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HYGROSCOPIC PROPERTIES OF BIOLOGICAL MATERIALS AND THE BINDING ENERGY OF MOISTURE*

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The binding energy of moisture with biological materials is determined from sorption isotherms for yeast at different temperatures.

Modern drying theory is based on the theory of heat and mass transfer and the concept of forms of moisture bonds with materials. Drying of moist materials is a thermophysical process in which the form of binding of moisture with the material is important. Therefore, discovery of the drying mechanism and its molecular nature is necessary for establishing scientifically substantiated optimum drying conditions.

Most microbiological preparations subject to drying are suspensions, whose dispersion medium is, in turn, a solution of organic and inorganic compounds. A microbial cell itself also contains 80–85% water. Some of the water is free and some is bound. Any decrease in the amount of water in the cell brings about drastic changes in the whole colloidal system. Protein compounds are basic components of a bacterial cell, and therefore too large losses of water result in coagulation of the protein, which is an irreversible process equivalent to death of the cells.

The drying process must not disturb the ability of the cell to metabolize; however, suppression of the life cycle does not always lead to death of the cell, and inactivation only occurs in the case of irreversible changes in the cell structure.

The objective of drying of living microorganisms is to suppress the life processes in the cells by decreasing the water content to a level at which the cells become "anabiotic."

The word "anabiosis" usually means temporary cessation of life processes or their deep suppression, after which the cells can be fully resuscitated.

It is known that the presence of a certain amount of water in a cell is a necessary condition for nutrition and respiration of microbes. According to E. V. Maistrakh [1], up to 35% of the entire amount of water can be removed from a living cell. In the process of adaptation to unfavorable living conditions, many microorganisms lose a certain percentage of water.

The question of the state of the vital functions in freeze-dried microorganisms has not been answered so far. Some researchers believe that freeze-drying terminates completely the metabolic processes in microorganisms, while others suggest that freeze-drying deeply suppresses the life processes.

Drying and dehydration processes can be theoretically substantiated and the time and energy necessary for water removal from biomass can be evaluated accurately only with complete knowledge of the properties of bound water contained in the cell.

At present P. A. Rebinder [2] and S. M. Lipatov [3] have developed the concept of forms of moisture bonds with capillary-porous colloid materials. In the drying of moist materials the moisture bond with the solid skeleton is disturbed and this distortion consumes some energy. With this in view, the forms of moisture bond are classified on the basis of the value of the binding energy in accordance with Rebinder's scheme.

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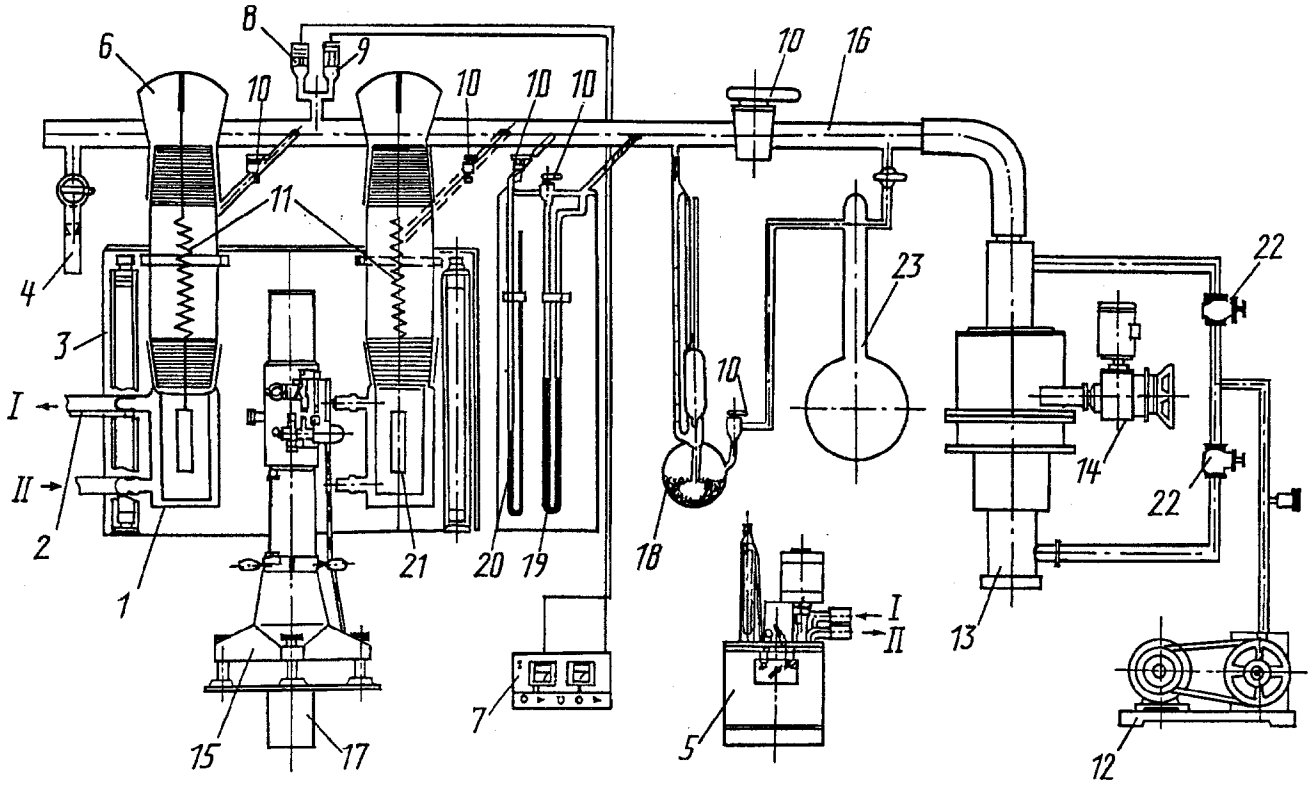

Fig. 1. Schematic of the experimental setup: 1) sorption cylinder; 2) coupling for supply of thermostating liquid; 3) lighting lamp; 4) ampoule with sorbate; 5) TL-150 ultrathermostat; 6) ground lids; 7) VIT-2 vacuum gauge; 8, 9) LT-2 and LM-2 vacuum gauges; 10) vacuum cocks; 11) quartz springs; 12) VN-1-2M pump; 13) N-13-2 pump; 14) electric drive of the valve; 15) KM-6 cathetometer; 16) header; 17) cathetometer table; 18) McLeod gauge; 19) oil pressure gauge; 20) mercury pressure gauge; 21) specimens; 22) vacuum valve; 23) initial vacuum bulb.

As is known, the vapor pressure over the surface of moist materials decreases due to the moisture bond with the material and the free energy decreases accordingly. It is natural that the stronger the moisture bond, the higher the binding energy. Binding of moisture with the material is accompanied by evolution of heat, and therefore some work is to be done to detach absorbed water molecules from the surface, and it is this work that characterizes the strength of the moisture bond with the material.

Consequently, the stronger the moisture bond, the higher the value of P_v and, on the other hand, for free water P_v can reach P_s and φ becomes equal to unity and the energy is equal to zero. In drying the moisture content of the material decreases continuously and starting from a certain moment (from the hygroscopic moisture content), the water vapor pressure over the material surface diminishes gradually, while the binding energy rises, i.e., it rises as φ falls. In the hygroscopic region the binding energy can be determined from sorption isotherms, i.e., from the relation $u_e = f(\varphi)$.

We investigated the hygroscopic properties of biological materials by the vacuum sorption method, because the popular strain-gauge technique requires a long experimentation time and can induce decomposition of the biological materials studied.

Decomposition can be accompanied by an increase in the material weight, and byproducts of the biochemical process can accumulate during experimentation. Therefore we used the vacuum sorption method to find the relation $u_e = f(\varphi)$ for biological preparations. The gravimetric method with the use of a McBain quartz balance allowed us to carry out investigations at low water vapor pressures (1.33-1333.2 N/m^2) in a fairly broad temperature range (20-90°C).

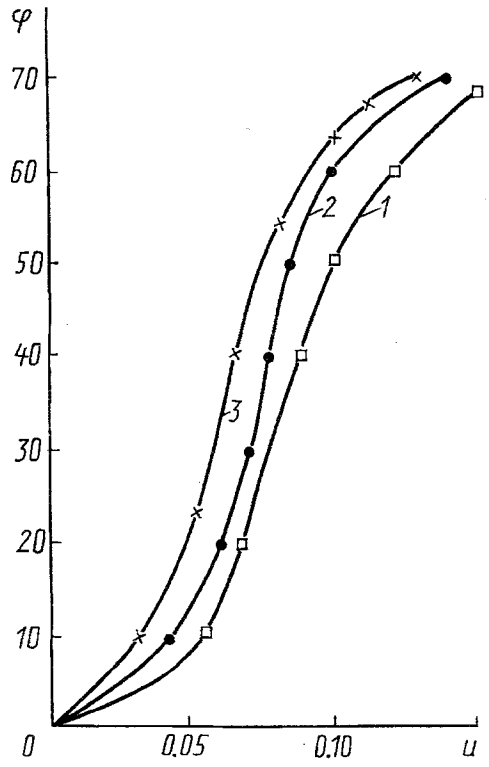

Fig. 2. Sorption isotherms for yeast: 1) 18°C; 2) 30°C; 3) 50°C. φ, %; u, kg/kg.

The scheme of the experimental setup is shown in Fig. 1. The main working part of the setup is glass cylinders 1 with ground removable lids 6 connected to springs 11, which function as a sorption balance. The springs are made of fused quartz. Specimens of the test material 21 were suspended by the quartz springs with glass filaments. The amount of sorbed moisture was recorded by the extension of the spring, determined with KM-6 cathetometer 15. The extension of the spring is equivalent to a change in the weight of the specimen. The sorption balance is highly sensitive, ensuring an accuracy of weighing within $5 \cdot 10^{-9}$ kg.

The two-stage vacuum suction system of the setup consists of roughing-down vacuum mechanical pump 12 of VN-1-2M type, N-1S-2 high-vacuum pump 13, systems of connecting pipes with a nitrogen trap, vacuum valves 22, and leaks. All joints are sealed and intended to provide and maintain a $0.13\text{-}0.13 \cdot 10^{-2}$ N/m^2 vacuum in the system.

The water vapor pressure necessary for the experiments is established by admitting a certain amount of vapor from ampoule 4, containing twice-distilled water. Air contained in the twice-distilled water was removed by freezing three times.

The pressure-measuring part of the vacuum sorption setup consisted of U-shaped mercury gauge 20, U-shaped gauge 19 filled with VKZh-4 organosilicon liquid, ionization thermocouple vacuum gauge 7 of VIT-2 type as a unit with LT-2 8 and LM-2 pressure gauges 8 and 9, and McLeod gauge 18.

The sorption cylinders are equipped with water jackets, to which water was supplied from TL-150 ultrathermostat 5 to maintain the required temperature in the cylinders.

Copper-constantan thermocouples were embedded in the working section of the sorption cylinders to control the operation of the thermostating system. In the experiments the deviation of the temperature from the preset value did not exceed ±0.5°C. Control experiments were conducted to find the effect of the temperature and pressure of the water vapor and the experimentation time on the extension of the quartz springs. These experiments were carried out with specimens made of a hydrophobic material (Teflon).

The control experiments have shown that in the range of P_v studied the value of the vapor pressure in the system has no effect on the extension of the spring, while changes in the temperature induce some extension, depending on the quality and length of the spring. This error was corrected by temperature corrections that were

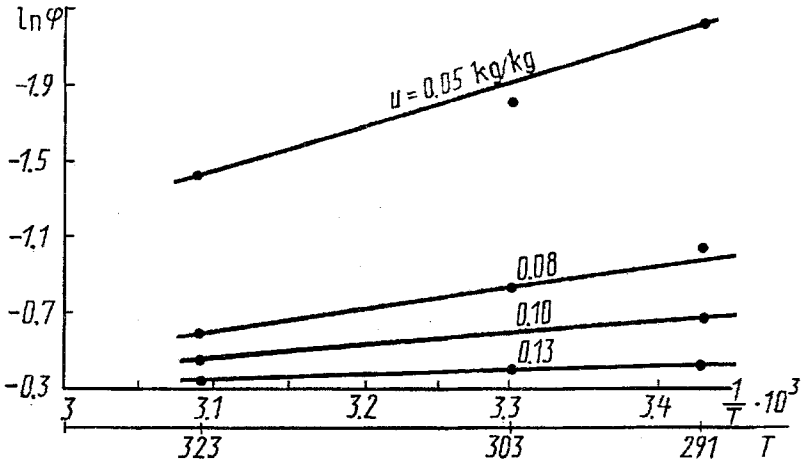

Fig. 3. Calculation of the heat of sorption. T, K.

added before and after every experiment and were included in the calculation of the moisture content of a specimen. The effect of the experimentation time on the sensitivity of the spring was determined by calibration of every spring before and after every experiment.

In the experiments the weight of the specimen dehydrated at 20-35°C and a pressure of 0.0133-0.133 N/m^2 until stabilization of the readings of the quartz springs was taken as the absolutely dry weight.

The experiments showed that the kinetic curves of water vapor sorption from microbiological preparations are similar in their general shape to kinetic curves obtained in sorption of water vapor from air at atmospheric pressure.

It should be noted that moisture absorption was more intense under vacuum than at atmospheric pressure and the same partial pressure of water vapor. This can be explained by the fact that in vacuum sorption, water vapor molecules can easily penetrate microcapillaries and be sorbed on the airfree material surface.

Sorption isotherm curves (Fig. 2) obtained in the vacuum sorption setup for yeast are described by the equation

$$u_e = u_{0.5}(T)\left(\frac{\varphi}{1-\varphi}\right)^{1/n}, \quad n = 3, \tag{1}$$

$$u_{0.5}(T) = 0.1 \exp\left(-1.65 \cdot 10^{-2}(T - T_0)\right) \quad \text{at} \quad T \le 30^\circ\text{C}; \quad T_0 = 20^\circ\text{C}.$$

If $T > 30^\circ$C, $u_{0.5} = 0.08$.

The obtained relations $u_e = f(\varphi)$ for yeast and entobacterin were used to determine the binding energy of moisture with these materials. Not only qualitative but also quantitative estimation of the binding energy is used more and more often in practical calculations of drying.

As is known, the relation between the external pressure and the liquid pressure is expressed by the equation [4]

$$\ln \frac{P_v}{P_s} = \ln \varphi = -\frac{P_w v}{RT}. \tag{2}$$

Differentiating Eq. (2) with respect to temperature for the case of constant moisture content (i.e., when $P_w v$ is independent of temperature), we obtain

$$\left[\frac{d\left(\ln \frac{P_v}{P_s}\right)}{d\left(\frac{1}{T}\right)}\right]_{u=\text{const}} = -\frac{P_w v}{R}.$$

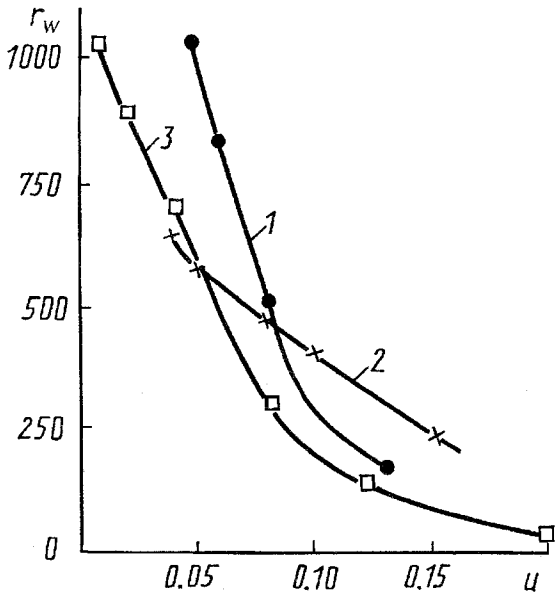

Fig. 4. Heat of sorption of yeast (1), entobacterin (2), and potatoes (3). r_w, kJ/kg.

The product $P_w v$ is the binding energy of moisture with the material.

As was mentioned above, the binding energy can be calculated from sorption isotherms. To do this, the natural logarithm ln φ for a certain moisture content is plotted versus $1/T$ and then the obtained curve is differentiated. In Fig. 3 this curve is plotted from the sorption isotherms for yeast shown in Fig. 2. The calculation results show (see Fig. 4) how much energy is required to resist the binding energy r_w for yeast (curve 1). In the same figure one can see curve 2 obtained in the same way as curve 1 for a bacterial preparation of entobacterin of a sporophyte (a preparation for plant protection). For comparison of the binding energy, curve 3 for potatoes taken from [4] is shown in Fig. 3.

In drying, cohesive forces of moisture molecules with material molecules are overcome and moisture evaporates, and therefore, in the drying process some energy is spent on the phase transformation and overcoming the binding force of moisture with the material. One can see from Fig. 4 that in the drying of microbiological materials to a final moisture content $W = 3-5\%$, the binding energy is insignificant. Therefore, in the energy balance of a drier for thorough drying of microbiological materials heat spent on overcoming the binding force of moisture with the material should be added to the heat of phase transformation.

NOTATION

P, pressure, Pa; r_w, binding energy of moisture with the material, J; R, gas constant, J(kg·K); T, temperature, °C; u, moisture content, kg/kg; v, specific volume, m^3/kg; $\varphi = P_v/P_s$, relative humidity of the medium. Subscripts: w, water; v, vapor; e, equilibrium; s, saturation.

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