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DETERMINATION OF LIQUID VAPOUR ADSORPTION AND DESORPTION ON AND FROM SOLIDS BY MEANS OF THE DERIVATOGRAPH II.

Determination of kinetics and isotherms of adsorption and desorption of water vapour on silica gel

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Studies of water adsorption and desorption on silica gel with a modified derivatograph are described. The dynamic gas chromatography step profile method was used to determine isotherms of adsorption and desorption from the TG curve. The obtained isotherms agree with those from other methods. The properties of surface liquid layers can be investigated by this method.

Kinetic adsorption investigations give valuable information on the filling of macropores and micropores in minerals. The rate of adsorption of a gas or vapour on a solid depends, among other things, on the diffusion coefficient, which in turn depends on many factors, such as the porosity, the granule zone radius, the adsorbate concentration in the carrier gas and in the adsorbent, and the physicochemical properties of the surface [1–3].

The desorption of a vapour or gas from a mineral surface is a reversible process relative to adsorption. The results of desorption process investigations provide interesting conclusions concerning the bonding energy of molecules adsorbed on the solid surface, the activation energy [4, 5] or the adsorbed molecules, and the vicinal adsorption layer structure [3].

There are two recognized methods of measuring the adsorption and desorption of liquid vapour: static and dynamic.

In the static methods [1], the sample investigated is placed in a liquid vapour atmosphere. When equilibrium is attained, the amount of adsorbed vapour and the equilibrium pressure are checked. The difference between the adsorbate introduced

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into the measuring system and that remaining in the gas phase can also be measured. The static methods are usually used for the examination of separate liquid vapour in a vacuum apparatus in which the sample investigated has previously been outgassed in high vacuum in order to remove the trace substances adsorbed on the solid surface. For the determination of adsorption values by means of the method described above, a McBain balance, vacuum microburettes and desiccators filled with sulphuric acid of suitable concentration are used. This method can only be applied to liquid adsorption measurements and does not permit examination of the desorption process. It is also time-consuming, and in the case of a small surface area of the sample investigated it is less precise or even impossible to carry out. Further, this method requires the application of a sophisticated vacuum apparatus.

Dynamic methods [6, 7] are based on the principles of adsorption gas chromatography. Measurements of adsorption on a solid surface are carried out indirectly by recording conductivity detector readings [8]. In this case, changes in the concentration of the adsorbate flowing out together with the carrier gas from the chromatographic column filled with the adsorbent investigated are noted. Apparatus similar to chromatographs equipped with a capacity detector is also used [9]. The capacity changes in the capacitor filled with the sample on which water adsorption takes place are then recorded. This method can also examine the kinetics of water adsorption and desorption on minerals. Dynamic measurements require expensive and sophisticated apparatus (chromatographs). Measurements take much time because the apparatus must previously be calibrated.

The derivatograph has been used to determine the amount of moisture [10], and also indirectly for the estimation of water adsorption isotherms on solids [11]. The samples investigated were placed in desiccators over sulphuric acid solutions of suitable concentration, i.e. in a water vapour atmosphere with a given relative humidity. After saturation, the samples were carried over to a crucible and the water contained in the sample was evaporated in the derivatograph in order to determine the amount of adsorbed water. Taking into consideration the water weight loss during the thermodesorption process and the water vapour pressure over sulphuric acid solution, the adsorption isotherms can be plotted.

In this part of our publication we present a method of calculation of kinetic data and isotherms of adsorption and desorption of water on silica gel on the basis of experimental data obtained with a modified derivatograph.

Experimental

Silica gel (0.15–0.3 mm fractions of 467 m^2/g surface area, Machery Nagel and Co., Germany) applied in chromatographic columns was used in our experiments.

Water adsorption and desorption were studied using a Q–1500 D (MOM, Hungary) modified derivatograph. The details of the method and the apparatus are given in [12].

Results and discussion

1 Kinetics of adsorption and desorption

Kinetic investigations of the adsorption and desorption of water on silica gel were made with a modified derivatograph utilizing the TG curve [12]. In this method, TG curves (Fig. 1) having the conventional shapes of adsorption and desorption curves corresponding to the amounts of adsorbed and desorbed water are obtained [4, 6, 7]. In Fig. 1, sector *BC* of the TG curve corresponds to the kinetics of water vapour adsorption on the silica gel surface, and sector *DE* to the kinetics of water vapour desorption from this surface at 20°. From the relationship presented in this Figure, it appears that adsorption equilibrium is established after 9 h 20 min, whereas the process of water desorption from silica gel takes 3 h 10 min.

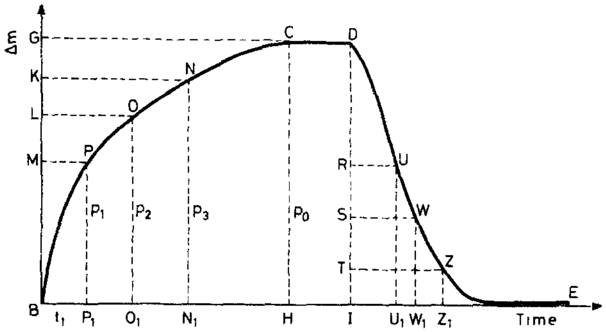

Fig. 1 TG curve corresponding to adsorption and desorption of water on silica gel at 20 °C. BC – adsorption of water, CD – plateau, DE – desorption of water

2 Isotherms of adsorption and desorption of water on silica gel

Isotherms of the adsorption and desorption of water on silica gel are plotted from the TG curve (Fig. 1) by the step profile chromatographic method (Glueckauf's method) [6, 13]. The details of the method are given in [6, 7, 13]. This method is used mainly for adsorption isotherm determination. The isotherms are calculated on the basis of the front shape of the descending line of the frontal chromatogram. In this method, adsorbate (in this case water vapour) at constant concentration in the carrier gas (nitrogen saturated with water vapour at the measuring temperature) is introduced into the measuring cell until maximum sample saturation has been attained. Adsorption curve *BC* (Fig. 1) is then obtained. After the adsorption equilibrium has been reached (maximum adsorption value, plateau—region *CD*), adsorbed water is removed from the surface with dry nitrogen, and the descending line *DE* is then obtained.

In practice, adsorption and desorption isotherms are determined by graphical integration of suitable areas [6, 7, 13]. In Fig. 1, area *BCG* designates the total amount of adsorbed water and area *DIE* the amount of desorbed water. Area *BPM* corresponds to the amount of water adsorbed after time t_1. The same refers to the other points for the other time ranges.

Water vapour pressures are defined from the height of the TG curve. Maximum height *CH* corresponds to saturated vapour pressure p_0 at 20° (adsorption equilibrium). As the balance indications are proportional to these of the recorder, individual heights, e.g. PP_1, OO_1, NN_1, correspond to the pressures of water vapour in adsorption equilibrium at a given moment (i.e. p_1, p_2, p_3, etc.).

Isotherms of adsorption and desorption of water were determined from the TG curve [12] using the method described above. Figure 2 shows the isotherms of adsorption (*A*) and desorption (*B*) obtained at 20°. These are isotherms of types II and III in the BET classification. The isotherm shape is conditioned by the

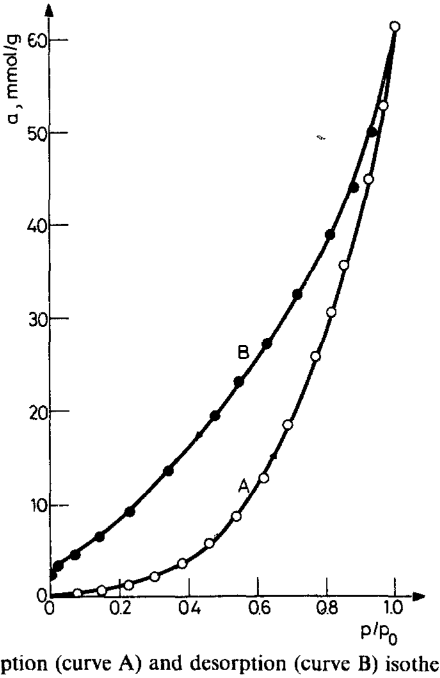

Fig. 2 Water vapour adsorption (curve A) and desorption (curve B) isotherms on silica gel at 20 °C

formation of a polymolecular adsorption water layer on the silica gel surface. These isotherms are similar to those obtained by Barraclough [14] and Kisielev [15]. From Fig. 2, it appears that the adsorption capacity of silica gel (maximum adsorption value) is 61.6 mmol/g. This value corresponds to the formation of 5.6 statistical water monolayer on the silica gel surface. It was calculated on the basis of the silica gel surface area (467 m^2/g), assuming that the surface occupied by one water molecule is 7.06 $Å^2$. The Figure also proves that the adsorption and desorption isotherms form hysteresis loops. Hysteresis loops result from the heterogeneity of the mineral pore structure, in which pores and micropores are not filled simultaneously [16]. The presence of hysteresis loops also demonstrates the irreversible character of the water adsorption process on the silica gel surface at 20°, as some water is attached to the surface more strongly in the form of "bonded" or "vicinal" water. Very drastic action, such as high vacuum or high temperature, is required to remove it from the solid surface. The amount of "bonded" water existing on the silica gel surface is 2.2 mmol/g. This amount was determined by heating silica gel up to 300° after the desorption of water with dry nitrogen at 20° [12]. Very similar adsorption and desorption hysteresis loops for water on carbosil (modified silica gel) at 24° have been obtained with the gravimetric adsorption method [14]. The maximum adsorbed amount on the sample outgassed at 900° (67 m^2/g surface area) is 6.11 mmol/g (3.89 statistical water monolayers). The amount of "bonded" water on carbosil is 0.6 mmol/g. The quasi-isothermal thermodesorption of water from silica gel (150 m^2/g) showed that, as concerns surface forces, 21.31 mmol/g of water (6.04 statistical water monolayers) remains [1]. The literature data presented above suggest the reality of the results obtained using this method.

Conclusions

A modified derivatograph made it possible to measure continuous weight changes at a constant temperature simply and precisely. It is also possible with this apparatus to register sample temperature changes caused by adsorption and desorption, as well as to determine adsorption and desorption heats. An important advantage of this apparatus is the possibility of its application for measurements of liquid adsorption and desorption on solids with very different grain sizes and very different surface areas. With this apparatus, adsorption and desorption phenomena at constant temperatures and the properties of surface liquid layers (e.g. kinetics of adsorption and desorption, adsorption capacity, statistical liquid layers adsorbed on solid surface, amount of bonded liquid, etc.) can be investigated. A knowledge of these properties is of great importance in many branches of physical chemistry and technology (adsorption, catalysis, chromatography, enrichment of useful minerals). The measurement method presented in this paper also makes application of the derivatograph possible (after not very complicated and inexpensive modification) for the measurements described here.

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Zusammenfassung — Die Untersuchung der Adsorption und Desorption von Wasser an Silikagel mittels eines modifizierten Derivatographen wird beschrieben. Die dynamische gaschromatographische Stufenprofilmethode wurde zur Bestimmung der Ad- und Desorptionsisothermen aus den TG-Kurven herangezogen. Die erhaltenen Isothermen stimmen gut mit denen nach anderen Methoden bestimmten überein. Die Eigenschaften flüssiger Oberflächenschichten können mit dieser Methode untersucht werden.

Резюме — С помощью модифицированного дериватографа изучена адсорбция и десорбция воды на силикагеле. Метод ступенчатой динамической газовой хроматографии был использован для определения изотерм адсорбции и десорбции на основе кривой ТГ. Полученные изотермы согласуются с таковыми, найденными на основе других методов. Описанным методом можно исследовать свойства поверхностных жидких слоев.