav, W. R. P. Raj and H. M. Cheung, *J. Colloid Interface Sci.*, 152 (1992) 376.
- 7 P. Staszczuk, M. Jaroniec and R. K. Gilpin, *Microbalance Techniques: Proceedings of the 25th VMT Conference at Siegen, Multi-Science Publication, Essex, 1994*, p. 101.
- 8 P. Staszczuk, *Powder Technology*, 34 (1983) 161.
- 9 P. Staszczuk, *J. Thermal Anal.*, 29 (1984) 217.
- 10 P. Staszczuk and M. Jaroniec, *J. Thermal Anal.*, 38 (1992) 2041.
- 11 V. Dondur and D. Vucelic, *Thermochimica Acta*, 68 (1983) 91.
- 12 V. Dondur and D. Vucelic, *Thermochimica Acta*, 68 (1983) 101.
- 13 V. Dondur and D. Vucelic, *Thermochimica Acta*, 68 (1983) 113.
- 14 S. Brunaur, P. H. Emmet and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 15 P. Staszczuk, *J. Thermal Anal.*, 38 (1992) 2325.