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Abstract

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ALLOTROPY OF LIQUIDS DURING CONDENSATION OF THEIR VAPORS IN QUARTZ CAPILLARIES

In observing the behavior of columns of water and of certain other liquids drawn into glass capillaries, Fedyakin ([1]) noted the formation of "secondary" columns with a lower vapor pressure, without which their formation and growth would be incomprehensible.

In the work of Deryagin ([2]) and Fedyakin it was shown that the viscosity of the secondary columns is several times greater than the bulk value of the viscosity, which is retained by the primary columns. In this case, movement of the secondary columns leads to a decrease in viscosity, while stopping leads to its restoration. The growth of secondary columns of water proceeds progressively if the surrounding atmosphere has a relative humidity greater than 93% ([3]).

To explain this behavior of "special" columns of liquids, an assumption was made about their special structure, different from the structure of the same liquid in bulk ([2]). Because of the unusual character of such an assumption, which contradicts data on the thickness of the boundary layer of a liquid with an altered structure ([4]), since the columns were observed in capillaries with a radius on the order of 1 μ, it is natural to try to reduce the observed facts to more trivial causes. The only possibility of such an explanation may be connected with the transition into the liquid columns of products of glass leaching, which lower the vapor pressure and increase their viscosity. As analysis of the behavior of "primary" and "secondary" columns shows, and especially special experiments carried out recently, the basic facts cannot be reduced to leaching; the latter may, however, during prolonged observations somewhat disturb the basic regularities and affect the correctness of the measurements.

In view of this, it is of special interest to study the formation and properties of special columns in quartz capillaries, which is the simplest way not only to refute the explanation of these properties by leaching, but also to measure them most accurately. In addition, in the present work the influence on the time of formation and the rate of elongation of the columns of the air pressure P, the relative saturation of the space with liquid vapor P/P_s, and the radius of the

Fig. 1. Schematic of a chamber for investigating the formation of an anomalous column

Figure 1: Fig. 1. Schematic of a chamber for investigating the formation of an anomalous column

capillary r was studied. Thanks to this, it proved possible finally to establish the nature of the phenomenon expressed in the title of the article.

The apparatus (see the diagram in Fig. 1) consists of a cylindrical glass chamber 5 with a flat window, from which air could be pumped out through stopcock 1, a manometer 4, and a side tube 9 connected through a tube with the liquid under investigation. With the aid of two Höppler thermostats and water jackets 2 and 10, it was possible to maintain the desired temperature in the chamber and a specified temperature difference between it and the liquid in the side tube. Owing to this, it was possible to obtain in the chamber, for the vapors of the given liquid, any value of P/P_s, determined from the readings of thermometers in the chamber and in the water jacket around the side tube, with the aid of a graph, close to a straight line, of the dependence of $\lg P_s$ on $1/T$, where T is the absolute temperature, measured with an accuracy of 0.02°. A capillary 7 was placed vertically in the chamber.

The length of the columns in it was measured with a KM-6 cathetometer under side illumination.

First of all, it turned out that, when the air is removed, columns appear at $P/P_s = 0.95$–0.97 much more rapidly—for water and acetone, usually after half an hour to an hour, whereas at atmospheric pressure even 2–3 days are often insufficient for this. The subsequent growth of the columns also proceeds several tens of times faster. Approximately the same relation is also observed in the condensation growth of columns in glass capillaries. This shows that leaching of the latter cannot play the principal role in the growth of anomalous columns, which is controlled first of all by diffusion of vapor through the air in the capillary.

Fig. 1. Schematic of a chamber for investigating the formation of an anomalous column

Since the space around the capillaries was always undersaturated with vapor, only "anomalous" columns could form in the capillaries. How is it to be explained that not one column, but several, was more often formed? Does this not indicate a difference in their vapor pressures and, consequently, their belonging to different phases?

The last question must be answered in the negative: with unequal vapor pressures, in the end only the column (or columns) with the lowest possible vapor pressure would remain; the others would evaporate, in any case after the vapor pressure outside the capillary had been reduced to the equilibrium vapor pres-

Fig. 2. Dependence of the rate of change in the length of water columns on the relative pressure in a quartz capillary: r = 12 μ, t = 20°

Figure 2: Fig. 2. Dependence of the rate of change in the length of water columns on the relative pressure in a quartz capillary: r = 12 μ, t = 20°

sure of the column located closest to the capillary opening. Observations of such a case revealed only the opposite tendency—toward an increase, not a decrease, in the number of columns. Along with this, certain slow variations in the lengths of the columns are often observed—the growth of some at the expense of others—which can be explained by the nonideal thermostatic uniformity of the temperature along the capillary. To explain the multiple birth of columns it is sufficient to take into account that, in contact with vapor supersaturated relative to the "special" columns, the capillary walls must become covered with so thick a film that the instability of the cylindrical liquid-gas interface known from capillarity theory [5] can no longer be eliminated by the action of the molecular field of the solid substrate, as occurs for equilibrium adsorption layers in contact with undersaturated vapor. The instability of the cylindrical surface first leads to its transformation into an unduloid, the bulges of which subsequently give rise to new columns. The nutrient material for the "embryos" can be transported both by vapor diffusion and by film motion. In both cases the driving force is small differences in chemical potential, caused by differences in curvature of different sections of the unduloid surface and inseparably connected with their instability when the surface is sufficiently extended.

Fig. 2. Dependence of the rate of change in the length of water columns on the relative pressure in a quartz capillary:
$r = 12\ \mu,\ t = 20°$

Under these conditions, in order to study the kinetics of condensation or evaporation on the outer surface of the "outermost" column, it is necessary to measure the total length of all columns (if there are several of them). The results of one of many such observations are presented in Figs. 2 and 3, where the abscissa gives the values of P/P_s, and the ordinate gives the rate of change

of the total length of the columns, $\Delta h_c/\Delta\tau$. In all cases a regular dependence of $\Delta h_c/\Delta\tau$ on P/P_s is obtained, indicating the correctness of the chosen method. The intersection of this curve with the abscissa axis obviously determines the equilibrium vapor pressure of the columns. Table 1 gives values of P_a/P_s for columns of various liquids in capillaries of different radius. It is noteworthy that the value $P_a/P_s = 0.93$ for columns of water in quartz capillaries coincided with the value 0.93 in a glass capillary ([3]) of radius $1.5\,\mu$. This provides additional proof of the small role of glass leaching. Extremely important is the independence, revealed in Table 1, of the vapor pressure from the capillary radius, up to capillaries with radii of $30\,\mu$. This shows that, upon condensation of vapors in quartz or glass capillaries, a bulk liquid phase arises which is an allotropic modification of an ordinary liquid.

Fig. 3. Dependence of the rate of change in the length of methyl alcohol columns on the relative pressure in a quartz capillary: $r = 19\,\mu,\ t = 20^{\circ}$

It is difficult to overestimate the significance of this conclusion for understanding the nature of the liquid state. Since in the cases studied the allotropic transformations yielded polar liquids, in whose structure hydrogen bonding plays a significant role, one may assume as a working hypothesis that the formation of columns occurs as a result of the following: under the influence of hydrogen bonding with the hydroxyls of the glass, a polymolecular adsorption layer initially arises, with a special structure and with a modified framework of hydrogen bonds. Upon further condensation of vapor, this unusual structure grows by an autoepitaxial mechanism, which until now had been observed only in solid and liquid crystals. Apparently, this phenomenon is facilitated by vapor undersaturation, owing to which a liquid with normal structure cannot arise at all and compete with the growth of the anomalous allotropic modification. However, it is quite possible that, after formation of the anomalous sublayer, it can grow in the form of a special modification of the liquid also at vapor pressures greater than the vapor pressure of the normal liquid (but less than some critical value), if the appearance of the latter is associated with the activation energy for formation of its nucleus.

Table 1

Name of substance	Glass grade	Capillary radius, μ	P_a/P_s
Pure water (bidistillate)	Quartz glass	12	0.93 ± 0.005
Pure water (bidistillate)	Same	21	0.93 ± 0.005
Pure water (bidistillate)	Same	5	0.93 ± 0.005
Pure water (bidistillate)	Glass No. 46, No. 23	1–5	0.93 ± 0.005
Acetone	Quartz glass	3	0.95 ± 0.003
Acetone	Same	8	0.95 ± 0.003
Acetone	Same	15	0.95 ± 0.003
Methyl alcohol	Quartz glass	19	0.94 ± 0.005
Methyl alcohol	Same	6	0.95 ± 0.005
Acetic acid	Quartz glass	23	0.95 ± 0.008

Confirmation of the views developed is provided by the fact that, in a capillary wetted from the inside with a film of "normal" water, anomalous columns do not form if the walls are not dried beforehand. This observation also refutes the attempt to ascribe the difference in properties of primary and secondary columns to the fact that, in contact with the former, a protective film of silicic acid gel is formed on the glass surface. Obviously, during drying of the glass such a film would have been preserved and would have continued to hinder the nucleation of "anomalous" columns.

It would now be premature to attempt to give a concrete explanation of the reasons why the special liquid phase, whose chemical potential is lower than that of the normal liquid, is unstable under ordinary conditions.

Here it is necessary to confine ourselves to two remarks: 1. The drop in viscosity during the motion of the special column indicates the mechanical weakness of the framework of its hydrogen bonds. Analogously, graphite, despite the lower value of its chemical potential, is considerably less strong than diamond. However, apparently, unlike liquid columns, the destruction of graphite does not lead to the formation of a diamond lattice. Moreover, taking into account the fundamental difference between the liquid and solid aggregate states, one should not expect a complete analogy, and the allotropy of the liquid and solid states must have fundamental differences. In order to show that destruction during flow of the more stable state and its transition to the less thermodynamically stable one (and, at rest, return to the original state) does not contradict thermodynamics, it is sufficient, however, to refer to the thixotropic gel–sol transformation under the action of stirring. At the same time, one should not seek a concrete explanation of the facts observed by us in thixotropy as such, since in quartz capillaries a gel simply cannot arise, while in glass ones the strictly Newtonian viscosity of the special columns is also incompatible with the properties of a gel.

To summarize: there remains no doubt that in quartz (and also glass) capillaries, upon condensation of unsaturated vapors of a number of polar liquids, columns of liquid arise with a lower chemical potential, but with physical properties different from those of the normal bulk phase.

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