THE INFLUENCE OF ADSORPTION FILMS UPON THE EVAPORATION OF WATER FROM THIN CAPILLARIES

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The contribution of surface transfer via a polymolecular adsorption film to the evaporation of water from quartz capillaries was measured. The results showed quantitative agreement with the theory of transfer based on experimentally observed isotherms of adsorption for plane surfaces.

Measurements of the evaporation of water from individual cylindrical capillaries (d = 1-50 μ) drawn from quartz glass (99.99% SiO_2) have shown that mass transfer occurs not only in the gas phase but also in the liquid film on the surface of capillaries [1-3]. The kinetics of water evaporation from capillaries is characterized by curves $1/v = f(x)$ which are shown in Fig. 1. Evaporation took place in an evacuated chamber in which a certain relative vapor pressure p_0/p_s was maintained by the McBain technique. The flow of vapor in the capillaries corresponds in this case to the interval 0.1-10 of the Knudsen number $K = \lambda/d$. For this interval, the transition from viscous to molecular flow, a vapor-transfer equation was obtained in [4]. The dashed line in Fig. 2 was calculated from this equation [4] and indicates the dependence of the

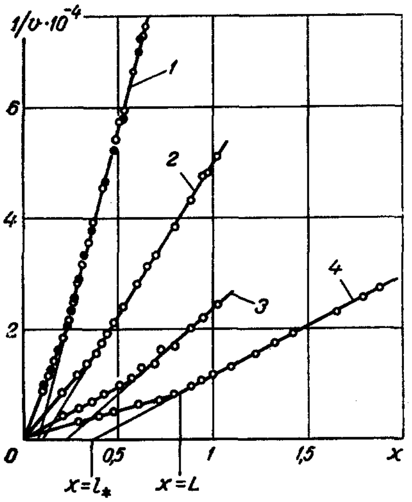

Fig. 1

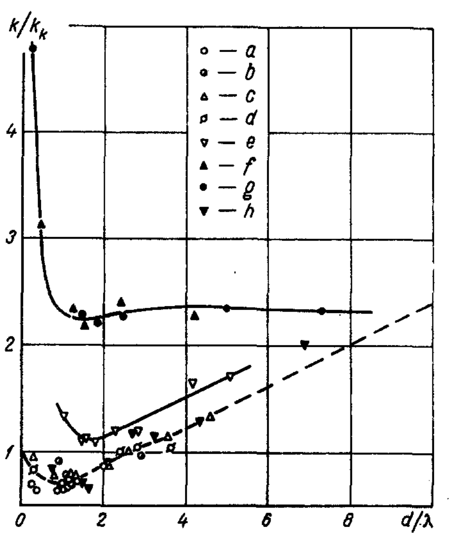

Fig. 2

Fig. 1. Experimentally obtained functions $1/v = f(x)$ for water evaporation from quartz capillaries of $p_0/p_s = 0.97$ and $t = 20.9°C$ (x cm; $1/v \cdot 10^{-4}$ sec/cm): 1) d = 2.3 μ; 2) 7 μ; 3) 13 μ; 4) 22 μ.

Fig. 2. Dependence of the permeability coefficients upon the inverse Knudsen number; the functions were obtained from observations of water evaporation from quartz capillaries; x > L: a) $p_0/p_s = 0$; b) 0.59; c) 0.64; d) 0.75; e) 0.86; f) 0.97; g) 0.985; h) hydrophobized capillaries with $p_0/p_s = 0.86-0.91$. The dashed line denotes the calculations which were made according to [4] for vapor flow.

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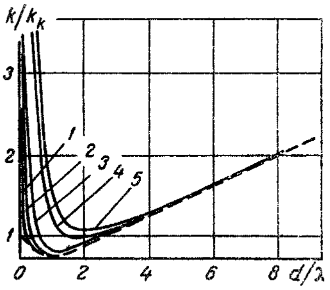

Fig. 3. Dependence of the permeability coefficients upon the inverse Knudsen number; calculations with Eq. (3) and the experimental adsorption isotherm of Eq. (4): 1) $p_0/p_s = 0$; 2) 0.5; 3) 0.86; 4) 0.98; 5) 0.99; the dashed line represents the calculations for vapor flow according to [4].

relative permeability coefficient k/k_k upon $1/K$, the coefficient characterizing the average vapor pressure in the capillaries. The k values which appear in the mass-transfer equation

$$v = (k/\rho)\ (\Delta p/x), \tag{1}$$

are shown in Fig. 2 where they are expressed as a ratio to the permeability coefficient $k_k = (4d/3)\ (\mu/2\pi RT)^{1/2}$ for molecular flow.

The goal of our investigations was to compare experimental data with transfer theory, which describes the flow of vapor in capillaries. The simple geometry of the porous space of capillaries allowed this comparison (which is not possible in the case of porous bodies) with high accuracy. But before proceeding to the comparison, we must discuss the possible mass-transfer mechanisms arising from an analysis of the measured evaporation rates. As can be inferred from Fig. 1, the mass-transfer rates agree with Eq. (1) only for $x < L$. For $x > L$, the curves $1/v = f(x)$, become linear and cut off sections l_* on the abscissa. This anomaly of the evaporation has been explained in [2]. It was assumed that for $x < L$, there remains a wetting film behind the receding meniscus, and the length l of this film increases in proportion to x. When a certain limiting value $l = l_*$ has been reached, the length of the wetting film section becomes stable, which, in turn, reduces the evaporation rate and changes the slope of the curves $1/v = f(x)$ at $x = L$.

Experimental and theoretical k_1 values were compared in [1] for the first section of the curves $1/v = f(x)$, i.e., for $x < L$. Here we make a comparison of the second section of the evaporation curves, i.e., for $x > L$. The mass transfer is in this case the same as [2]. The surface of the capillary near the meniscus is covered by a wetting film over the length of the section $l_* = \text{const}$. Since the mass transfer involves mainly the liquid phase in the section l_*, the evaporation is shifted over the distance l_* closer to the mouth of the capillary. The experimental values of the permeability coefficient are therefore obtained with the equation

$$k_2 = \rho v (x - l_*) / (p_* - p_0), \tag{2}$$

for $x > L$, where $(x - l_*)$ denotes the distance between the mouth of the capillary and the point of evaporation.

The k_2 values obtained in this fashion are much greater than the theoretical values calculated with an equation of [4]. It is possible that an additional transfer of liquid occurs in a thin polymolecular film which covers the entire surface of the capillary from the end of the section with the wetting film to the mouth. The discontinuous transition occurring at $p = p_*$ from a thin wetting film to a thinner adsorbed film is a consequence of the instability of water films in a certain thickness interval [5, 6]. The step-like change in the thickness of the water film on quartz has been confirmed recently by direct microscopical observations in which the polarimetric technique was employed [7].

Figure 2 is a comparison of the theoretical k values (dashed line) with the experimental values (dots) calculated with Eq. (2). The first group of experimental points (a-d) refers to vapor pressures which are far from the saturation pressure in the chamber ($p_0/p_s \leq 0.75$). The points are grouped close to the dashed line which corresponds to the theoretical calculations of [4]. Since for $p_0/p_s < 0.75$, the adsorption of water on the surface of quartz does not exceed a monolayer [5], the contribution of surface flow is not noticeable for all practical purposes. The experimental results are in good agreement with the theoretical values, which confirms the validity of the transition theory of vapor transfer [4]. As in the case of other gases flowing through capillaries [8-11], the k/k_k values of water vapor pass through a minimum at $K \sim 1$.

At higher p_0/p_s values (points e-g), deviations from the theory are noticeable. These deviations may be related to an additional transfer into the adsorption film. It is generally accepted that the film thickness increases sharply when p_0/p_s tends to unity [5]. For example, for $p_0/p_s = 0.97$ and 0.985, the experimental k_2 values are several times greater than the theoretical values (dashed curve). The differences increase with decreasing diameter of the capillary. The conclusion that film flow is the reason for the observed increase in the evaporation rate at p_0/p_s is confirmed by experiments with hydrophobized capillaries. As can be inferred from Fig. 2 (points h), when no polymolecular adsorption film (which is not formed on a hydrophobic surface) is present, the k_2 values agree almost completely with the theoretical values which account only for the flow in the gas phase, though the experiments were made for $p_0/p_s = 0.86$ and 0.91.

The permeability coefficient of mass transfer in capillaries can be represented as a sum of coefficients k_v and k_l which account for the flow in the gas phase and in the liquid film, respectively. The fact that the permeability coefficients are additive is a consequence of the linear pressure coefficients in the transfer equations, and of the condition $v_v + v_l = \text{const}$, which is satisfied in any cross section of the capillary. When the adsorption isotherm $h(\varphi)$ of water on the surface of capillaries is known, the values of the permeability coefficient for film flow can be obtained from the following equation of [1]:

$$\frac{k_l}{k_k} = \frac{\rho RT\sqrt{2\pi RT/\mu}}{v_m p_s \eta d^2 (1-\varphi_0)} \int\limits_{\varphi_0}^{\varphi_*} \frac{[h(\varphi)]^3}{\varphi}\, d\varphi, \tag{3}$$

where $\varphi = p/p_s$; $\varphi_0 = p_0/p_s$; and $\varphi_* = p_*/p_s$. Equation (3) was used to calculate k_l. The calculations were based on the isotherm of water adsorption on a plane glass surface [5]:

$$\ln(h_1/h) = B(1-\varphi). \tag{4}$$

The following values were assumed for the calculations: $h_1 = 7.5 \cdot 10^{-7}$ cm; $B = 40$; $\rho = 1$ g/cm^3; $T = 296$°K; $v_m = 18$ cm^3/mole; $\mu = 18$ g/mole; $\eta = 0.01$ Poise; and $\varphi_* = 0.998$. Figure 3 displays the results of the k_l/k_k calculation for several φ_0 values in the function $1/K = d/\lambda$. It follows from a comparison of the calculated values (Fig. 3) with the experimental values (Fig. 2) that the agreement is only qualitative since the contribution of the film flow increases when p_0/p_s approaches the value unity and also when the diameter of the capillaries decreases. This conclusion had been drawn some time ago in [12, 13] where an evaporation theory with proper account for film flow was developed. But the isotherms of the disjoining pressure of wetting films which are formed when a liquid layer reduces its thickness were considered in [12, 13].

Differences between theory and experiment may be related to a deviation of the adsorption isotherm of water in quartz capillaries from the isotherm of a plane glass surface, the latter isotherm being used in our calculations. For example, much greater thicknesses of polymolecular films were obtained in [14] for the adsorption on the surface of quartz capillaries. Estimates show that the differences decrease considerably when h_1 increases.

Another possible reason is that water viscosity and water density values of the bulk of the material were used in the calculations, because the physical properties of polymolecular films are not fully known. Observations of the evaporation of water from capillaries provide a possibility of studying these properties. But the adsorption isotherms of water on the surface of capillaries must be obtained for those studies.

The results of our investigations show that the hydrophilic nature of the surface and the dimensions of the capillaries have a noticeable influence upon the evaporation rate of water. Film flow intensifies the mass transfer in thick wetting films [1, 12, 13, 15], as well as in thinner polymolecular films which are formed by adsorption from the gas phase. Changes in the thickness and structure of surface films in thin porous bodies are one of the controlling mechanisms of internal mass exchange.

NOTATION

d is the diameter of capillary;
v is the evaporation rate, cm/sec;
x is the distance between the meniscus of the liquid and the mouth of the capillary;
p is the vapor pressure of the liquid;
p_s is the pressure of saturated vapor;
λ is the free path length of vapor molecules;
ρ is the density of the liquid;
v_m is the molar volume of the liquid;
η is the viscosity;
Δp is the pressure difference of the vapor over the meniscus and near the mouth of the capillary;
μ is the mass of a mole of the liquid;
R is the gas constant;
T is the temperature, °K;
p_0 is the vapor pressure in the chamber;
p_* is the vapor pressure in the capillary over the transition point from the wetting film to the adsorbed film;
h is the thickness of the adsorption film;
h_1 is the thickness of the film for $\varphi = 1$;
B is the constant of isotherm (5).

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