The changes in permittivity of the system *n*-butane—silica gel*

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On dielectric isotherms of the *n*-butane sorbed on wide-porous silica gel a hysteresis behaviour was observed at 0°C at the frequency of 1 MHz. The major ascending branch of the dielectric isotherm showed breaks in permittivity while the jumps in permittivity of the system appeared on the descending branch. The discontinuities in the course of dielectric isotherm were found in the positions where the inflexion points appeared on the isotherm. An attempt was made to interpret the experimental results qualitatively in terms of the electrostatic theory of intermolecular forces and the theory of capillary condensation.

Было обнаружено гистерезисное поведение на диэлектрических изотермах *н*-бутана сорбированнсго на широкопористом силикагеле при температуре 0°C и частоте 1 MHz. Проявляется переломом на главной восходящей ветви диэлектрической изотермы и скачками на нисходящей ветви диэлектрической проницаемости. Разрывности на диэлектрической изотерме были найдены в местах, где на сорбционной изотерме появляются точки перегиба. С помощью электростатической теории межмолекулярных сил и теории капиллярной конденсации была сделана попытка на качественное объяснение полученных результатов.

Dielectric measurements of the changes in the capacity of a capacitor filled with adsorbent as a function of the amount of the gas sorbed provide interesting information on the behaviour of the whole system [1]. As found for the sorption of polar or non-polar vapour on silica gel [2], these relationships denoted as dielectric isotherms frequently fall into two linear parts.

In spite of some investigations in this line [1, 2], the relationship between the number of linear parts of the dielectric isotherm and the shape of the sorption isotherm has not been cleared so far. Furthermore, the contribution of the hysteresis behaviour found on sorption isotherms to the course of the relationships representing the major branches of the sorption—desorption cycle of dielectric isotherm has not been verified reliably [3].

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In order to clear up these problems, a device was developed for measuring the changes in permittivity accompanying the vapour sorption on porous dielectrics, which was sensitive enough with respect to small changes in the quantities measured [4]. The results of the changes in permittivity measured on this device were qualitatively interpreted for the system *n*-butane—wide-porous silica gel in terms of the electrostatic theory of intermolecular forces and the theory of capillary condensation.

Experimental

The design of the experimental device was determined by the properties of the studied system *n*-butane—silica gel and the necessity to protect the surface of adsorbent against the vapours of vacuum greases and mercury though there was no evidence that these impurities affected the results of measurement in a disturbing manner [1].

The mercury cut-offs of long-termed operational reliability [5] were used for the device and an effective protection against mercury vapour was elaborated.

Fig. 1 shows a diagram of the sorption part of the device for the measurement of the changes in permittivity of a system on porous dielectrics. In a glass jacket *1* the cylindrical capacitor *3* with a sample of adsorbent is hanging on metal rods *2*. These rods are joined to circular brass plate equipped with a die inserted into the groove of the copper sleeve *5* sealed to the covar neck of the glass jacket *1*. The vacuum-tight joining of circular plate *4* with the sleeve *5* is made of Wood's metal. The centre of the plate *4* holds a mounting with a spiral quartz balance *6* and the cell *7* filled with a sample of the same adsorbent as placed in the cylindrical capacitor *3*. The amount of adsorbate corresponding to one mass unit of adsorbent in the capacitor *3* is determined from the stretching of the balance with an accuracy of ± 0.02 mg g^{-1}.

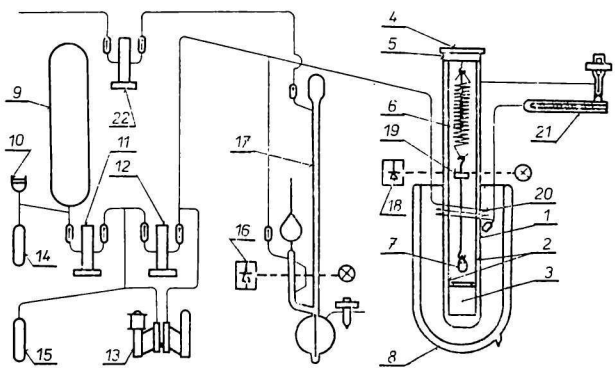

Fig. 1. Diagram of the sorption device with capacitor.
1. Glass jacket; *2.* metal rods; *3.* capacitor with a sample of adsorbent; *4.* circular brass plate; *5.* copper sleeve; *6.* spiral quartz balance; *7.* cell for adsorbent; *8.* Dewar vessel; *9.* gas reservoir; *10.* Prytz lock; *11.*, *12.*, *22.* mercury cut-offs; *13.* electromagnetic mercury cut-off; *14.*, *15.* condensation vessels; *16.*, *18.* adjustable photoelectric scanner; *17.* combined mercury manometer; *19.* diaphragm; *20.* spiral tube; *21.* mercury vapour trap; *22.* mercury cut-off.

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The capacitor is connected with the measuring device by means of a screened conductor going through a vacuum-tight porcelain bushing inserted into an excentrically drilled hole in the circular plate *4*.

A constant temperature of the sample of adsorbent in the capacitor *3* and cell *7* is achieved by means of an equilibrium bath of melting ice placed in Dewar vessel *8*. The adsorbate is kept in the cylindrical reservoir *9* filled through the Prytz lock *10*. The gas enters the measuring chamber of the device through the mercury cut-offs with magnetic manual control *11*, *12* or electromagnetic mercury cut-offs *13* with a partition of porous glass. The pressure of the adsorbate fed into the measuring chamber of the device is regulated by the temperature of liquid adsorbate in the condensation vessels *14*, *15*.

At isothermal measurements the cut-off *13* is actuated by a photoelectric scanner *16* responding to the variations of the position of the mercury meniscus in the left arm of combined manometer *17*. The equilibrium pressure of adsorbate was measured with an accuracy of ± 0.05 torr.

At isosteric measurements it is possible to actuate the lock *13* by means of the photoelectric scanner *18* adjusted to the variations of position of the diaphragm *19* sealed to the mounting of the cell *7* of the spiral quartz balance *6*.

Before entering the jacket *1* the gas passes through the spiral tube *20* dipped into the bath of melting ice which is a part of the hold-up of mercury vapour *21*. In the hold-up there is a spiral made of golden wire from which mercury may be stripped *in vacuo* of the order 10^{-6} torr at the temperatures between 200 and 250°C. Therefore it is not necessary to remove the golden spiral from the device. By the method of atomic absorption it was found that gold retained 99.6 weight % of mercury vapour. The concentration of mercury vapour in the gas passed through the hold-up averaged to 9 ng l^{-1}.

The device is separated from the evacuation equipment by the mercury cut-off *22* connected to the right arm of the manometer *17*.

The evacuation equipment is an all-glass equipment of usual kind. It consists of a mercury diffusion pump equipped with a freezing trap of mercury vapour cooled with solid carbon dioxide and a freezing trap cooled with liquid nitrogen which serves for protection against the penetration of vapour traces from the oil rotary pump. During evacuation the pressure is measured by means of a manometer equipped with a thermocouple with Penning's gauge. The value of vacuum obtained was of the order of 10^{-6} torr. All glass parts were made of "Sial" glass.

The cylindrical capacitor is of a coaxial type (Fig. 2). It consists of the external cylindrical jacket *1* into which the cylinder *3* is pressed by means of the ring *2*. Into the intermediary space thus formed a hollow cylindrical jacket *4* is put. This jacket is braced up by three pairs of distance balls *5* fixed by means of screws with the threads cut into the holes of the external jacket *1*. All metal parts are made of brass and well silvered.

The jacket *4* is electrically connected with the measuring device by a silver conductor led along one of the brass rods *6* holding the capacitor. The silver conductor is isolated by a glass capillary from the screening pipe of stainless steel soldered to the rod *6*. The capacitor is screened from the top by the cup *7* screwed to the cylinder *3*.

The theoretical value of capacity C of the capacitor without dielectric (adsorbent) was 31.3 pF and was calculated for two cylindrical capacitors. The calibration with benzene (relative permittivity $\varepsilon = 2.7663$) gave somewhat higher value of capacity ($C = 33.68 \pm 0.02$ pF) because the theoretical value did not include the boundary effects which are hardly to evaluate.

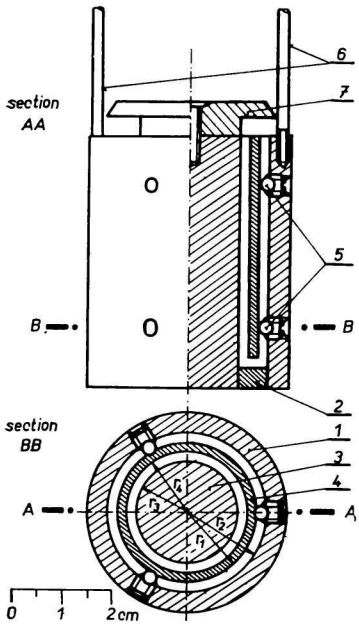

Fig. 2. Sectional view of the cylindrical capacitor. *1.* External jacket of capacitor; *2.* ring; *3.* internal cylinder; *4.* hollow cylindrical jacket; *5.* glass distance balls; *6.* supporting rods; *7.* screening cup.

The voids of 2 mm width between the cylinders were filled with the adsorbent grains of 0.10—0.15 mm size.

Assuming that the adsorbate shows dielectric properties similar to a liquid, the change in capacity will be biased by the amount of substance adsorbed as well as by the difference between the permittivities of adsorbate in gaseous and sorbed state. A change in permittivity is favourable for these measurements because the permittivity of substances in gaseous phase is practically equal to one while it is substantially higher provided the substances are in liquid phase [6, 7]. (In this case the concept of permittivity covers the relative static permittivity ε.) From the measurements with rising frequencies it follows that after the frequency has reached a certain value, in general, the permittivity decreases from the static value to the value of "optical" permittivity. During the transition between these limiting values the system goes through the region of anomalous dielectric dispersion where the absorption of energy in dielectric takes place [8].

The measurements of capacities must be performed at a frequency outside the dispersion region lest the heat released should disturb the established adsorption equilibrium. Practically the region of frequencies from zero to 10 MHz can be considered. At the frequency of 1 MHz which is usual for high frequency measurements in the range of laboratory temperatures the relaxation times of simple molecules are so small that the quantity measured is practically identical with the static permittivity. For precise measurements of capacity (permittivity) at this frequency the bridge, resonance, and interference methods are available [9].

According to present experience the instruments functioning on the basis of the resonance method show a high sensitivity and also fulfil the condition of long-termed stability. The preliminary experiments showed that for the measurements of the change in capacity the sensitivity of instrument is to be 0.01 pF. Because of the long duration

of experiments a considerable stability of long periods of time corresponding to ± 0.02 pF is also required.

A thermionic crystal oscillator with a quartz cut of a frequency $f_Q = 1$ MHz in grid circuit was used in the instrument. In the anodic circuit of electron-tube there is an oscillation LC circuit in which the capacity of measuring capacitor with the adsorbent measured represents a part of the resonance capacity. The change in capacity is read on the scale of a variable capacitor which is parallel-connected with the measuring capacitor. A milliampermeter is connected in the inlet of anodic current. As the power supply of the instrument, a two-way rectifier with usual filtration and stabilizing discharge tube is used.

The variable capacitor is tightly connected with a circular scale which enables one to read the angle changes by one minute and serves for measuring the changes in capacity of the measuring capacitor.

The measuring capacitor is fixed in the adsorption device. Its connection with the measuring instrument is secured by a solid coaxial line. Routine checks on the stability of the instrument are carried out by means of comparing capacitors with a capacity approximately equal to the capacity of the measuring capacitor. The comparing capacitors as well as the measuring capacitor are connected with the anodic resonance circuit by means of a pneumatically controlled mercury change-over switch.

The changes in capacity are measured by the substitution method.

Chemicals

The measurements were performed at 0°C with wide-porous silica gel. This material had the specific surface of 385 $m^2\ g^{-1}$ and the effective diameter of pore necks was 4.4 nm [10]. Butane was spectrally pure. It was prepared from *n*-butanol by high-pressure hydrogenation in the presence of WS_2 [11].

Before measurement the capacitor with a sample of silica gel was evacuated for 20 hrs at 180°C and at a pressure of the order of 10^{-6} torr.

Results and discussion

As shown by a number of studies [12–16], the surface atoms of silicon are bonded with one, two or three hydroxyls. In case of *n*-butane which is a non-polar adsorbate the electric field of surface hydroxyls will induce a dipole moment proportional to the polarizability of the molecule. Besides the electrostatic component, the attractive dispersion component of intermolecular forces plays an important part at higher surface concentrations.

The role of the surface atoms of silicon and oxygen is assumed to be small in comparison with that of hydroxyl groups.

Fig. 3 shows the plot expressing the change in capacity of the system due to the sorption corresponding to the major ascending branch of hysteresis loop. The change in capacity ΔC and the sorption a correspond to the total amount of adsorbent placed in the capacitor.

Each bending of the sorption isotherm is preceded by a rapid change in the polarizability of molecules. Within the limits of experimental errors the permittivity

in the given region is a linear function of the amount of gas sorbed. An exception is observed only at the beginning when the first doses of adsorbate do not contribute to the change in permittivity and in the polarizability of molecules.

Starting from the point A the polarizability increases rapidly, which indicates increasing interactions between the molecules of n-butane and surface hydroxyls and a weakening of the intramolecular hydrogen bonds in this region. This statement is supported by a considerable initial volume expansion of porous glass accompanying the sorption of n-butane [17]. In the point B the surface concentration of adsorbate is so high that the attraction among the molecules of butane due to the effect of the dispersion component of intermolecular forces rises suddenly. The interaction between the molecules adsorbed and the surface hydroxyls weakens and thus the polarizability of the sorbed molecules decreases. The point B may be regarded as origin of the two-dimensional condensation which — according to the degree of further decrease in polarizability in the point C — may turn into capillary condensation.

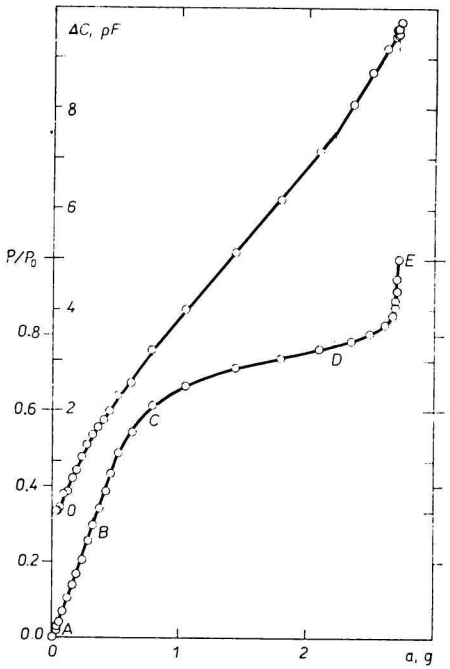

Fig. 3. Major ascending branch of the dielectric (at the top) and sorption isotherm (at the bottom) of n-butane on wide-porous silica gel.
ΔC — change in capacity of capacitor; P/P_0 — relative pressure in gaseous phase; a — mass of the gas adsorbed on a sample of silica gel placed in capacitor.

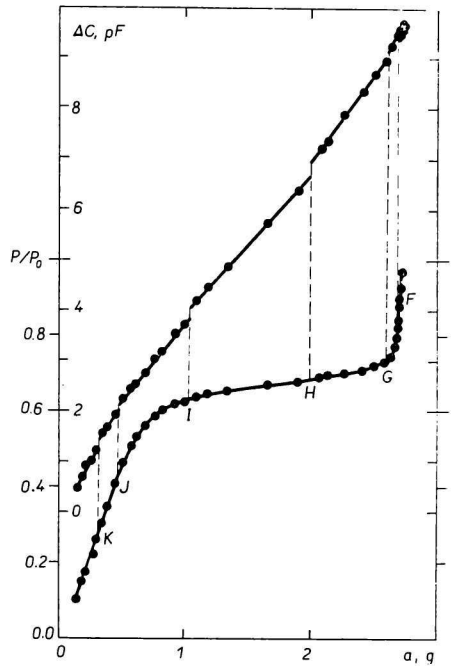

Fig. 4. Major descending branch of the dielectric (at the top) and sorption isotherm (at the bottom) of n-butane on wide-porous silica gel.
ΔC — change in capacity of capacitor; P/P_0 — relative pressure in gaseous phase; a — mass of the gas sorbed on a sample of silica gel placed in capacitor.

In the point *D* a sudden increase in polarizability of molecules is observed. According to the theory of capillary condensation this point reflects the state in which the curvature radii of menisci of the liquid adsorbate start to increase. This results in a compression of the liquid in pores, an increase in attractive dispersion component among the molecules of adsorbate, and a contribution to the decrease in polarizability of the molecules. Conversely, if the electrostatic induction component of the attractive forces due to the interaction between the molecules of butane and surface hydroxyls grows stronger, an increase in polarizability of the molecules is observed. This case occurs if the molecules of butane orientate themselves in the direction of their maximum polarizability, their longitudinal axis being parallel with the electrostatic field of surface hydroxyls. Consequently, the molecules of adsorbate orientate themselves in the directions perpendicular to the surface of adsorbent. This is obviously the case of a superposition of two opposite effects the second one of which plays a much more important part.

In the preceding stages of sorption there prevailed the direction of orientation of molecules with the longitudinal axis parallel with the surface. The hydroxyl groups previously screened are liberated by the perpendicular orientation of molecules and enter into bonded states with other molecules of adsorbate only at high surface concentrations which manifests itself in the points *D* and *E* where the polarizability increases.

This strong interaction may account for the high maxima on the curves representing the differential heats of normal paraffins sorbed in wide-porous silica gel [10, 18].

Because of the accompanying heat effects, the sharp changes in polarizability in the last points suggest the phase transitions of the first order.

The plot in Fig. 4 illustrates the changes in capacity of the system in the course of desorption. The major descending branch of the sorption hysteresis loop is at the bottom.

The dielectric isotherm consists of a series of stepwise arranged linear sections. To each bending on the descending branch of sorption isotherm corresponds a jump in permittivity of the system. The slopes of the straight lines change in the same sequence as in Fig. 3 and therefore we can apply the considerations concerning the changes in polarizability to the interpretation of processes taking place in desorption. The jumps observed on the dielectric isotherm indicate that during desorption the system passes through metastable states which is accompanied by spontaneous processes. It appears that the most simple interpretation of the jumps in permittivity may be based on the theory of capillary condensation [19] which postulates some metastable states of adsorbate connected with the rearrangement of the surface shape of liquid menisci in a given stage of the sorption—desorption cycle. The skeleton of silica gel is formed by the particles of spherical shape with pores showing a negative curvature of walls. They suggest bottle-shaped pores with a greater number of necks.

The structure of silica gel skeleton determines the shape and curvature of menisci of the liquid. By reducing the external pressure as far as the point *F* the menisci of bowl-like shape are formed in the necks of pores filled with the condensed adsorbate. The curvature of these menisci increases and in the point *G* they change spontaneously into the menisci of an approximately spherical shape. A depletion of the necks of pores sets in and in the point *H* the spherical menisci start breaking

open into the content of pores. Then the menisci of saddle-shaped form arise and after further desorption they slip in the point I to the contact points of spherical particles of the skeleton. These menisci lose their stability in the point J where the capillary condensation turns into a two-dimensional condensation. A further spontaneous change in surface structure of the adsorbed layer of molecules is likely to take place in the point K.

The jumps in permittivity observed on the descending branch of dielectric isotherm suggest the phase transitions of higher order because we were not able to reveal any corresponding distinct changes in the course of the differential heats of normal paraffins on wide-porous silica gel determined calorimetrically.

Conclusion

From the changes in polarizability it ensues that the effect of force on the molecules sorbed depends on the surface concentration of adsorbate. The polarizability of molecules changes abruptly when the surface concentration exceeds a certain critical limit. This state is characterized by a point of inflection on sorption isotherm. Therefore the complexity of the course of sorption isotherm depends on the number of states through which the system passes within the whole range of surface concentrations of adsorbate.

The linear relationships between the permittivity of the system and the amount adsorbed exhibit two kinds of discontinuities: the breaking points on the ascending branch and the jumps on the descending branch of the dielectric isotherm. This different behaviour causes the revealed dielectric hysteresis. If we compare the major branches of the sorption—desorption cycle of a dielectric isotherm, we find out that they are in close vicinity. The sensitivity and stability of the experimental device enable us to distinguish safely the differences in the course of both branches of dielectric isotherm.

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