COEFFICIENTS OF MASS DIFFUSION IN GRANULATED POLYMERS, INDUSTRIAL CLOTHS, AND CERAMICS WITH AN ORGANIC PLASTICIZER

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Data are presented on the coefficients of mass diffusion for a broad class of materials, derived by the method of nonsteady flow under isothermal conditions.

Data on the diffusion coefficients for a bound substance are extremely limited and cannot presently be used systematically in the calculation work of design bureaus. This is caused by certain methodological difficulties which arise in the course of experiments, as well as by the absence of a corresponding standard apparatus which permits reliable determination of these coefficients.

Analysis of the known methods of determining the mass-diffusion coefficients a_m [1-8], as well as earlier experiments, have pointed to the possibility of using the Luikov [1] method of nonsteady moisture flow under isothermal conditions for this purpose, with the use, according to [9], of the following modified formula in the calculations:

$$a_m = \frac{\pi}{\tau}\left[\frac{M_s}{2(u_0 - u_b)\gamma_0}\right]^2. \qquad (1)$$

The basic procedural elements for these experiments are described in [10], with the methodological features based on consideration of the specifics of the test materials and the need for properly satisfying the experimental conditions which follow from the solution of the heat-conduction problem for a system of two semi-infinite bodies for boundary conditions of the fourth kind, as well as for the maintenance of isothermal conditions in the experiment. Particularly important is the proper choice of geometric dimensions for the containers housing the test materials, since the duration of the experiments may differ substantially, depending on the initial parameters of the specimens and the control standard. Initially we compared the times τ_{st} during which the specified steady temperature field was actually established through the cross section of the materials (the test material and the control standard) with the time τ_{ex} of the experiment to satisfy the obvious condition $\tau_{ex} \gg \tau_{st}$. The experimental error is thus reduced to a minimum.

The experiments showed us that from the standpoint of moist granulated polymers with $d_{eq} = 3.4$-4.0 mm it is most efficient for the demountable copper beaker with a diameter of 40 mm and $h = 124$ mm to be cylindrical in shape. A special device was used to sample the granular material at various levels; it involved the use of a small circular spatula adjusted with a micrometer screw, thus making it possible to sample the disperse material through the height of the charge.

As regards the determination of the diffusion coefficients for industrial paraffin in the dross of high-frequency ceramics (SK-1 steatite used extensively in practice), we find that unique conditions prevail. As is well known, the transfer of mass takes place between semifinished products fabricated of high-frequency ceramics and the adsorbent cannot be regarded as the simple runoff of the paraffin binder into the adsorbent exclusively under the action of gravitational forces [11, 12]. The process of mass transfer for an industrial binder in this case can be written as follows:

$$q_m = -a_m \gamma_0 \nabla u - D\gamma_0 \nabla P. \qquad (2)$$

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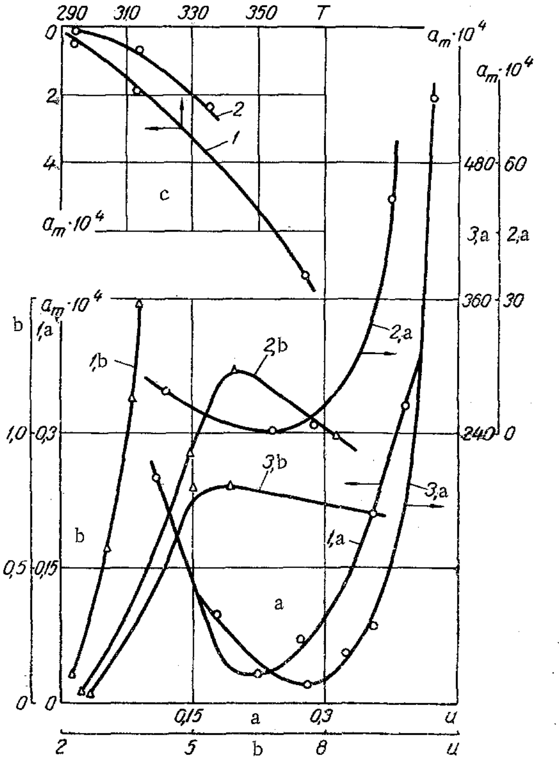

Fig. 1. The moisture-diffusion coefficient a_m (m^2/h) in a charge of granulated polystyrene (a) (curves 1, 2, and 3, respectively, for T = 293, 313, and 363°K) and for granulated capron (b) (curves 1, 2, and 3, respectively, for T = 363, 313, and 293°K) as a function of their moisture content u (%), as well as the a_m of the filter paper as a function of the temperature for a moisture content of u = 0.05 kg/kg (curve 1, the authors' data) and 0.1 kg/kg (curve 2, the data from [15]) (c).

We can therefore provide for uniquely defined conditions of mass transfer in a dross–standard system when the system is contact under isothermal conditions. If the process proceeds with intensities not too great – when the specific-pressure gradient is small and can be neglected – it proved possible to employ the above-indicated method of determining the diffusion coefficient for the bound material. Here we would point out that the transfer of mass between the dross and the adsorbent (the control standard) without preliminary heating of the latter, as shown experimentally, proceeds at a relatively low intensity [13].

As regards a system consisting of a thermoplastic material (SK-1 dross) and the control standard, we found the optimum geometric beaker dimensions to be a diameter of 25 mm and h = 110 mm. The latter must be designed in a demountable configuration in the longitudinal plane of the cylinder. The specimens were first poured out in the form of cylinders 25 mm diameter and h = 55 mm, with various initial paraffin mass contents. Filter paper was used as the control standard. Determination of the boundary, middle, and end layers in these specimens presented no difficulties, since the materials at these heating temperatures cut easily.

Figure 1a shows the diffusion coefficient for the moisture in a charge of granulated polystyrene as a function of the material's moisture content and temperature. As follows from the figure, the curves exhibit extrema near u = 0.25%.

As a model of a colloidal material we can use one with numerous micropores of molecular dimensions, which is actually characteristic of a wide range of polymer granulates consisting of high-order polymer chains [1, 14]. In this connection, the nature of the change in a_m in the charge of granulated polystyrene must be recognized as valid.

The nature of the relationship $a_m = f(u, T)$ in a charge of granulated capron (Fig. 1b) has a form that is typical for colloidal capillary-porous materials. The singular point on the curves corresponds to the instant at which the internal microstructure of the polymer is saturated with moisture.

Mass transfer takes place not only in the complex quasicapillary granulate system, but (with an increase in the material's moisture content) in the manner of selective diffusion, which governs the characteristic reduction in a_m.

On the basis of the method developed in [8] for the generalization of the experimentally derived data on the moisture-diffusion coefficients a_m we constructed derivative curves which enabled us successively to find functional relationships of the form

$$1/a_m = f(u,\ T);\quad a_0/a_m = f(u - u_{ex});\quad a_0 = f(T)$$

and from these derive generalized empirical relationships of the form

$$\frac{a_0}{a_m} = 1 \pm k(u - u_{ex}) \tag{3}$$

for ranges of variation in moisture content in the polystyrene $0.27 \le u \le 0.40\%$ and in granulated capron $2.5 \le u \le 4.50\%$, which are of practical value.

The quantity a_0 corresponds to the value of a_m when $u = u_{ex}$, where u_{ex} is the moisture near the extremum on the curves $a_m = f(u, T)$, equal to 0.27 and 2.5%, respectively, for polystyrene and granulated capron.

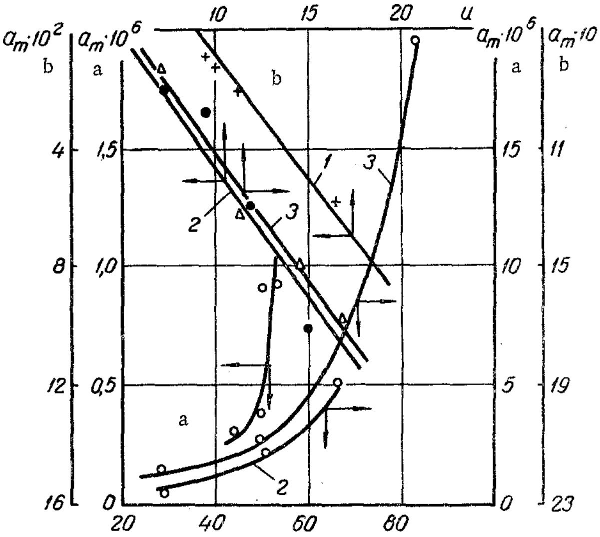

Fig. 2. The diffusion coefficient a_m (m^2/h) for industrial paraffin in filter paper as a function of its mass content u (%) (a) and of the dross mass content u (%) (b): 1) T = 333°; 2) 363°; 3) 393°K.

The quantity a_0 is a function exclusively of the material properties and of the absolute temperature:

$$a_0 = m \left(\frac{T}{1000} \right)^n . \tag{4}$$

The constants in (3) and (4) for the polystyrene are equal to: k = -9.3; m = $7.6 \cdot 10^5$; n = 20; and for the capron: k = -0.52; m = $1.58 \cdot 10^7$; n = 4.

Figure 2b shows the experimental results from the determination of the diffusion coefficient for industrial paraffin in the SK-1 dross (steatite). In the relatively wide range of dross mass content the relationship $a_m = f(u, T)$ proved to be linear, thus enabling us to obtain a generalized empirical relationship

$$a_m = ku + nT - 0.7, \tag{5}$$

in which k and n are empirical coefficients, respectively, equal to 0.0087 and 0.0018. The formula is valid for $9 \leq u \leq 17\%$ and $335 \leq T \leq 400°K$.

This series of experiments also enabled us to find a number of other mass coefficients for materials of practical significance.

Figure 1c shows the relationship for the moisture-diffusion coefficient a_m in the case of filter paper with a specific moisture content of u = 0.05 kg/kg over a wide temperature range ($293 \leq T \leq 370°K$). It should be pointed out here that the comparison of published data with respect to a_m for filter paper in the range $0.1 \leq u \leq 0.3$ and $293 \leq T \leq 333$ [15] with our data showed excellent agreement from the standpoint of the physics of the process.

Figure 2a shows the graphical relationship between the paraffin diffusion coefficient in filter paper in the form $a_m = f(u, T)$. In this case we find a strong relationship between a_m and the absolute temperature of the material, this relationship reflecting the significant change in the viscosity properties of the industrial paraffin with a change in the temperature of the latter.

We know of no data in the literature on the moisture-diffusion coefficients in industrial cloths used in the paper industry. Nevertheless, for meaningful calculations of the rapid processes of contact heat and mass transfer in a cloth–paper system the knowledge of these coefficients is vital [16].

Experiments to determine a_m were conducted with various types of cloths used extensively in actual practice: cotton terry cloth with $\gamma = 2440$ g/m^2 and wool with $\gamma = 1840$ g/m^2. From an experimental standpoint, in this case it proved more convenient to use the demountable measuring cylinder consisting of two equal parts connected by a special threaded sleeve (Fig. 4b). We thus avoid the substantial errors in determining the amounts of moisture moving through the contact area of the test materials. The use of demountable cylinders of a light metal permits the direct determination of the mass in each half with an analytical balance.

As before, the experiments were carried out in a water ultrathermostat at temperatures of t = 50 and 90°C. The duration of the experiment during which the moisture content at the ends remains constant was determined in preliminary tests and, depending on the initial moisture content and temperature, came to $\tau = 0.5$-4 h.

The moisture content of the cloths being tested was less in each of the experiments than the maximum hygroscopic values.

The initial moisture content of the control standard (the filter paper) varied from 5 to 7%, depending on the parameters of the ambient medium (φ_m, t_m). The experimental results are shown in Figs. 3 and 4.

As we can see from the curves, the diffusion coefficient a_m as a function of moisture content for the two types of cloths are similar and characterized by the existence of a maximum which exhibits a tendency to shift slightly toward the lower moisture contents with a rise in temperature.

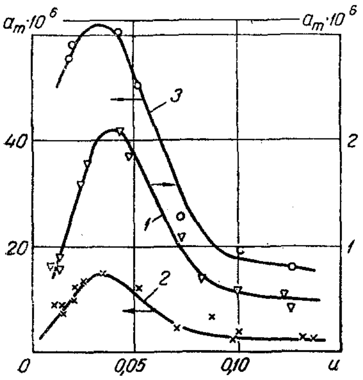

Fig. 3

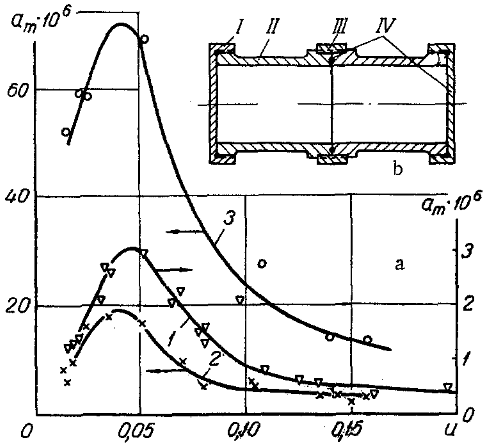

Fig. 4

Fig. 3. The moisture-diffusion coefficient a_m (m^2/h) in cotton cloth as a function of its moisture content u (kg/kg): 1) T = 291°; 2) 323°; 3) 363°K.

Fig. 4. Moisture-diffusion coefficient a_m (m^2/h) in wool as a function of its moisture content u (kg/kg) (a) (curve 1, 291°; curve 2, 323°; curve 3, 363°K) and the measuring cylinder for the determination of a_m (b) (I, cover; II, cylinder; III, sleeve; IV, rubber spacers).

This type of curve can be explained by analyzing the physicochemical properties of the fibers in the test materials, since it is these which determine the manner in which the moisture is bound to the cloths, and also the structural-mechanical features of the latter.

Cotton and wool are natural fibers. In terms of their physicochemical structure, they are amorphous-crystalline materials. According to the concepts of cohesive structure in fiber materials, these are made up of segments (micelles) formed by clusters of molecules of various dimensions and degrees of crystallinity, linked to each other by common molecular chains.

An industrial fiber represents a cluster of elementary fibers. Cotton and wool fibers can be treated as a porous medium exhibiting a tremendous surface area. In cotton fibers, for example, the pore volume makes up 35-40% of the fiber volume [17], while the magnitude of the inside surface of a wool fiber is approximately 10^6 cm^2 per 1 g of wool [18]. The substantial magnitude of the inside surface of natural fibers governs their high adsorptivity of moisture which, in contact with fibers, first of all, penetrates into the spaces between the crystallites (micelles), producing molecular swelling, and the moisture then enters into some interaction with the micelles themselves.

The transfer of mass between the cloth and the control standard results from two processes – moisture adsorption by the fibers and moisture diffusion into the depth of the cloth, resulting from the difference between the partial vapor pressures of the cloth and the standard. The diffusion of mass in the pores is a substantially slower stage of the process than the actual adsorption occurring at the contact surface of the cloth and governs the kinetics of the process. In the general case, moisture diffusion in a cloth can proceed as follows: through the pore space which is governed by the fabric structure; along the pore surfaces; and through the very fibers of the cloth, exhibiting high hygroscopicity. The molecular mean free path of the water vapor at standard barometric pressure and normal temperature for the cloths is of the order of 10^{-5} cm.

We used the Dumanskii [19, 20] method to determine the pore diameters for cotton and wool cloths; this method is based on the fact that the liquid distribution through the height of a pore system drawing in moisture from any type of vessel depends on the number of capillaries which make up this system, and on the radii of these capillaries, which are of the order of 10^{-3} cm. Consequently, we can assume normal vapor diffusion through the cloth.

We know [1] that with diffusion transfer in the hygroscopic range of moisture contents under isothermal conditions, the diffusion coefficient as a function of the moisture content can be determined by $(\partial\varphi/\partial u)_T$ which is proportional to the slope of the tangent to the sorption isotherms of the materials.

Analysis of the sorption isotherms for cotton and wool [15, 18] revealed that they exhibit the S-shaped form typical of colloidal capillary-porous bodies. The initial isotherm segment exhibits the convexity of the curve toward the moisture-content axis that is characteristic of monomolecular adsorption, and the quantity $(\partial\varphi/\partial u)_T$, proportional to the slope of the tangent to the sorption isotherm of the material, increases with an increase in u.

According to [1], the transfer of matter (by vapor diffusion for the most part) corresponds in Figs. 3 and 4 to the range of moisture contents under consideration, and as a result a_m increases with a rise in u to some maximum. For cotton cloth the latter is near the moisture content u = 0.03-0.04 kg/kg, which is also in agreement with the indirect data of [17] for cellulose fibers (cotton). Wool exhibits a higher sorption capacity than cotton. The bound material in wool penetrates not only into the spaces between the crystallites, but into the crystallites themselves [18, 21]. It is probably by means of these features of wool fibers that we can explain the slight shift in the maximum on the $a_m = f(u, T)$ curves in Fig. 4 toward moisture contents higher than in cotton cloth.

At moisture contents approximately corresponding to polymolecular adsorption the sorption isotherms for wool and cotton are convex to the axis of ordinates (the moisture content of the air). The quantity $(\partial\varphi/\partial u)_T$ diminishes with a further rise in u. The subsequent range of moisture contents in which the fraction of matter transported in the form of liquid increases corresponds to this phenomenon in Figs. 3 and 4. The coefficient a_m diminishes with an increase in u.

Experimental data on moisture-diffusion coefficients in industrial cloths were processed according to a method described in [8] for a range of variation u = 0.05-0.15 kg/kg of cloth moisture content.

As a result of this procedure, we derived formulas in the form of (3), in which, for the case under consideration, $u_{ex} = 0.05$.

The coefficient a_0 as a function of temperature has the form

$$a_0 = m\left(\frac{T}{273}\right)^n.$$

For cotton cloth the constants in (3) and (4') are equal to $k = 36.2$; $m = 0.725 \cdot 10^{-6}$; $n = 15$; and for wool they are equal to $k = 45$; $m = 1.12 \cdot 10^{-6}$; $n = 15$.

It should be pointed out in conclusion that these values for the coefficient n in (4) and (4') apparently reflect the physicochemical and structural–mechanical features of the materials being investigated, and in analogy with the data in [8], in first approximation, can be extended to other similar materials.

NOTATION

a_m	is the mass-diffusion coefficient;
D	is the mass-diffusion coefficient governed by the vapor-pressure gradient;
M_s	is the quantity of matter moved during the time τ per unit area of contact between the test material and the control standard;
q_m	is the mass flux density;
T	is the absolute temperature;
u_0, u_b	are, respectively, the mass content of the material, initially and at the boundary;
γ_0	is the density of the dry material;
∇P	is the vapor-pressure gradient;
∇u	is the gradient of the specific mass content.

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