MECHANISM OF INTERNAL HEAT AND MASS TRANSFER IN GELS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS BY THE USE OF RADIOACTIVE TRACERS

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Radioactive tracers have been used to study the mechanisms of internal heat and mass transfer and shrinkage, and phase composition of the transferred liquid in the process of drying of gels of high-molecular-weight compounds.

Thorough investigations of the internal heat and mass transfer and shrinkage make it possible to set up means for controlling the technological processes for the drying of various food, chemical, and biological materials under optimal conditions and for obtaining products of high quality.

The internal heat and mass transfer in high-molecular-weight organic compounds (HMCs) differs significantly from the migration of moisture in capillary-porous solids [1-3]. The material selected for investigation was agar–agar. The radioactive tracer Na_2SO_4 marked with sulfur S^{35} was introduced into this material in advance. It was held for several days in a desiccator in order to establish a constant moisture content and tracer concentration over the entire volume of the material to be investigated.

Samples of the agar–agar at an initial moisture content of ~ 13 g/g have the structure of a gel. The quantity of water absorbed in the agar is about 0.3 g/g, and the remaining moisture is osmotically bound. The radioactive tracer is also dissolved in it. The concentration of the macromolecules governs the nature of their bonding. At concentrations of up to 20%, the structure formation of the gel occurs as a result of hydrogen bonds; at larger concentrations molecular contacts also arise as a result of hydrophobic interactions. Interactions between functional groups have a considerable influence on the kinetics of structure formation during the desorption of moisture from agar–agar gels. During the removal of moisture and the increase of the concentration of the HMC the interactions between the molecules increase. This leads to an increase in the time of relaxation of the resorption of the stresses arising during drying and to an increase in the nonrelaxable stresses in the skeleton of the surface layers of the sample which is formed [4-6].

The experiments were carried out with three- and fivefold replication in an apparatus by means of which it was possible to determine during the process of moisture desorption the changes in temperature, weight of the sample, its volumetric shrinkage, and surface radioactivity. For determining the volumetric shrinkage a special device was developed; this consisted of a mercury voluminometer which made it possible to determine changes in the volume of the sample inside the drying chamber throughout the entire experimental time. On the basis of these measurements calculations were made of the rate of the relative volumetric shrinkage $\alpha = d(V/V_0)/d\tau$, the shrinkage coefficient $k = (1/V_d)dV/du$, and the coefficient $\beta = \rho_w dV/dp$. The quantity β represents the ratio of the rate of shrinkage to the rate of removal of moisture from the sample. The initial dimensions of the spherical samples were 14 mm.

From an analysis of Fig. 1 it follows that the entire drying process occurred in the variable rate period. This is also indicated by the monotonic increase of the surface temperature of the sample. The initial period of heating up the sample is small with respect to time (see Fig. 2, curves 1", 2").

In the initial stages of drying at $\phi = 0.07$ the shrinkage of the material occurs intensively and is equal to the volume of the moisture which is removed. The moisture is evaporated from the surface of the deforming sample. The coefficient of volumetric shrinkage is constant, $k = 0.415$ (Fig. 2, curve 1'), while the air does not enter into the sample, since $\beta = 1$, and the density of the sample γ increases only insignificantly (Fig. 3a, curves 1, 1').

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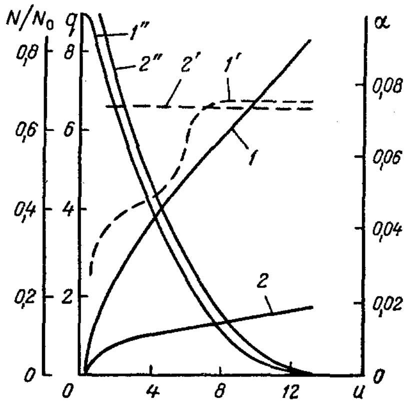

Fig. 1

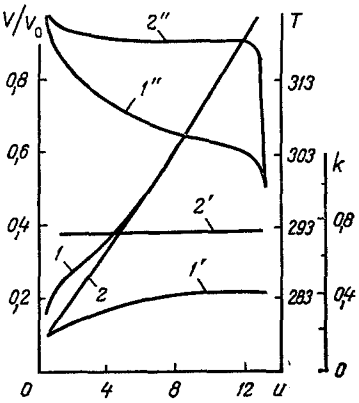

Fig. 2

Fig. 1. Curves for the rate of drying q, h^{-1} (curves 1, 2), the rate of shrinkage α (curves 1', 2'), h^{-1}, and relative radioactivity N/N_0 (curves 1", 2") of samples of agar–agar at a temperature of 323°K and relative moisture contents of the air of 0.07 (curves 1) and 0.76 (curves 2).

Fig. 2. Shrinkage V/V_0 (curves 1, 2), shrinkage coefficient k (curves 1", 2"), and surface temperature T (curves 1", 2") as functions of the moisture content of the samples. T is given in °K.

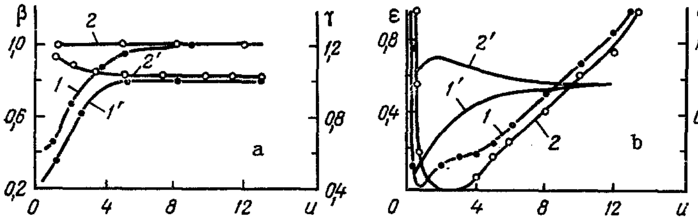

Fig. 3. Dependence of the coefficient β (curves 1, 2) and the density γ, g/cm³ (curves 1', 2') in (a) and of the phase change parameter ε (curves 1, 2) and the relative intensity of evaporation i/i_0 (curves 1', 2') in (b) on the moisture contents of the samples.

Intensive dehydration of the surface layers occurs during further drying. The concentration of the macromolecules in the surface layers increases. A dense surface skin is formed which hinders the uniform shrinkage of the sample. The rate of drying q and the relative rate of volumetric shrinkage α (Fig. 1, curve 1') decrease, the capillary pressure increases, and there is an increase in the state of bulk-stressing under the action of which the moisture is transferred from the inner layers to the surface of the sample where it is evaporated.

It should be noted that a meniscus is not formed at large moisture contents of the agar because of the low strength of the material. Menisci are formed only in the peripheral layer when this "pushes against" the strong skeleton of macromolecules being formed.

Mixed (combined) mass transfer occurs during the entire drying period, since $0 < \varepsilon < 1$ (Fig. 3b, curve 1). A surface skin is formed initially which then increases in thickness and strength with increasing time. Since the moisture content and the mobility of the macromolecules in the central layers of the material are higher than in the surface skin, the mobile macromolecules of the central layers can be transferred together with the moisture towards the surface and are deposited on the inner side of the peripheral skeleton. As a result of this cavities arise in the central part of the sample, and then continuous recesses, the volumes of which increase in the course of the drying process. The rate of drying q continues to decrease even though the internal moisture transfer during this period is characterized by maximum transfer in the liquid phase: ε is close to zero.

It can be assumed that air passes into recesses and the vapor of the liquid is removed through a system of pores and microcracks in the skeleton which are free of liquid. In this case, internal evaporation surfaces will occur. Consequently, the peripheral layer which is being formed will be under the influence of a double capillary pressure. Compaction and strengthening of the material in this layer occurs, but the density of the sample γ, which is calculated from its outside dimensions, decreases steadily (Fig. 3a, curve 1'). The presence of a double evaporation front is also indicated, in particular, by the sharp decrease in the value of the coefficient of volumetric shrinkage k and the fact that $\beta < 1$ for $u < 5$ g/g (Fig. 2, curve 1', and Fig. 3a, curve 1). On the temperature plots (Fig. 2, curve 1") no zone with a constant temperature of the material is observed. The temperature increases continuously during the entire drying period and tends towards the temperature of the surrounding medium. During the dehydration of the sample to a moisture content $u \approx 6$ g/g the temperature increases slowly (apart from the period of preheating of the material). This also indicates that as a result of the shrinkage the moisture content of the surface layer is reduced only insignificantly. During the subsequent further drying a more intensive increase of the sample temperature is observed than in the initial drying as a result of the external and internal evaporation of moisture and the decrease of the overall moisture content. A confirmation of the mechanism of the drying of agar samples given above is also provided by the plot of the ratio of the intensity of evaporation i to the initial value i_0, which decreases monotonically (Fig. 3b, curve 1').

Under milder conditions ($\phi = 0.76$) the process of dehydration of the material also occurs at a variable rate. Hence, the mechanisms of internal mass transfer are analogous during drying under both the drastic and the mild conditions, though there are also some differences in detail. The mechanism of the shrinkage and strengthening of the material also differs. As ϕ increases, the capillary pressure decreases, and the rapid dehydration of the surface layers of the material is not observed, so that under the milder drying conditions the formation of the skin on the surface of the sample occurs less intensively than at $\phi = 0.07$. The drying of the material with $\phi = 0.76$ and a uniform outside temperature occurs with a slowly falling rate and a constant relative volumetric shrinkage α (Fig. 1, curves 2, 2'). The zone from the initial moisture content to 4 g/g is characterized by a small capillary pressure and a monotonic increase in the transfer of radioactivity to the surface of the sample N/N_0. The small reduction in q also corresponds to the slow increase of the surface temperature of the sample, which slightly exceeds the wet-bulb temperature (Fig. 2, curve 2"). The small capillary pressure and the relaxable internal stress facilitate uniform shrinkage with a constant coefficient $k = 0.77$ (Fig. 2, curve 2'). When $u < 4$ g/g there is an increase in the density of the sample γ (Fig. 3a, curve 2') and a constant value of the coefficient $\beta = 1$ (curve 2). This indicates that the rate of volumetric shrinkage is equal to the rate of removal of water. During the further drying of the agar–agar, the concentration of macromolecules at the surface of the sample becomes somewhat higher than the concentration inside the sample. The intensity of evaporation increases sharply in the surface layer (Fig. 3b, curve 2') and the capillary pressure increases steadily, which leads to a "squeezing out" of the moisture with the tracer from the internal volume of the gel to the periphery, where the water evaporates. As a result of this the radioactivity of the surface increases and there is also an increase of the phase change parameter $\varepsilon \geq 0$ when $u < 4$ g/g (Fig. 3b, curve 2). The temperature of the sample increases slowly during this stage of the drying process (Fig. 2, curve 2") and tends towards the temperature of the surrounding medium. The values of the phase change parameter averaged over the entire drying period are 0.56 and 0.62 for the drastic and mild conditions of drying the agar–agar, respectively. This indicates that even at relatively low temperatures and high values of ϕ in the medium, more than a half of the moisture in the material is removed in the form of vapor. Under the mild conditions significant skin formation is not observed and internal drying cavities are not formed. The dried samples have a uniform, homogeneous structure. The samples dried under more drastic drying conditions have large internal recesses which remained in place and intersected the samples after drying.

Thus, for easily deformable high molecular weight materials such as agar–agar internal mass transfer is characterized mainly by a mixed (combined) mechanism of moisture transfer. The investigations which have been carried out using radioactive isotopes have made it possible to study in more detail the mechanisms of internal heat and mass transfer during the drying of such materials. They represent further developments of the work of A. V. Lykov [1] on the study of the mechanisms of the drying of colloidal capillary-porous materials.

NOTATION

V_0, V, V_d, initial volume of sample, volume at moisture content u, and volume of absolutely dry material, respectively; ΔP, change in mass of the moist material; ρ_w, density of water; N/N_0, ratio of the current value of the radioactivity at the surface of the sample to the maximum value at the end of drying; i/i_0, ratio of the moisture flux through the sample surface to its initial value; ϕ, relative moisture content of air.

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TEMPERATURE DEPENDENCE OF THE TRANSPORT COEFFICIENTS OF MONATOMIC GASES

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We study the range of applicability of the power-function approximation for the temperature dependence of viscosity and thermal conductivity of monatomic gases.

The temperature dependence of the transport coefficients of gases and their mixtures is often described by the power function

$$\mu(T) = \mu_0 \left(\frac{T}{T_0}\right)^n, \tag{1}$$

where the exponent n is different for different gases, and μ_0 is the value of the so-called reference point at temperature T_0. The quantity n, generally speaking, varies with temperature according to

$$n = \frac{d \ln \mu}{d \ln T}, \tag{2}$$

but in restricted temperature intervals one can, with some accuracy, use the value n = const. This dependence is used in theoretical modeling of a variant of the shock-tube method [1-4] in the measurement of the thermal conductivity of gases at temperatures 1000-6000°K (Table 1).

It was shown in [5-7] that the experimental results concerning the thermal conductivity of monatomic gases are described satisfactorily by the function (1) with n = const at high temperatures. As the temperature is lowered, however, the results deviate from this function towards higher values of thermal conductivity. From the point where this deviation starts, the limit of applicability of the function (1) was determined in [5-7] for each gas. In [8], these results were generalized to the viscosity of monatomic gases in order to obtain data at high temperatures at which no experimental investigations have been carried out. The temperatures of the reference point T_0 and the exponents n which were found in [5-7] are shown in Table 1. It should be noted that the experimental results concerning the high-temperature thermal conductivity are characterized by a large error. Consequently, the scatter of these data can affect the accuracy of determination of the parameter T_0 for the function (1).

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