ON THE MECHANISM OF FORMATION OF WATER COLUMNS WITH SPECIAL PROPERTIES DURING THE CONDENSATION OF WATER VAPOR IN WIDE FRESHLY DRAWN GLASS CAPILLARIES

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 541.12.013.5

PHYSICAL CHEMISTRY

N. N. FEDYAKIN, Corresponding Member of the Academy of Sciences of the USSR, B. V. DERYAGIN,
A. V. NOVIKOVA, M. V. TALAEV

ON THE MECHANISM OF FORMATION OF WATER COLUMNS WITH SPECIAL PROPERTIES DURING THE CONDENSATION OF WATER VAPOR IN WIDE FRESHLY DRAWN GLASS CAPILLARIES

In works ([1]-[3]) it was shown that, in comparatively wide glass capillaries (with a radius of 1-15 μ), columns of water and of a number of other polar liquids exhibit sharply different properties depending on whether they are formed by capillary suction or by condensation from vapor. In the first case the properties of the columns coincide with the properties of the same liquids in bulk; in the second, a difference in properties is observed—for example, a considerably reduced (for water, by 7%) saturated-vapor pressure. It was suggested that, in the process of the condensation formation of columns, under the influence of the glass surface, liquids with a special structure, different from the ordinary one, are obtained. In view of the unusual character and extreme paradoxicality of this assumption, it is natural to try to explain the observed facts in a more trivial way.

In essence, the only possible other explanation may consist in a change in the properties of the liquids under the influence of the products of leaching of the glass. It is necessary, however, also to explain why the process of leaching of the glass affects only the behavior and properties of the condensate columns, and does so very strongly.

An attempt to explain this difference was made in our laboratory by B. V. Zhelezny on the basis of the ideas of I. V. Grebenshchikov and his followers that the action of small volumes of water on the surface of glass differs fundamentally from the action of large volumes. In the first case the interaction products remain in place and cause secondary reactions, which leads to further destruction; in the second case the interaction products are removed, and a protective film is formed on the surface. Briefly, this is expressed in the proposition that the action of small volumes of water approaches the action of alkalis on glass ([4], p. 218).

Fig. 1. Schematic diagram of a bridge for measuring the electrical conductivity of liquids in capillaries

Figure 1: Fig. 1. Schematic diagram of a bridge for measuring the electrical conductivity of liquids in capillaries

The present work is devoted to the presentation of new facts (in addition to those given earlier) that refute this explanation.*

Electrical conductivity of water in glass capillaries

In order to show that condensate columns do not contain such concentrations of dissolved substances as could account for so large a decrease in saturated-vapor pressure (7% for water), it is simplest to measure the electrical conductivity. We measured the electrical conductivity of both "normal" and "anomalous" water. For this purpose platinum wire electrodes were introduced into the capillaries, and the resistance of the liquid was measured by the usual bridge circuit (Fig. 1). A sound generator was used as the current source, and an oscillograph as the indicator. Cascade resistances up to

---

* We do not give the details of this explanation, which does not belong to us, since the conclusions from the observations described below do not depend on these details.

100,000 ohms each. In measuring the resistance of the liquid in the capillaries, the oscillation amplitude was observed to pass through a minimum. The accuracy of the measurements did not exceed 10% and was determined by the sensitivity of the oscilloscope; however, for answering the question posed this accuracy was more than sufficient. During the experiment, the space between the electrodes in the capillary was within the field of view of the microscope (to monitor possible formation of gas bubbles and rupture of the liquid). Capillaries made of glass No. 23 were used in the experiments. The results are given in Table 1.

From Table 1 it is evident, first of all, that the conductivity of the anomalous columns always remains, even after 6 months in the capillary, at such a low level that it is, undoubtedly, incompatible with the assumption that the lowering of their vapor pressure is due to the presence of dissolved substances. It is also seen that even with a very large contact surface (a suspension of ground glass films) the concentration of dissolved substances remains considerably less than 1%.

Fig. 1. Schematic diagram of a bridge for measuring the electrical conductivity of liquids in capillaries

Effect of alkalis on the condensation of water vapor in capillaries

The role played by leaching of glass in the process of condensation of water vapor on the glass surface can also be clarified in another way, if a small amount of alkali is introduced beforehand and the kinetics of its absorption of water vapor is studied. We took two capillaries 8 cm long, with radii of 10.5 and 1.1 μ, and partially filled them with water. Into the free ends we introduced a 50% NaOH solution. The lengths of the alkali columns were, respectively, 32 and 37.6 μ. Owing to absorption of water vapor by the alkali solution, these columns should lengthen, while the water columns should shorten. As is known from works (1, 2), the lengthening of columns of "special" liquid, at least over the course of 1-1.5 months, occurs approximately uniformly at a rate of ~2.8-3 μ/hour.

If the cause of condensation is leaching, then under favorable initial conditions the increase of the column of NaOH solution should proceed indefinitely.

Table 1

Liquid studied	d (μ)	l (mm)	R (MΩ)	σ (ohm^{-1}·cm^{-1}·10^{-4})	C (%)
Distilled water was in the capillary for 1 h	65	2.38	20	3.52	$0.12 \cdot 10^{-2}$
Distilled water was in the capillary for 7 h	171	2.1	1	9.1	$3.4 \cdot 10^{-2}$

Liquid studied	d (μ)	l (mm)	R (MΩ)	σ (ohm^{-1}·cm^{-1}·10^{-4})	C (%)
Suspension of ground glass films (0.1-1 μ) with concentration (by weight) 20%, settled for 20 days	72	4.2	2	53	$18.5 \cdot 10^{-2}$
	82	2.5	1.55	15.3	$5.3 \cdot 10^{-2}$
"Anomalous" column was in the capillary for 6 months					
	100	2.1	2	7.5	$2.62 \cdot 10^{-2}$
"Anomalous" column formed in "vacuum" and was in the capillary for 7 days					
Tabulated value of σ for 0.1 N NaOH solution	–	–	–	116	$40 \cdot 10^{-2}$

Fig. 2

Figure 2: Fig. 2

Liquid studied	d (μ)	l (mm)	R (MΩ)	σ (ohm^{-1}·cm^{-1}· 10^{-4})	C (%)
Tabulated value of σ for 10% NaOH solution	–	–	–	3130	10.0

Note. d is the diameter of the capillary, l is the distance between the electrodes, R is the resistance, σ is the conductivity. In the last column the alkali concentration corresponding to the obtained conductivity is given.

Figure 2 shows the results of the experiments. Curves 1 and 2 characterize the dependence of the elongation of a column of alkali solution on time in capillaries of radii 10.5 and 1.1 μ, respectively. Curve 3 was drawn on the assumption that the vapor pressure of the solution decreases only as a result of the decrease in concentration due to absorption of vapor. Curves 1 and 2 pass above curve 3 and then run parallel to the abscissa. Consequently, in the initial period of time the glass is destroyed and the alkalis dissolve. Straight line 4 represents the growth of the "special" column formed by vapor condensation. The cessation of growth of the columns with NaOH solutions indicates the cessation of dissolution of the alkalis. However, it is necessary to determine the result of the interaction of the NaOH solution with the glass.

Fig. 2. Dependence of the length of the formed column on time.
1 –50% NaOH, $\Delta l_0 = 32$ μ, $r = 10.5$ μ; 2 –50% NaOH, $\Delta l_0 = 37.6$ μ, $r = 1.1$ μ; 3 –curve for the growth of the column in the absence of interaction of the alkali with the glass; 4 –elongation of the "anomalous" column.

For this purpose, the column of liquid formed during condensation of vapors in a capillary of radius 10.5 μ was evaporated. After evaporation in air (with a humidity of 0.62%), there remained a column 40 μ long, consisting of gel. Apart from this column, neither crystals nor other particles were found on the walls of the capillary. This was readily established by examining the capillary under a microscope with side illumination. That the residue is a gel is revealed by placing the capillary between crossed nicols in a polarization microscope.

Figure 3a shows a microphotograph of the residue.

It should be noted that after evaporation of 1% (and even 0.1%) solutions of alkalis or salts, crystals are readily detected on the walls of the capillary. Their

Figure 3

Figure 3: Figure 3

crystalline structure is also established with the aid of a polarization microscope. Figure 3b shows a microphotograph of the walls of a capillary after evaporation of a 1% NaOH solution between crossed nicols. The light spots are the image of crystals deposited on the walls of the capillary. Consequently, indefinitely prolonged condensation of moisture due to the hygroscopicity of glass is impossible. Taking into account the insufficiency of the data, nothing can be said about chemical interactions as a result of which the alkalis are, as it were, "neutralized," i.e., the glass ceases to be destroyed and the vapor pressure remains close to that normal for water. As was already stated above, the final result of the interaction proved to be gels, which at low concentration cannot substantially lower the vapor pressure.

Rate of evaporation from capillaries of columns of normal and anomalous water

A comparison of the evaporation kinetics from a capillary of "normal" and "anomalous" liquids is instructive. As was shown in (1), if a capillary is partially filled with liquid and sealed at both ends, then in its free part a column of liquid with special properties arises, uniformly lengthening with time, i.e., a "distillation" of the liquid takes place. The following experiment was carried out. In a capillary ($r = 34\ \mu$), over 5 months, a column of "anomalous" water 3.5 mm long was obtained. At the opposite end there remained a column of "normal" water of almost the same length. Both ends were cut off at points 1 mm from the liquid menisci.

Fig. 3. *a* —residue after evaporation of a column of solution formed as a result of absorption of vapor by a column of 50% NaOH solution, in a capillary with $r = 10.5\,\mu$ and $\Delta l = 500\,\mu$, $\Delta l_0 = 32\,\mu$; *b* —end of the capillary after evaporation of a 1% KCl solution, photographed through crossed nicols. The light spots are salt crystals on the walls.

The rate of evaporation from both capillaries was measured simultaneously with the aid of a microscope. Evaporation took place in air with a relative humidity of 60% and a temperature of 10°.

Figure 4 shows curves expressing the dependence of the rate at which the menisci recede on their distance from the open ends of the capillaries. Circles denote the evaporation rates of the "normal" liquid, crosses those of the "anomalous" liquid. As shown in (12), the evaporation kinetics of the normal liquid from capillaries with radii greater than 0.1 μ is satisfactorily described by the known Stefan equation.

In Fig. 4 the solid curve is plotted from the Stefan equation for the given

Fig. 4. Dependence of the evaporation rate on the distance from the meniscus to the orifice. Curve 1 is plotted according to Stefan' s formula for the evaporation rate of water at $t = 20^\circ$ and air humidity 60%. $a, ,$ —rates of shortening of the "normal" column (a), the "anomalous" column of the same capillary (), and the column of a 1% KCl solution ().

Figure 4: Fig. 4. Dependence of the evaporation rate on the distance from the meniscus to the orifice. Curve 1 is plotted according to Stefan' s formula for the evaporation rate of water at $t = 20^\circ$ and air humidity 60%. $a, ,$ —rates of shortening of the "normal" column (a), the "anomalous" column of the same capillary (), and the column of a 1% KCl solution ().

conditions. The points for "normal" water lie satisfactorily on this curve. The rate of recession of the "anomalous" liquid, as is clear from the figure, is almost twice as great as that of the "normal" liquid. More intense evaporation cannot occur here, since the vapor pressure of the "anomalous" liquid is lower than that of the "normal" liquid. Thus the only remaining possibility is that, owing to properties still unknown but inherent in it, "anomalous" water migrates along the surface of the capillary walls much more intensively than normal water. This migration probably has the character of intensive film motion.

Fig. 4. Dependence of the evaporation rate on the distance from the meniscus to the orifice. Curve 1 is plotted according to Stefan' s formula for the evaporation rate of water at $t = 20^\circ$ and air humidity 60%. $a, ,$ —rates of shortening of the "normal" column (a), the "anomalous" column of the same capillary (), and the column of a 1% KCl solution ().

For comparison, the evaporation kinetics of solutions from capillaries of dimensions of the same order were measured. In Fig. 4 the squares denote the evaporation rates of a 1% solution. As the water evaporates, the salt concentration increases and the evaporation rate slows down.

Conclusions

1. Condensation of unsaturated water vapor in wide glass capillaries cannot be explained by leaching of the glass.
2. The condensed liquid differs in its physical properties from the bulk liquid, which can be explained only by a difference in their structure.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
25 V 1965

References Cited

1. N. N. Fedyakin, *Koll. zhurn.*, **24**, 4 (1962).

2. B. V. Deryagin, N. N. Fedyakin, *DAN*, **147**, 402 (1962).

3. N. N. Fedyakin, *Proceedings of the Second Conference on Surface Forces*, "Nauka," 1964.

4. *Handbook for Glass Production*, 1, Moscow, 1963.

Note: Figure translations are in progress. See original paper for figures.