The influence of the ionizing radiation on the adsorbate in the metastable state*

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The influence of the ionizing radiation on capillary condensed water in porous glass and silica gel was studied. The ionizing radiation generates vapours nucleation centres in the liquid and can initiate a transition of the adsorbate from a metastable to a stable state. From an analysis of the conditions of growth of these nucleation centres it follows that ionizing radiation influences capillary condensed equilibria only in pores of certain forms and dimensions. This effect was evident in ink-bottle pores. For the first time, the experiments actually proved the existence of the negative pressure in capillary condensed adsorbate in the porous adsorbent. From the results one can judge on the dimensions as well as on the form of the mesopores.

Было изучено влияние ионизирующей радиации на конденсированную воду в капиллярах пористых стекол и силикагела. Ионизирующая радиация генерирует парообразные зародышные центры в жидкости и может индицировать переход адсорбированного вещества из метастабильного в стабильное состояние. Из анализа условий роста этих центров следует, что ионизирующая радиация влияет на равновесие конденсированного в капиллярах вещества только в случае поров определенных форм и размеров. Этот ефект был очевиден в случае поров в стекле типа ,,чернильницовых бутылок“ В первый раз было экспериментально доказано существование отрицательного давления адсорбированного вещества капиллярно конденсированного в пористом адсорбенте. Из результатов этой работы также можно сделать заключение о размерах и о формах мезопоров.

In connection with the concepts that explain phenomena of the adsorption hysteresis with the negative pressure of the adsorbate [1], the idea has been expressed in our laboratory on the necessity of influencing the adsorption hysteresis by ionizing radiation.

The capillary condensed adsorbate in the pores thus finds itself under negative hydrostatic pressure $-P$ which depends on the relative pressure of the vapour of the adsorbate above the pores, according to the relation

$$-P = \frac{RT \ln p/p_s}{v}, \tag{1}$$

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where P — negative hydrostatic pressure,
R — gas constant,
T — temperature,
v — molar volume of the adsorbate,
p/p_s — relative pressure of the adsorbate vapours.

In the metastable liquid, the ionizing radiation forms in its course microscopic vapour bubbles (nucleation centres) and initiates under proper conditions (*i.e.* under conditions suitable for the growth of nucleation centres) the transformation of the adsorbate to the stable state.

At temperatures considerably smaller than the critical temperature, the liquid in the mesopores is in a metastable state because of the influence of the existing negative pressure (which depends on the curvature of the meniscus of the liquid in the pore according to Laplace equation $-P = 2\sigma/r$). The adsorbate remains in the liquid phase at a pressure lower than that which corresponds to the tabelated tension of the saturated vapours at a given temperature. It becomes the question of the overheated liquid which can be realized in section AB (Fig. 1) of the isotherm of the real gas.

In order to form microscopic bubbles, a sufficient energy must be transmitted into the defined element of volume of the liquid by the ionizing radiation. This energy is called LET (linear energy transfer) and represents the amount of the transfered energy for a path length unit of an ionizing particle which passes through the investigated medium. If the LET, expressed as $\mathrm{d}E/\mathrm{d}s$ (E — energy of the particle, s — course of the particle), is sufficiently high it can cause the formation of nucleation centres.

The growth of the nucleation centres (microscopic bubbles of the vapour formed by a certain kind of radiation at the given energy) is possible also when a sufficiently high value of the negative hydrostatic pressure in the adsorbate is attained. (This

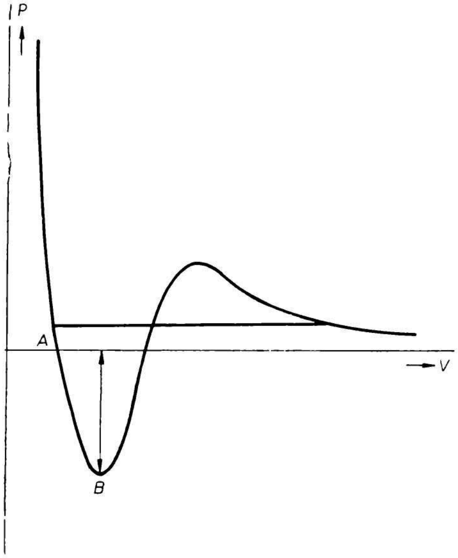


Fig. 1. P—V isotherm of the real gas.

pressure provides the energy for the growth of the nuclei when the value of the LET is not sufficiently high.) It is necessary to guarantee the suitable sterical conditions for the growth of the bubbles because the negative pressure according to the Laplace equation dependens on the radius of the meniscus of the liquid surface in the pore.

In cylindrical bilaterally accessible pores, where the adsorption hysteresis can appear [2], the capillary condensation equilibrium is not influenced by the ionizing radiation. It is also similar in the conic or unilaterally accessible pores, where the adsorption hysteresis does not appear. The ionizing radiation which penetrates into these pores can form nuclei in the condensed phase, which disappear after the interruption of the radiation. This results in the fact that the radius r_2 of the nucleus cannot surpass the value of the meniscus radius r_1 that corresponds to the equilibrium pressure (Fig. 2*a*).

In pores with narrow entrances and large cavities where the radius of the nuclei r_k may surpass meniscus radius r_3 (which corresponds to the equilibrium pressure) the inequality of pressures in the condensed phase causes the growth of the nuclei. The growth of the nuclei results in the desorption of the condensed phase from the main part of a pore. The necessary condition for that is also $r_4 > r_k$, where r_4 is the radius of the cavity (Fig. 2*b*).

Experimental

The influence of X-rays on the capillary condensed water was studied. The first adsorbent was silica gel with a low coordination number of globules of SiO_2 which has a porous structure similar to that of pores with a conical shape. The second sample prepared by *Zhdanov* (Leningrad) was a porous glass containing broad pores (radius ~10 nm) with very narrow entrances of critical dimensions 0.3 nm. This glass shows molecular sieve properties. The experiments were made on the usual type of adsorption balance with a quartz spiral. The bottom of the apparatus was adapted for the X-irradiation of the sample. Where the radiation beam enters the apparatus, the glass was replaced by a beryllium window, which is virtually transparent to the X-rays. The

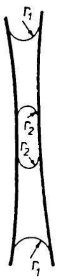
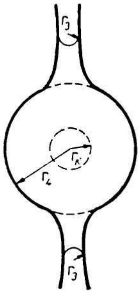


Fig. 2a. Tubular tapered pore: r_1 — equilibrium radius of meniscus of condensed phase; r_2 — radius of nucleus; $r_1 > r_2$.



b

Fig. 2b. Ink-bottle pore: r_3 — equilibrium radius of condensed phase; r_4 — radius of cavity; r_k — radius of the nucleus; $r_4 > r_k$.

samples were irradiated by X-rays (Mikrometa II apparatus, Chirana, ČSSR), 50 kV with an X-ray tube with a beryllium window. The dosimetry of the X-beam was determined by means of a ferrous sulfate dosimeter using the value $G_{Fe^{3+}} = 13.1$ [8]. The samples were irradiated for a period from 30 to 40 min by the dose rate $I = 10^{10}$ eV cm^{-3}. Isotherms were measured at 20°C.

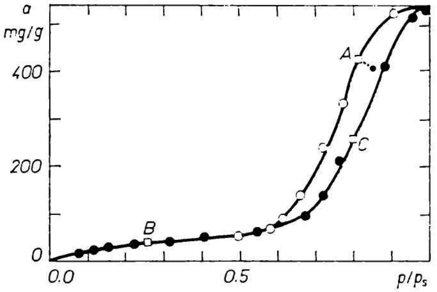


Fig. 3. Adsorption isotherm of H_2O on silica gel at 20°C.
● Adsorption; ○ desorption; □ radiation.

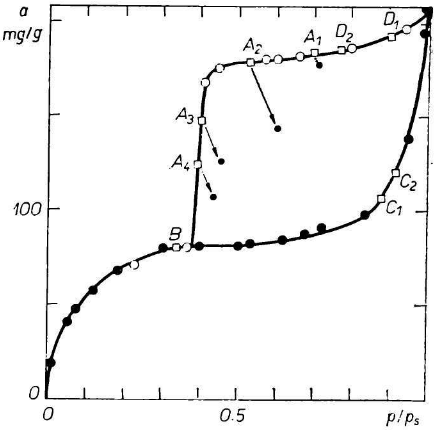


Fig. 4. Adsorption isotherm of H_2O on porous glass at 20°C.
● Adsorption; ○ desorption; □ radiation.

The water isotherm of the silica gel used shows a narrow hysteresis loop (Fig. 3). The radiation in the region of the desorption branch causes a slight shift of the initial point A on the desorption branch toward the decreasing adsorbed quantity. After the termination of the radiation, the system returns into its initial state. The radiation at a low relative pressure on the reversible section of the isotherm (point B) and on the adsorption branch of the hysteresis loop (point C) had no influence whatever. As mentioned before, the reversibility of the process is due to the conical form of the pores of the used silica gel.

Another situation arose when a sample of the porous glass was used (Fig. 4). The water isotherm on this adsorbent has a broad hysteresis loop, typical for materials with ink-bottle type of pores. The effect of X-radiation became evident on the desorption branch of the isotherm only with relative pressures below 0.7 (which corresponds to the negative pressure 4.823×10^7 Pa and more). In points A_1, A_2, A_3, and A_4 the system was irradiated by the X-rays. We observed a shift of these points in the direction of the arrows in Fig. 4. At points B, C_1, C_2, D_1, and D_2 the radiation did not effect any influences.

Discussion

It was proved that only with the ink-bottle pores there can be expected an effect of the ionizing radiation on the desorption branch of the isotherm in the proximity of the characteristic relative pressure h_0/l.

A similar concept has been developed independently by *Rao* and *Nayar* [3]. These authors have proved the influence of the electric discharge on water entrapped in silica gel. Nevertheless, the electric discharge has strong heat effects, hence the results of Rao and Nayar are not indisputable proof of the given assumptions.

The situation is analogous to the case of bubble chambers [4—6]. The mechanism of the origin of the bubbles in both cases is identical, since the two processes can be described by the same mathematical-physical relations. It is necessary to include individual forms of the energy which participate in the formation of the nucleus. The energy E which is necessary for the formation of a bubble consists of the components E_a and E_b

$$E = E_\mathrm{a} + E_\mathrm{b},$$

where

$$E_\mathrm{a} = \frac{4}{3} \pi r^3 N_\mathrm{b} h_\mathrm{s}$$

and

$$E_\mathrm{b} = \int_0^r \left(p_0 + \frac{2\sigma}{r} \right) 4\pi r^2 \,\mathrm{d}r.$$

(r — radius of the bubble, N_b — moles of the adsorbate per bulk unit in gaseous phase, h_s — molar heat of vaporization of the adsorbate, p_0 — exterior pressure, σ — surface tension of the adsorbate.)

E_a represents the energy which is necessary for the evaporation of the microscopic bulk of the liquid, E_b is the energy corresponding to the volume work at the formation of a bubble.

The energy which the ionizing particle loses on its course in the condensed media corresponds to the diameter $D = 2r$ of the nucleation centre and can be expressed as

$$E_1 = \frac{\mathrm{d}E}{\mathrm{d}s} 2r.$$

This energy is available in the spherical area of a diameter $2r$ and equals the energy used at the formation of a nucleation centre of a radius r

$$\frac{\mathrm{d}E}{\mathrm{d}s} 2r = \frac{4}{3} \pi r^3 N_\mathrm{b} h_\mathrm{s} + \frac{4}{3} \pi r^3 p_0 + 4\pi r^2 \sigma.$$

From this relation the radius of the nucleation centre can be expressed

$$r = \frac{-2\pi\sigma + \left[4\pi^2 \sigma^2 + \frac{4}{3} 2\pi \left(\frac{\mathrm{d}E}{\mathrm{d}s}\right) (N_b h_\mathrm{s} + p_0)\right]^{1/2}}{\frac{4}{3} \pi (N_\mathrm{b} h_\mathrm{s} + p_0)}$$

From the experiments it follows that there exists a certain region of the hysteresis loop where the X-radiation with the energy of 40 × 10^3 eV causes the desorption [7].

In the other part of the hysteresis loop the radiation does not affect the capillary condensation equilibria. The influence of radiation begins at negative pressures from 4.823×10^7 Pa upwards.

Our experiments have for the first time proved directly the existence of the negative pressure in the capillary condensed adsorbate in the porous adsorbent. On the basis of the obtained results it was possible to propose a method for the determination of the porous structure of adsorbents, mainly with regard to the dimension and the form of the mesopores.

Further studies of this system are in progress.

References

1. Kadlec, O. and Dubinin, M. M., *J. Colloid Interface Sci.* ***31***, 479 (1969).
2. De Boer, J. H., in *Proceedings of the 10th Symposium of the Colsten Research Society held in the University of Bristol.* (D. H. Everett and F. S. Stone, Editors.) P. 68. Butterworths, London, 1955.
3. Rao, S. K. and Nayar, B. C., *J. Colloid Interface Sci.* ***38***, 45 (1972).
4. Sette, D. and Wanderlingh, F., *J. Acust. Soc. Amer.* ***41***, 1074 (1966).
5. Seitz, F., *Phys. Fluids* ***1***, 2 (1958).
6. Kato, R., *J. Appl. Phys.* ***42***, 204 (1971).
7. Volková, J., Fojtík, A., and Kadlec, O., *Trudy chetvertoi vsesoyuznoi konferentsii po teoreticheskim voprosam adsorptsii*, Leningrad, 1974, in press.
8. *Report of the International Commission of Radiobiological Units and Measurements (ICRU)*, January, 1961.

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