DISTRIBUTION OF MOIST AND DRY PORES IN A MOIST POROUS MATERIAL (A PROBABILITY MODEL)

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We propose a model and a method for the calculation of the concentrations of completely fluid-filled, partially moist, and dry pores in a moist porous material. The method is based on the probability approach in which the distribution of fluid in pores is accomplished by means of "scattering" through the pores in random fashion of quantities of fluid whose volume is dependent on the wetting angle.

When a porous material is saturated to a moisture content ω a portion of the pores may remain dry. As ω increases the fraction of dry pores diminishes and when $\omega = 1$ it is equal to 0. Krisher has introduced the function $b(\omega)$ equal to the ratio of the moist-air volume V_{ma} in a porous body to the entire volume of air within the pores [1]:

$$b = \frac{V_{ma}}{V_{ma} + V_{da}} . \tag{1}$$

He makes use of this function in his model to calculate the thermal conductivity of moist materials. This is shown graphically in Fig. 1. Based on the data derived by Krisher [1], the function $b(\omega)$ from [2] was approximated by the relationship

$$b(\omega) = 1 - \exp(-7\omega). \tag{2}$$

A fundamental drawback of this method is the fact that the numerical values for the function $b(\omega)$ derived by Krisher through solution of the reciprocal problem for the thermal conductivity of moist materials, i.e., in using the experimental data on thermoconductivity, he substituted these data into his moist-material model which was comprised of a collection of plates oriented parallel and perpendicular to the flow of heat, and he determined the values of $b(\omega)$. Thus an error generated by the model itself was introduced into the calculation.

The approximation formula (2) does not satisfy the limit transition for the case in which $\omega = 1$, since in this case b must be equal to 1, nor has its dependence on the wetting angle ϑ been taken into consideration.

Let us determine the fraction of the moist and dry pores for a given moisture content, utilizing the probability approach. With this in mind, we will represent a porous body in the form of a collection of a large number of cells in communication with each other. The process of saturating the material with moisture will be treated as the "scattering" in random fashion, through the cells, of quantities of fluid with a volume v_f. In this connection we make only one assumption, namely: any number of such individual quantities of fluid may enter any given cell. This will be valid provided that v_f will be smaller than the pore volume v_{por} of a single cell. The validity of this assumption in the case of small ω is obvious, since in this case the probability of multiple entry into a single cell will be infinitesimally small (the number N of cells is infinitely large). However, if the moisture content is sufficiently large, the moist cells will be in contact with each other and therefore, when a particular quantity of fluid enters a cell the fluid will spread out over the entire cluster of moist cells.

Let us introduce the quantity γ which represents the fraction of the number of dry cells and let us also introduce the quantity β which is the ratio of the number n of events to the entire number N of cells in the system. Let us first take a look at the dry material ($\gamma = 1$) and project n_1 events as a result of which the fraction $\gamma(\beta_1)$ of cells will remain dry. We will then project an additional n_2 events. Since the events occur in a random manner, on the average the quantities of moisture entering the moist cells will be proportional to the fraction of moist and dry cells, and the fraction of dry cells after the second series of events will become equal to

$$\gamma(\beta_1 + \beta_2) = \gamma(\beta_1)\gamma(\beta_2). \tag{3}$$

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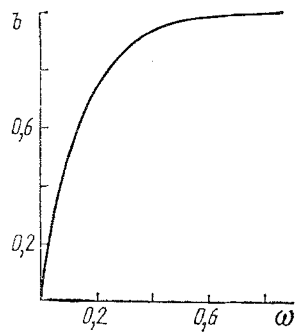

Fig. 1. Ratio of the moist-air volume in a porous body to the entire volume of air in the pores, as a function of the moisture content [1].

We know that the function satisfying (3) has the form

$$\gamma(\beta) = Ca^{p\beta}. \tag{4}$$

Let us determine the constants C, a, and p. When $\beta = 0$, γ is equal to 1 and, consequently, C = 1. When $\beta \ll 1$, the function $\gamma(\beta)$ must equal $1 - \beta$ since in this case the probability of entering (repeatedly) a single cell is negligibly small. If we expand $\gamma(\beta)$ in series, we can write

$$\gamma(\beta) = 1 + p\beta \ln a. \tag{5}$$

When we take into consideration that in this case $\gamma(\beta) = 1 - \beta$, we will express p from (5):

$$p = -\frac{1}{\ln a} \tag{6}$$

and we will substitute into (4)

$$\gamma(\beta) = a^{-\beta/\ln a} = \exp(-\beta). \tag{7}$$

We will write the expression for the moisture content ω:

$$\omega = \frac{n v_{\text{f}}}{N q_{\text{por}}} = \beta\omega_0, \tag{8}$$

where ω_0 is the moisture content equal to the ratio of the volume of fluid in a single event to the pore volume within the cell. Using (7) and (8) we obtain

$$\gamma(\beta) = \exp\left(-\frac{\omega}{\omega_0}\right). \tag{9}$$

Formula (9) must satisfy the following limit transitions: $\gamma = 1$ for $\omega = 0$ and $\gamma = 0$ for $\omega = 1$. We might take note of the fact that the second condition will be satisfied only in the event that ω_0 tends to 0. As a result $\gamma(\omega)$ degenerates into the function

$$\gamma = \begin{cases} 1 \text{ when } \omega = 0, \\ 0 \text{ when } \omega \neq 0, \end{cases} \tag{10}$$

which in turn presupposes the total absence of dry pores when $\omega \neq 0$. This circumstance was utilized in the construction of a model for moist porous materials in [3], where it was assumed that all of the pore cells had been filled in identical uniform fashion with moisture. We can make use of this assumption only in the case of small wetting angles, when it serves a useful function for the fluid to wet as large an area as possible of the surface of the pore space. In the case of large wetting angles, where the fluid does not wet the surface of the pores, the assumption with respect to uniform distribution of fluid through the pores becomes invalid. In particular, it was demonstrated in [4] that when $\vartheta \geq 150°$ the fluid is distributed through granular material in the form of individual batches.

Let us now imagine that ω_0 is not an infinitely small quantity. This will lead to a situation that in a system with an increasing moisture content ω the number of cells entirely filled with fluid will increase as well. Consequently, the fraction of cells over which the moisture can be distributed is reduced.

Let us introduce the following quantities: $\alpha = N_{fil}/N$ is the fraction of cells entirely filled with fluid; $\sigma = N_m/N$ is the fraction of cells that are moist but are not entirely filled with fluid. These quantities satisfy the equation

$$\alpha + \sigma + \gamma = 1. \tag{11}$$

We can also write the following expression:

$$\omega = \alpha + \tilde{\omega}\sigma, \tag{12}$$

where $\bar{\omega}$ is the average moisture content of the fluid in the moist cells. For the sake of simplicity we can assume that $\bar{\omega} = \omega$.

Let us assume an infinitely small number dn of events. In this case $(1 - \alpha)$ will not change and in analogy with (3) we can write

$$\begin{gathered} \gamma(\beta + d\beta) = \gamma(\beta)\,\gamma(d\beta), \\ d\beta = \frac{dn}{N(1-\alpha)}. \end{gathered} \tag{13}$$

With consideration of (13) the differential $d\gamma$ will be as follows:

$$d\gamma = \gamma(\beta + d\beta) - \gamma(\beta) = \gamma(\beta)\,\gamma(d\beta) - \gamma(\beta) = \gamma(\beta)(\gamma(d\beta) - 1). \tag{14}$$

Here

$$\gamma(d\beta) = \gamma(dn) = \exp(-d\beta) = \exp\left(-\frac{dn}{N(1-\alpha)}\right). \tag{15}$$

Let us expand γ(dn) in series and limit ourselves to the first term of the series

$$\gamma(dn) = 1 - \frac{dn}{N(1-\alpha)}. \tag{16}$$

When we substitute (16) into (14) we have

$$d\gamma = -\gamma\,\frac{dn}{N(1-\alpha)}. \tag{17}$$

From (11) and (12) let us express α as follows:

$$\alpha = \frac{\omega\gamma}{1-\omega}. \tag{18}$$

Utilizing (8), we will make the substitution

$$\frac{dn}{N} = \frac{d\omega}{\omega_0}. \tag{19}$$

Substituting (18) and (19) into (17) yields

$$d\gamma = -\frac{\gamma\,d\omega}{\omega_0\left(1 - \frac{\gamma\omega}{1-\omega}\right)}. \tag{20}$$

We derived an ordinary first-order differential equation with the following initial condition:

$$\gamma(0) = 1. \tag{21}$$

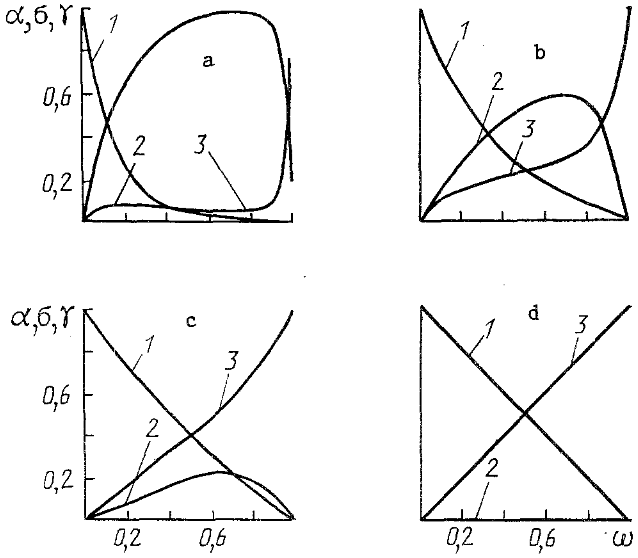

Fig. 2. The concentration of dry, partially moist, and completely fluid-filled pores (curves 1, 2, 3) as functions of the moisture content at various wetting angles ϑ: a) $\vartheta = 0$, $\omega_0 = 0.16$; b) $\vartheta = 45°$, $\omega_0 = 0.41$; c) $\vartheta = 90°$, $\omega_0 = 0.72$; d) $\omega_0 = 1$.

The quantity ω_0 can be selected on the basis of considerations such that in the entry of the fluid into the cell it has the possibility of becoming distributed over all of the cells formed into a single cluster. The minimum value of ω_0 in this case will be equal to the first critical moisture content $\omega_0 = \omega'$ [3]. For wetting angles equal to 0, 45, and 90°, the values of ω' will equal, respectively, 0.16, 0.41, and 0.72.

Equation (20) with initial condition (21) was solved numerically on a computer. The results from the calculation of the relationships between ω and γ, α, and σ can be seen graphically in Fig. 2. The fraction γ of dry cells as a function of ω diminishes monotonically, and this rate of diminution depends on ϑ. The fraction of moist cells will be nonmonotonic in nature. When the moisture content changes from zero signal will increase to some maximum value and it will then drop down to zero when $\omega = 1$. This is explained by the fact that in the case of low moisture content as a result of the filling of the cells with moisture the fraction of moist cells increases due to the reduction in the fraction of dry cells, and the number of cells entirely filled with moisture in this case is insignificant. As ω increases, the fraction of filled cells will increase, and as a result of this the fraction of moist cells begins its reduction down to zero. The maximum fraction of moist pores with an increase in the wetting angle ϑ will shift in the direction of lower values of ω.

For purposes of verification we undertook a calculation with $\omega_0 = 1$. In this case, there will exist within the system only two types of cells: dry and those that are entirely filled. The dependence of γ and α on ω must be linear. In this case,

$$\gamma = 1 - \omega, \quad \alpha = \omega, \tag{22}$$

which is fully confirmed by calculation (Fig. 2d).

In conclusion, let us note that the derived result can be utilized in the calculation of the conductivities (thermal conductivity, electrical conductivity, etc.) for moist porous materials in the case in which it becomes necessary to take into consideration the distribution of the fluid in the pores as a function of the wetting angle.

NOTATION

ω, volumetric moisture content of the fluid; ω', critical value of the moisture content; b, ratio of moist-air volume in the pores to the entire volume of air in the pores; ϑ, wetting angle, deg; v_ℓ, volume of the elementary portion of fluid, m^3, v_{por}, pore volume, m^3; N, number of cells; n, number of events; α, σ, γ, concentration of pores entirely filled with fluid, partially moist, and dry, in a porous material.

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THE P-ρ-T DEPENDENCE OF DIETHYL SUCCINATE

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We have derived experimental results with respect to the P-ρ-T dependence of diethyl succinate. Based on these results we have compiled an equation of state which allows us to calculate the thermal properties of the material.

Diethyl ethers of succinic acid are used extensively in the chemical industry for the production of dyestuffs, alkyd resins, succinates, light-sensitive materials, etc. However, the literature contains inadequate information with respect to the thermophysical properties of these materials. With this in mind, we undertook an investigation into the P-ρ-T dependences of diethyl succinate at pressures of 0.1-49.1 MPa and temperatures ranging from room temperature to 500 K. The substance tested to a total chemical purity of 98.6%.

The measurements were carried out by means of a hydrostatic suspension method with a maximum error of 0.1% over the entire investigated range of parameters of state. A new experimental setup was designed and constructed for the purposes of this study, and it made use of elements from other experimental units designed by the authors [1, 2]. This unit differs from the ones with which we are familiar in that the sensor coil is positioned outside of the medium being studied, thus making it possible to simplify its operation and to raise operational reliability.

The elements of the suspension system were calibrated by a method of hydrostatic suspension in water (bidistillate) with the aid of VLA-200G-M-type analytical balances, using the method familiar from [3-5]. The parameters of the elements of this suspension system (the volumes) were as follows: a silver steel core 0.4210 cm^3, the filament 0.0047 cm^3, and a solid quartz float 2.8173 cm^3. In a vacuum the system weighed 9.5253 g.

The density was measured from the isotherms. Nine isotherms yielded 58 experimental density values, each of which is the result from the averaging 3-4 multiple measurements. These quantities have been tabulated in Table 1. The literature provides information with respect to density at 20°C for diethyl succinate [6], and these are in agreement with our data with an error of 0.1%.

The temperature of this material was measured during the experiments by means of a platinum resistance-type PTS-10 thermometer of the first category, in conjunction with a U-309 potentiometer unit.

Pressure was generated and measured by means of an MP-600 type piston manometer of the 0.05 class. In order to separate the oil of the piston manometer from the material being tested in the compression vessel, we made use of a thin-walled Capron (polycaprolactam resin) tube out of BF-6 cement whose sensitivity was 0.0001 MPa. The material of the divider was inert with respect to the substance being tested. This was verified by suspension of the tube prior to and subsequent to the measurement.

Analysis of the experimental material demonstrated that for the given substance the following equation of state is most appropriate [7, 8]:

$$P = A(T/T_{\text{boi}})\rho^2 + B(T/T_{\text{boi}})\rho^8, \tag{1}$$

where P is the external pressure, MPa; T is temperature, K; ρ is density of the liquid, g/cm^3; T_{boi} is the normal boiling point; $A(T/T_{boi})$ and $B(T/T_{boi})$ have been calculated by the method of least squares for each of the isotherms and described analytically in the form of the T/T_{boi} polynomial:

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