

DETERMINING THE HYGROSCOPIC CHARACTERISTICS  
AND THE MASS TRANSFER COEFFICIENTS OF MOISTURE  
SORPTION FOR DISPERSE MATERIALS SOLUBLE IN WATER

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UDC 541.183

Results are shown of an experimental study concerning the hygroscopic characteristics of materials soluble in water. Data have been obtained pertaining to the coefficients of internal mass transfer in such materials.

It is well known that the processes of moisture transfer within disperse materials govern the behavior of such materials during their thermohumidity treatment. Based on this premise, knowing the coefficients of internal mass transfer and the hygroscopic characteristics of soluble products will certainly be worthwhile for engineering calculations, for the regulation and the automation of technological processes, for thorough desiccation, for long-term preservation and the proper conveyance of manufactured goods, etc.

Experience of recent years has shown that the sorption method of analysis is useful for these purposes [1]. With the aid of static and kinetic sorption curves, one can by a well known procedure [2-4] determine the hygroscopic point of a given material  $W_{cr}$  (critical moisture content in a body at a given air temperature and relative humidity, above which a saturated solution begins to form at the surface), the specific isothermal moisture holding capacity  $C_m$ , the moisture diffusivity  $a_m$ , and the moisture conductivity  $\lambda_m$ .

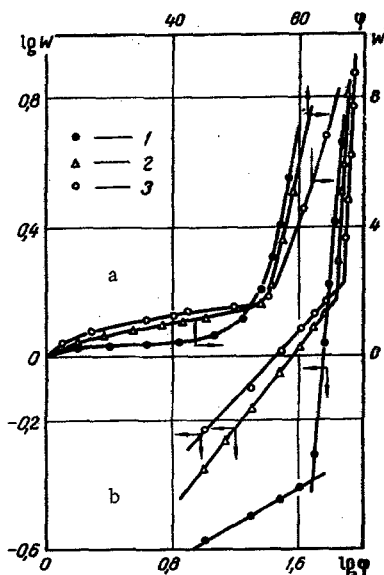


Fig. 1. Sorption isotherms for mineral fertilizers, (a) in natural coordinates and (b) in logarithmic coordinates, at 293°K: specimen No. 1 (1), specimen No. 2 (2), specimen No. 3 (3). Moisture content  $W$  (%).

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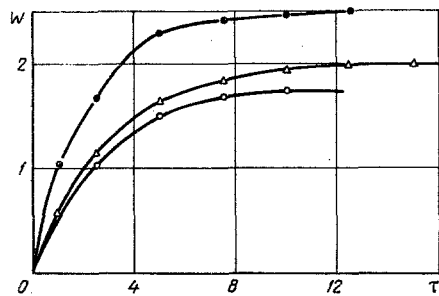


Fig. 2

Fig. 2. Kinetics of moisture sorption by materials soluble in water, at  $\varphi = 70\%$  and a  $293^\circ\text{K}$  temperature.

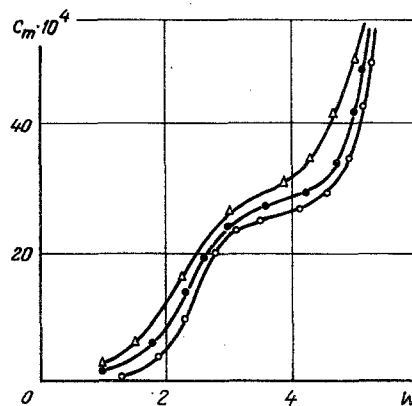


Fig. 3

Fig. 3. True specific isothermal moisture holding capacity  $C_m$  (mole/J) of specimens, as a function of the moisture content.

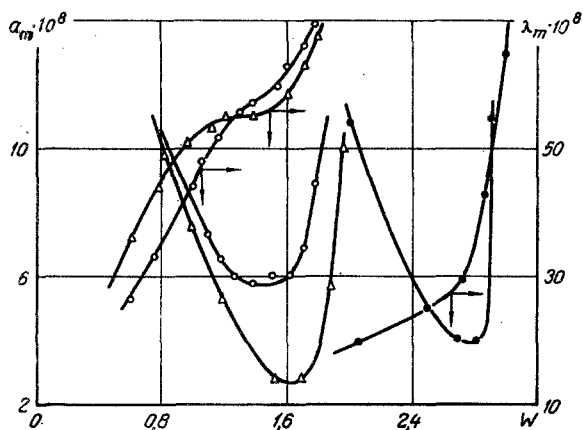


Fig. 4. Moisture diffusivity  $a_m$  ( $\text{m}^2/\text{sec}$ ) and moisture conductivity  $\lambda_m$  ( $\text{kg}/\text{m} \cdot \text{sec} \cdot \text{J}/\text{kg}$ ) of specimens, as functions of their moisture content  $W$  (%).

No. 3 consisted of ammonia polyphosphate powder resulting from the neutralization of phosphoric acid essence with ammonia at  $473\text{--}483^\circ\text{K}$ , 12% nitrogen and 60%  $\text{P}_2\text{O}_5$ .

During moistening the specimens by sorption under a given water vapor pressure, the layer in a sorption cell was 2-3 mm thick and 1.0-1.5 cm in diameter. The quantity of sorbed water was determined from the change in the length of a quartz spring, by measurement with a model KM-6 micrometer through a window in the apparatus with a 0.001 mm precision. The accuracy of such weighing was  $(0.7\text{--}1.0) \cdot 10^{-3}$  mm. The null position of the spring, to correspond to the weight of a perfectly dry specimen, was set under a  $0.133 \text{ N}/\text{m}^2$  pressure and at a  $383^\circ\text{K}$  temperature. The procedures for the test preparation of specimens and for the test performance, namely plotting the isotherms and the sorption kinetics curves, were similar to those described in [5]. The sorption kinetics curves were plotted at a 70% relative pressure of water vapor and, by numerically differentiating these curves, we obtained from them the rates of change in the moisture content. All tests were performed at a  $293^\circ\text{K}$  temperature.

On the basis of the obtained test data, we have plotted the sorption isotherms shown in Fig. 1. The isotherms for all three fertilizers are similar and follow the adsorption of the third kind according to the BET theory [6].

These isotherms have been plotted here in logarithmic coordinates too. Each curve is broken into two straight-line segments at a point characteristic of each specimen. According to [4], the coordinates

For the experiment the authors used vacuum-sorption scales of the MacBen-Bacre design, updated with complete thermostatization within  $\pm 0.05^\circ\text{C}$ .

The study was made on three specimens of nitrate-phosphate mineral fertilizers soluble in water and produced at the Nitrate Fertilizers Plant in Rovno. Specimen No. 1 was prepared by mixing liquid ammonia polyphosphates with granulated ammonia nitrate (2-3 mm grains). The ammonia polyphosphates had been obtained by neutralizing phosphoric acid essence with ammonia at a temperature within  $473\text{--}483^\circ\text{K}$ . This procedure yielded ammonia polyphosphates containing 12.6% nitrogen and 58% phosphorus on a  $\text{P}_2\text{O}_5$  basis. After mixing and granulating, the fertilizer contained 25.4% nitrogen and 25%  $\text{P}_2\text{O}_5$ . Specimen No. 2 was prepared with ammonia polyphosphates containing 12.3% nitrogen and 60.5%  $\text{P}_2\text{O}_5$ . The final granulated fertilizer product contained 23.3% nitrogen and 27.1%  $\text{P}_2\text{O}_5$ . Specimen

of this characteristic point determine the hygroscopic properties of a specimen when its moisture content has reached a certain definite level  $W_{cr}$ . To the left of the break point the isotherm represents possible modes of moisture sorption by the fertilizer (chemisorption, adsorption, and capillary vapor condensation), to the right of the break point the isotherm represents saturation dissolution at the grain surface and subsequently throughout the entire volume of material. In this case, evidently, the bond of sorbed moisture is osmotic. Thus, in terms of their hygroscopic characteristics, the test specimens of mineral fertilizers cover almost the entire gamut of moisture bonds typical of capillary-porous colloidal materials.

It also follows from Fig. 1 that the quantity of moisture held by adsorptive and capillary bond forces constitutes only an insignificant part of the total moisture content. These data provide an indication about the relative hygroscopic quality of the selected fertilizer grades. The hygroscopic point of a specimen does not, however, tell anything about the rate of moisture adsorption from an ambient vapor-air mixture at a given temperature and humidity. Information about this can be obtained from the sorption kinetics curves for the specimens shown in Fig. 2.

According to Fig. 2, the quantity of adsorbed moisture as a function of time at a fixed relative atmospheric humidity follows the same trend for all three specimens and approaches a Langmuir curve. This indicates that the moisture transfer within the hygroscopic range of specimens is effected mainly by the activated Knudsen diffusion mechanism, similar to the mass transfer in microporous sorbents [7].

The true specific moisture holding capacity  $C_m$  as a function of the moisture content in the specimens (Fig. 3) reflects changes in the moisture storing characteristics during the sorption of water vapor. The  $C_m(W)$  curves plotted from the sorption segments show that, at moisture contents up to the hygroscopic point of a specimen,  $C_m$  increases with increasing  $W$  as the same monotonic function for all materials. When the moisture content reaches the hygroscopic level, then the trend of the  $C_m(W)$  curves changes and inflection occurs approximately at the points where specimens begin to dissolve at the surface. The further increase in  $C_m$  is almost linear, which indicates that moisture is stored in specimens by a process of dissolution uniformly progressing from the surface into the volume.

The  $a_m(W)$  curves in Fig. 4 characterize the rate of moisture transfer in specimens. The trend of these curves is typical of capillary-porous colloidal materials such as clay, for example, which swell up due to internal dissolution [8]. At low moisture contents the moisture transfer within a specimen is effected by diffusion of vapor through micropores, then the moisture diffusivity of the material is high. As the moisture content in a specimen increases, the moisture diffusivity decreases and the effective diameter of microcapillaries becomes smaller owing to the film of adsorbed moisture.

Within the initial range of capillary condensation the bond energy of moisture is comparable to the bond energy of moisture in the last layers of polymolecular moisture, while coefficient  $a_m$  remains almost constant. Subsequently, this coefficient increases rapidly to high values. This has, evidently, to do with the massive absorption of water vapor by capillary condensation processes and by dissolution of specimen fragments, when the moisture content reaches the necessary critical levels.

It is well known that the moisture conductivity  $\lambda_m$  under isothermal conditions determines, in a moist capillary-porous colloidal material, the magnitude of the moisture current per unit gradient of chemical mass-transfer potential. Information about the  $\lambda_m(W)$  relation for disperse materials soluble in water is almost completely lacking in the technical literature. The moisture conductivity as a function of the moisture content has been calculated for the specimen materials by the formula  $\lambda_m = a_m C_m \gamma_0$  and is shown in Fig. 4.

The  $\lambda_m(W)$  curves indicate that the moisture current density is insignificant within the range where the moisture bond is adsorptive. This is related to the low isothermal mass holding capacity. As the moisture content in a specimen increases, the mass transfer capability increases too, even though the diffusivity  $a_m$  decreases. The increase in conductivity  $\lambda_m$  within this range of moisture contents is entirely due to the rapid increase in the specific isothermal mass holding capacity of specimens. From there on the conductivity  $\lambda_m$  of all specimens increases appreciably, as a result of the simultaneous increase of  $C_m$  and  $a_m$ .

Thus, on the basis of our tests and calculations, which agree completely with the theoretical concepts in phenomenological thermodynamics of irreversible processes, we may state that disperse materials soluble in water are subject to the same laws of internal mass transfer as capillary-porous colloidal materials moistened by sorption of water vapor. This revelation makes it feasible to apply in practice the basic concepts of modern heat and mass transfer theory pertaining to capillary-porous colloidal materials.

## NOTATION

$\varphi$	is the relative pressure of water vapor;
$W$	is the moisture content;
$\tau$	is the time;
$a_m$	is the moisture diffusivity;
$\lambda_m$	is the moisture conductivity;
$C_m$	is the specific isothermal moisture holding capacity of a specimen.

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