EFFECT OF TRAPPED AIR AND ANOMALOUS CONDENSATE ON THE EVAPORATION OF WATER FROM CAPILLARIES

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The effect of trapped air bubbles and of columns of anomalous condensate on the evaporation of water from quartz capillaries is analyzed. It is shown that these phenomena may retard the removal of moisture and may cause a redistribution of liquid in the capillary volume.

Porous bodies not saturated with moisture contain inclusions of trapped air which separate liquid-filled pores. In order to simulate the behavior of such systems during evaporation, liquid was poured into cylindrical capillaries and, at the same time, air bubbles were injected to various distances from the inlet. In this way, the water in a capillary channel was broken up before evaporation by an air column 0.3-5.0 mm long. Capillaries 50-300 μ in diameter were used here which had been drawn over an oxygen burner from fusing-grade quartz. The diameter of each capillary was measured on the ocular scale of a microscope. The capillaries were filled with deaerated and twice-distilled boiling water.

The capillaries were sealed at one end and placed in a desiccator; a saturated salt solution just covering the bottom maintained a constant relative humidity of air φ_0 in this enclosure. The tests were performed at $T_{amb} = 295.5°K$ and at various φ_0 levels within the range 0.32-0.98. In order to eliminate the effect of convective air currents in the desiccator, the capillaries were supported in a rubber membrane covering a few small chemistry beakers with the same salt solution. A membrane was pulled over the open end of a beaker and fastened around its edges with clamps. The beakers were placed on a porcelain tray inside the desiccator. The rubber membrane was punctured in several places with a needle

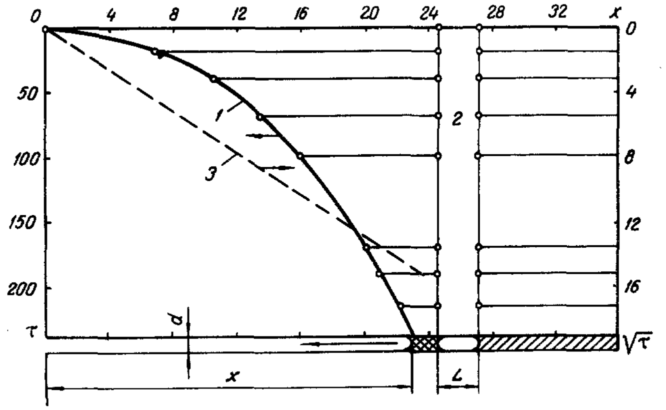

Fig. 1. Evaporation of water from a quartz capillary with the diameter d = 180 μ and containing a trapped air bubble (2) L = 2.6 mm long; $\varphi_0 = 0.4$, T = 295.5°K. 1) $x = f(\tau)$; 3) $x = f(\sqrt{\tau})$. x, mm; τ, h.

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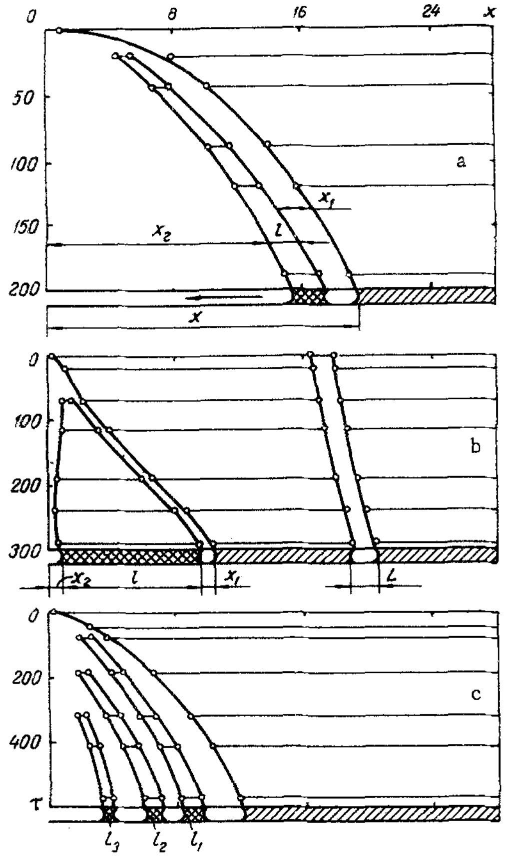

Fig. 2. Evaporation of water from quartz capillaries in which secondary columns of anomalous condensate (length l mm) have formed: T = 295.5°K; τ, h; x, mm; a) d = 40 μ, $\varphi_0 = 0.58$, $x_1 = 2.2$ mm; b) d = 130 μ, $\varphi_0 = 0.95$, $x_1 = 0.5$ mm, and water contains a trapped air bubble L = 1.3 mm long; c) d = 130 μ, $\varphi_0 = 0.93$, and several secondary columns (l_1, l_2, l_3) have formed successively.

and the capillaries were inserted through these pinholes. They were thus "suspended" above the salt solution and held in place by the friction against the rubber membrane, at a constant distance of 0.5 cm from their inlet ends to the surface of the solution.

In view of the long testing time (up to 15-20 days) at high φ_0 levels, the desiccators were placed in a chamber where temperature fluctuations did not exceed ±1°C. The temperature fluctuations were smoothed out by placing the desiccators in thermally insulated enclosures.

The trend of evaporation was observed through a microscope and, for this purpose, the capillaries were periodically removed from the desiccators. One series of measurements involving 6-8 capillaries in one beaker did not take longer than 15-20 min. Measurements were made in 24 h intervals at the beginning and in 72-120 h intervals later on. With the aid of the guide screws under the microscope, we measured x, L, and also the distance from a capillary inlet to the meniscus at the boundary of the air column inside. These distances could be measured accurately within 0.1 mm.

The relation $x = f(\tau)$ was plotted on graphs, one of which is shown in Fig. 1. The solid lines here indicate the position of the evaporating meniscus (curve 1) and of the air column (curve 2) in the capillary in the course of the test. The dashed line (3) represents the same graph replotted in x, $\sqrt{\tau}$ coordinates. The slope k of curve 3 is related to the diffusivity of water vapor as follows:

$$k = \frac{\sqrt{\tau}}{x} = \sqrt{\frac{RT}{2v_m D p_s (\varphi_s - \varphi_0)}}. \qquad (1)$$

The values of D in Eq. (1) were calculated from the data of several test series at $\varphi_0 = 0.40-0.58$, when vapor diffusion had become the main mechanism of transport and the effect of film flow in wide capillaries had become negligible [1, 2]. Our calculations (with T = 295.5°K, $v_m = 18$ cm^3/mole; $p_s = 20.5$ mm Hg and $\varphi_s \sim 1$) have yielded the mean value of diffusivity D = 0.25 ± 0.015 cm^2/sec, in close agreement with known tabulated values of D = 0.249 cm^2/sec [3, 4] under the same conditions. Thus, evaporation from wide capillaries under isothermal conditions and with air bubbles present proceeds in accordance with known theoretical concepts. The fully understood jump of the evaporation rate occurs only after the evaporation of all the liquid between the inlet and an air bubble. It was important here that the position of an air bubble in a capillary remained unchanged during the evaporation process (Fig. 1). Consequently, the pressure in the segments of liquid separated by an air bubble was the same and depended only on the curvature of the menisci.

The situation became different, however, when water was evaporating from the same capillaries into an atmosphere with a higher humidity level. A formation of secondary liquid columns near a capillary inlet, causing the mode of evaporation to change, was observed sometimes at $\varphi_0 = 0.58$ and always at $\varphi_0 = 0.93-0.95$. Let us first examine Fig. 2a. Before the beginning of evaporation, the water level in a capillary was full. Approximately a few days after the beginning of evaporation, a small secondary column of liquid $l = 1$ mm long was detected at a distance $x_1 = 2.5$ mm from the meniscus. The spontaneous formation of condensate in the free zone of a capillary was, apparently, of the same nature as the formation of secondary columns of anomalous liquids which had been discovered earlier by Fedyakin [5]. Columns of anomalous condensate during the evaporation of water from capillaries were also observed in [6, 7].

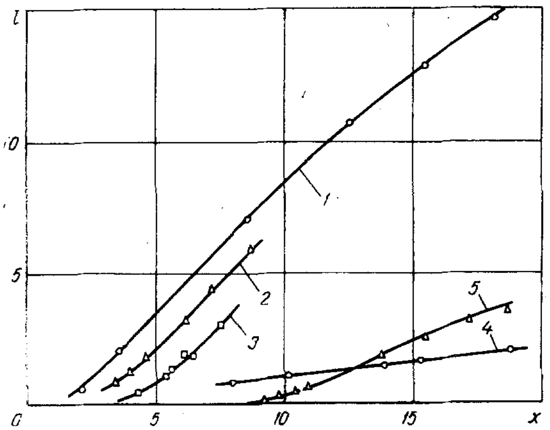

Fig. 3. Length of secondary columns l (mm) as a function of x defining the position of the meniscus of water evaporating from a capillary: 1) d = 40 μ, $\varphi_0 = 0.93$, $x_1 = 2$ mm; 2) d = 200 μ, $\varphi_0 = 0.95$, $x_1 = 1.5$ mm; 3) d = 100 μ, $\varphi_0 = 0.95$, $x_1 = 3.5$ mm; 4) d = 40 μ, $\varphi_0 = 0.58$, $x_1 = 2.5$ mm; 5) d = 31 μ, $\varphi_0 = 0.98$, $x_1 = 0.4$ mm.

A forming secondary column did not remain stationary, but moved behind the receding meniscus driven by the air-pressure drop (Fig. 2a). Water, while evaporating, condensed on the meniscus of the secondary column, the vapor pressure φ_* above which had been reduced [8, 9] by the presence in it of a dissolved nonvolatile component.† The rate of this mass transfer, at $\varphi_s \sim 1$, is

$$v_1 = \frac{v_m D p_s (1-\varphi_*)}{RTx_1}. \tag{2}$$

The mass transfer in the zone between a secondary column and the surrounding medium proceeds at the rate

$$v_2 = \frac{v_m D p_s (\varphi_* - \varphi_0)}{RTx_2}, \tag{3}$$

where $v_2 > 0$ corresponds to evaporation of plain water (solvent) from a secondary column (when $\varphi_* > \varphi_0$) and $v_2 < 0$ corresponds to condensation of water vapor from the surrounding medium onto a secondary column (when $\varphi_* < \varphi_0$).

Usually $\varphi_* < \varphi_0$ at the instant when a secondary column begins to form, and the latter continues to build up collecting water vapor from the liquid in the capillary on one side as well as from the surrounding medium on the other side. After the anomalous component has been diluted so much that φ_* exceeds φ_0, the mass transfer is effected by passage through the secondary column. On the right-hand meniscus of the secondary column the vapor condenses, while at the left-hand meniscus the water evaporates into the surrounding medium. The rate at which the length of a secondary column changes can be expressed as follows:

$$\frac{dl}{d\tau} = v_1 - v_2 = \frac{v_m D p_s}{RT}\left(\frac{l_a}{l x_1} - \frac{1-(l_a/l)-\varphi_0}{x-x_1-l}\right). \tag{4}$$

This equation has been derived with a logical change of variables $x_2 = x - x_1 - l$ (Fig. 2a) and on the basis of an approximate version of Raoult's law, the latter relating the vapor pressure φ_* to the concentration of the anomalous component in a secondary column [8]:

$$\frac{l}{l_a} \simeq \frac{1}{1-\varphi_*}. \tag{5}$$

Accordingly, the evaporation rate of the primary liquid in the capillary is

$$\frac{dx}{d\tau} = v_1 = \frac{v_m D p_s l_a}{RT l x_1}. \tag{6}$$

Eliminating τ from Eqs. (4) and (6), we obtain the following differential equation:

$$\frac{dl}{dx} = 1 - \frac{x_1 l - x_1 l_a - x_1 l \varphi_0}{x l_a - x_1 l_a - l_a l}, \tag{7}$$

where x_1, l_a, and φ_0 are constant under the given test conditions.

Equation (7) does not have a simple analytic solution and, therefore, we will only discuss it here. First we neglect all terms of second-order smallness, considering that $l_a \ll x$, $l \ll x$, and $x_1 \ll x$. Then

$$\frac{dl}{dx} = 1 - \frac{x_1 l (1-\varphi_0)}{l_a x} = 1 - A\frac{l}{x}. \tag{7'}$$

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† The formation of secondary columns of a nonvolatile anomalous component during evaporation has been confirmed by measurements of their thermal expansivity. It was discovered in all cases that the temperature at which the condensate ceased to form had dropped by a few degrees.

It follows from this equation that, if $1 > Al/x > 0$, the buildup rate of a secondary column $dl/d\tau > 0$ must lag behind the rate at which the meniscus of the primary liquid recedes, $dx/d\tau > 0$. In this case less liquid evaporates from the secondary column into the surrounding medium than is collected by condensation of vapor from the primary column. If $Al/x \ll 1$, however, then $dl/dx \sim 1$. This means that, under these conditions, a secondary column builds up at the expense of primary liquid: almost no mass transfer to the surrounding medium occurs, and the evaporation rate of the liquid is a minimum. Finally, if $Al/x > 1$, the length of the secondary column can decrease: $dl/dx < 0$, which corresponds to $dl/d\tau < 0$ when $dx/d\tau > 0$. In this case, the rate at which the liquid evaporates into the surrounding medium becomes higher than the rate at which the vapor condenses on the secondary column. As can be seen from this analysis, the conditions of mass transfer are governed by the parameter Al/x.

From this standpoint, then, we will now try to explain the experimentally derived relations $l = f(x)$, some of which based on several tests are shown in Fig. 3. For values of φ_0 close to unity, when A is small (curves 1-3), quite soon after the formation of a secondary column the $dl/dx \sim 1$ mode will prevail. At $\varphi_0 = 0.58$ (curve 4), when A is large, conditions of mass transfer in the transit mode will prevail; $0 < dl/dx < 1$. The values of A can also be rather large when the quantity of the anomalous component in a secondary column is small ($l_a \rightarrow 0$). Apparently, this case corresponds to curve 5, where (even though $\varphi_0 = 0.98$) dl/dx increases while lagging behind x and remaining smaller than unity, in agreement with Eq. (7').

We will now compare the evaporation rates of the liquid from a capillary into the surrounding medium v_2 in the presence of secondary columns and v_0 in the absence of secondary columns:

$$v_0 = \frac{v_m D p_s (1 - \varphi_0)}{RTx} . \tag{8}$$

The ratio of these velocities is

$$\alpha = \frac{v_2}{v_0} = \frac{x(\varphi_* - \varphi_0)}{x_2(1 - \varphi_0)} . \tag{9}$$

Since $x > x_2$ while $(\varphi_* - \varphi_0) < (\varphi_s - \varphi_0)$, hence the evaporation rate can either increase or decrease, depending on the position of the secondary column and on the concentration of the anomalous component in it. When x is small, the difference between x and $x_2 = x - x_1 - l$ being large, the evaporation may be accelerated, especially when also φ_* is close to φ_s. When $x \gg x_1 + l$, the difference between x and x_2 being small, the evaporation rate decreases: the lower φ_* is, the slower becomes the evaporation. Evaporation ceases at $\varphi_* = \varphi_0$ and, when $\varphi_* < \varphi_0$, even condensation of vapor in the capillary is possible. The causes of anomalous condensation are not yet quite understood. Similar problems concerning the modification which liquids undergo during condensation of their vapors have been analyzed in [10, 11].

Tertiary and further columns observed in many tests along with secondary ones complicate the pattern of mass transfer even more (Fig. 2c). According to this diagram, secondary columns appear approximately within the same capillary segment near the inlet and then extend deeper as the primary liquid evaporates.

The tests have also shown that, when the distance between the primary liquid and the secondary column is sufficiently large ($x_1 = 1$ mm), the presence of trapped air bubbles in the capillary has no effect on the evaporation process. The air bubbles remained stationary during the evaporation of liquid, also in the tests recorded in Fig. 1.

When a secondary column forms near an evaporating liquid (Fig. 2b), the pattern changes. According to the diagram, a trapped air bubble begins to move toward the sealed end of the capillary. This can be explained by the mass transfer which occurs through the bubble and by the resulting difference between the partial pressures on the left hand and on the right hand meniscus. Apparently, when the secondary column is near, it becomes possible for the anomalous component to penetrate – by way of surface diffusion – into the volume of liquid filling the capillary. The anomalous component, eventually distributed over the volume of liquid, will reduce the vapor pressure on the menisci according to Raoult's law. Since an air bubble represents a high resistance to diffusion, both the concentration of the anomalous component and thus also the partial pressure of vapor drop sharply at its ends, which in turn causes the mass transfer discussed earlier. This experiment demonstrates also how, at high φ_0 levels, the predominant mass transfer can proceed between the liquid and the secondary column without loss of moisture to the surrounding medium. According to Fig. 2b, the total volume of all the liquid in a capillary was conspicuously unchanged in the course of an experiment.

The peculiarities of mass transfer discovered in these experiments, due to the formation of secondary columns and the presence of trapped air, may evidently appear also during evaporation on porous bodies. By performing tests with individual capillaries, where columns can be easily detected by optical methods, it has been possible to study some characteristics of the physical mechanism on a model system. A scale of magnitude for evaluating the effect and the conditions of capillarity in bodies will have to be established in further studies.

NOTATION

L	is the length of an air bubble;
d	is the diameter of the capillary;
φ_0, φ_s, φ_*	are the relative humidity of air in the chamber, above the meniscus of evaporating water, and above the meniscus of a secondary column, respectively;
x	is the distance between the capillary inlet and the meniscus of the evaporating liquid;
τ	is the evaporation time;
D	is the diffusivity of vapor through air, cm^2/sec;
R	is the gas constant, erg/mole · °C;
T	is the temperature °K;
v_m	is the molal volume of liquid, $cm^3/mole$;
p_s	is the pressure of saturated vapor;
x_2	is the distance between the capillary inlet and the nearest meniscus of a secondary column;
x_1	is the distance between liquid in a capillary and a secondary column;
v_1	is the rate of mass transfer along the segment between the liquid and the secondary column, cm/sec;
v_2	is the rate of water evaporation from the secondary column into the surrounding medium, cm/sec;
l	is the length of the secondary column;
l_a	is the length of the secondary column, referred to only one anomalous component present.

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