EVAPORATION RATE OF CONCENTRATED ELECTROLYTE SOLUTIONS FROM FINE CAPILLARIES

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Solution concentration at the meniscus is elevated above the initial value, but does not vary during evaporation from capillaries. The reduction in evaporation rate as compared to water determined experimentally is in agreement with previously developed theory.

Calculations of the rate of evaporation of moisture from porous bodies are usually based on the characteristics of pure water: vapor pressure, density, and viscosity. However, in real objects subjected to drying and natural porous bodies the pore moisture is a solution of complex composition. During drying the solution becomes more concentrated in the evaporation zone, the extent and position of which depend on the structure of the porous body and external conditions.

The problems of convective diffusion of a dissolved substance near a free evaporation surface were solved in [1, 2]. The effect of reduction of vapor pressure above the solution upon its evaporation rate from a capillary was first considered theoretically by Zolotarev [3]. However, to the authors' knowledge, that theory has not been subjected to experimental verification.

The authors have conducted a series of comparative measurements of the evaporation rate of aqueous KCl solutions (C = 0.075-22.35% by weight) and pure water from quartz capillaries 1-20 μm in radius. The capillaries, 5-6 cm in length, were first filled with the working liquid, sealed at one end, and placed in a horizontal position within a thermostatic metal chamber with porolon thermal insulation [4, 5]. A constant relative humidity φ_0 was maintained within the chamber by use of a saturated salt solution. The following salts were used: NaCl ($\varphi_0 = 0.75$), KCl ($\varphi_0 = 0.85$), and KNO_3 ($\varphi_0 = 0.94$). Chamber temperature was maintained constant by an electronic temperature regulation system to an accuracy of ±0.1°. The chamber temperature was stabilized continually for several hours, using power from storage batteries [4]. To avoid condensation of vapor on the viewport installed in the chamber top, the chamber temperature was maintained several degrees above the maximum room temperature. Air pressure within the chamber was equal to atmospheric.

The chamber was mounted on the movable table of an IZA-2 horizontal comparator. Meniscus displacement during evaporation was measured to an accuracy of ±1 μm. Micrometer mechanisms producing lateral and longitudinal displacement of the chamber relative to the fixed reference microscope of the comparator were used to sight in the meniscus. The meniscus was observed with illumination from the side. To decrease background light the bottom of the chamber was blackened.

Tests were made of 10-12 capillaries containing water and solutions simultaneously. Since the quantity of water evaporated was less than 10^{-6} cm^3, and the volume of saturated solution was 2-3 cm^3, the ongoing evaporation could not change the humidity in the chamber. Observations of the change in meniscus position during evaporation were performed continually for 5-6 h.

Initially the desired regime ($\varphi_0 = \text{const}$, $T = \text{const}$) was created in the empty chamber. Then the lid was opened and the holder containing the capillaries was inserted rapidly. Before insertion, the open ends of the capillaries were cut off with pincers below the liquid-filled level. This moment was taken as the beginning of the experiment, $\tau = 0$. After opening the chamber and inserting the capillaries equilibrium values of φ_0 were established after 1-3 h,

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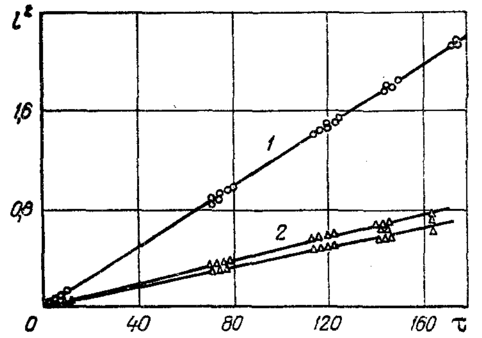

Fig. 1

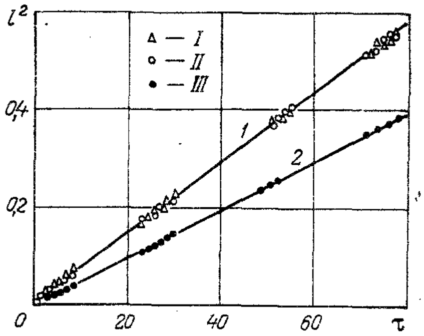

Fig. 2

Fig. 1. Square of the meniscus displacement l^2 in capillary versus evaporation time τ for $\varphi_0 = 0.75$ and $T = 300.6$°K: 1) water, capillaries Nos. 1, 5, 10 ($r \simeq 20$ μm); 2) KCl solution, C = 22.35%, capillaries Nos. 2, 3, 4 ($r \simeq 20$ μm) and Nos. 6, 7, 8, 9 ($r \simeq 1$ μm); l^2, cm^2; τ, h.

Fig. 2. Square of the meniscus displacement l^2 in capillary ($r \simeq 1$ μm) versus evaporation time τ for $\varphi_0 = 0.85$ and $T = 300.2$°K: 1) water, capillaries Nos. 5, 10 (points I); 0.075% KCl solution, capillaries Nos. 3, 8 (points II); 2) KCl solution, C = 7.45%, capillaries Nos. 1, 4, 7 (points III).

so that the initial intervals corresponding to nonsteady-state conditions were eliminated from consideration.

Figures 1-3 present some of the results obtained. The abscissa here denotes evaporation time τ, and the ordinate is the square of the distance from the open end of the capillary to the meniscus, l^2. The distance l was measured directly by the comparator.

The rate of displacement of the meniscus v in the capillary due to diffusion of vapor into the surrounding medium is equal to

$$v = \mu p_s D(\varphi_M - \varphi_0)/\rho R T l, \quad \text{cm/sec.} \tag{1}$$

Substituting $v = dl/d\tau$ and solving this equation, we obtain

$$l^2 = 2\mu p_s D(\varphi_M - \varphi_0)\tau/\rho R T = 4\alpha\tau. \tag{2}$$

Here α denotes a quantity constant under given experimental conditions. It follows from Eq. (2) that at constant temperature and relative vapor pressure the function $l^2(\tau)$ must be linear. As is evident from Figs. 1-3, $l^2(\tau)$ is actually linear, indicating satisfaction of Eqs. (1) and (2).

For water the values $\alpha = 8.85 \cdot 10^{7}$ ($\varphi_0 = 0.75$); $5.14 \cdot 10^{-7}$ ($\varphi_0 = 0.85$), and $2.6 \cdot 10^{-7}$ cm^2/sec ($\varphi_0 = 0.94$) calculated from the slopes of the $l^2(\tau)$ curves correspond exactly with theoretical values from Eq. (2), assuming $\mu = 18$ g/mole; $D = 0.257$ cm^2/sec; $\rho = 1$ g/cm^3; $T = 300.6$°K, and $\varphi_M = 1$. In practice the results for the low-concentration solution with C = 0.075% do not differ from those for water. This is because according to Rowle's equation the vapor pressure in this case is depressed only by hundredths of a percent. This follows, in particular, from Fig. 4, which shows reduction is vapor pressure above a KCl solution as a function of the solution's concentration. Due to the absence of accurate tabular data for KCl, curve 1 was constructed approximately. Its initial segment corresponds to Rowle's equation for ideal solutions (dashed line 2). This line (in analogy to the behavior of other solutions, e.g., NaCl [6]) joins the point corresponding to a vapor pressure (= 0.85) above the saturated KCl solution (C = 26.7% [6]. The dashed segment 3 indicates a supersaturated solution state.

As is evident from Figs. 1-3, for high-concentration solutions the evaporation rate is markedly lower than for water. However, the functions $l^2(\tau)$ remain linear, which indicates constancy of vapor pressure above the meniscus φ_M over the entire course of evaporation. Table 1 shows values of φ_M, calculated from Eq. (2) on the basis of the α values obtained

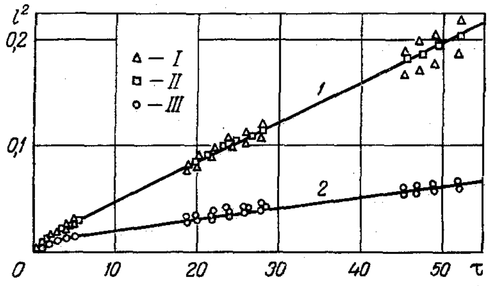

Fig. 3

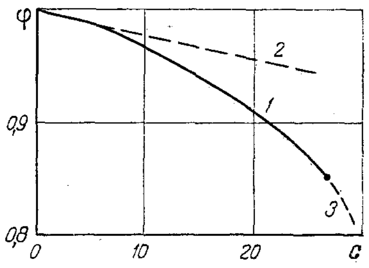

Fig. 4

Fig. 3. Square of meniscus displacement l^2 in capillary ($r \approx 1$ μm) versus evaporation time τ for $\varphi_0 = 0.94$ and $T = 300.6$°K: 1) water, capillaries Nos. 3, 7 (points I); KCL solution 0.075%, capillaries Nos. 4, 8 (points II); 2) KCl solution, $C = 7.45\%$, capillaries Nos. 1, 5, 9 (points III).

Fig. 4. Reduction in relative vapor pressure φ above KCl solution versus solution concentration C at $T = 300.6$°K. C, %.

from the graphs and the same values of μ, ρ, p_s, and D as obtained in water experiments. Since the electrolyte is nonvolatile, there appear in Eq. (2) only the characteristics of the volatile solution component, i.e., water.

The values of φ_M are lower than the vapor pressure φ_p above the initial solution, which is due to the concentration of the solution during evaporation. The constancy of φ_M during evaporation can be explained by Zolotarev's theory [3] that further growth in concentration (after rapid establishment of $\varphi_M = \text{const} > \varphi_p$) is compensated exactly by diffusion removal of electrolyte into the inner reaches of the capillary. This is valid, however, only in the absence of convection and for a semiinfinite capillary, which was the case in our experiments, since the capillaries were sufficiently narrow and the total capillary length was an order of magnitude larger than the l values reached in experiment.

Using Eq. (4), the φ_M values can be used to obtain the electrolyte concentration at the meniscus, C_M. As is evident from Table 1, where these C_M values are denoted as experimental, the electrolyte concentration near the meniscus is ≈ 25-65% higher than the concentration of the initial solution C, shown in the second column. We will compare these C_M values with theory. For low evaporation rates, as occurred in the experiments performed, we may use an approximate solution for isothermal conditions [3]:

$$C_M = C\left(1 + \sqrt{\pi\alpha/D_*}\right). \tag{3}$$

Substituting in this equation values of C and α from Table 1 and taking $D_* = 2 \cdot 10^{-5}$ cm²/sec, we obtain the theoretical values of C_M.

At $\varphi_0 = 0.75$ the agreement between experimental and theoretical C_M values is good. However, the C_M values exceed the saturated electrolyte concentration, which is 26.7%. Since precipitation of crystals would lead to a rapid reduction in evaporation, which was not observed, a slight supersaturation must be maintained in the meniscus zone. In connection with this it should be noted that, in contrast to [7], we found no "creep" of a saturated KCl solution film along the quartz surface. Examination of the capillaries with the microscope revealed no crystal seeds. Thus, the "creep" phenomenon does not occur under strictly isothermal conditions, as in our experiments.

At $\varphi_0 = 0.85$ and $\varphi_0 = 0.94$ the divergence of experimental and theoretical C_M values reaches 13-14%. This may be due to a number of causes: insufficient accuracy in the function φ(C) used (Fig. 4) or the effect of film transfer of moisture near the meniscus, not considered by the theory of [3]. The contribution of the latter, as is well known, increases with increase in φ_0 and decrease in capillary radius [5, 8, 9]. Unfortunately, in the experiments performed at $\varphi_0 = 0.85$ and 0.94 only very thin capillaries with $r \approx 1$ μm were used.

The presence of a film on the capillary surface near the meniscus, from which evaporation also occurs, leads to degradation of the conditions for removal of the electrolyte

TABLE 1. Change in Solution Concentration near Evaporating Meniscus in Capillaries

φ_0	C, %	$\alpha \cdot 10^7$, cm²/sec	φ_M	φ_p	C_M, %		No. of measurements
					exp.	theory	
0,75	22,35	3,0±0,2	0,84±0,005	0,902	27,6	27,2	7
0,85	7,45	3,4	0,953	0,98	12,2	9,2	3
0,94	7,45	7,0±0,3	0,96±0,001	0,98	11,0	8,2	3

accumulating in the evaporation zone, since the film is thin. This may produce elevated experimental C_M values in comparison to theory. However, this supposition requires further verification.

In conclusion, we note that the introduction of sodium lauryl sulfate in concentrations of $5 \cdot 10^{-4}$ to 0.5% caused no perceptible change in the evaporation rate of either water or the solutions, which agrees with data obtained earlier [10].

The results of this study confirm the validity of the solution evaporation theory presented in [3]. The solution concentrations at the meniscus under conditions of a semi-infinite capillary are actually increased, and do not change with time during evaporation. For a strict quantitative verification of the theory it is necessary to perform experiments with solutions for which the functions φ_0 (C) are known exactly. It would also be desirable to study evaporation from relatively short capillaries, which would permit consideration of the effect of pore finiteness, which is significant in practical drying applications. We note in this connection that in a number of experiments with large l values deviations from linearity of $l^2(\tau)$ were observed in the direction of reduced evaporation rate.

A more complex, but no less interesting problem is the study of evaporation of solutions, both components of which are volatile. The experimental method developed herein would be convenient for such studies, which have not only theoretical, but also, practical importance.

NOTATION

μ, mass of a mole of water, g/mole; D, diffusion coefficient of vapor through air, cm²/sec; φ, relative vapor pressure in chamber (relative air humidity); φ_M, relative vapor pressure above meniscus; ρ, density of water, g/cm³; R, gas constant, erg/mole·deg; T, temperature, °K; D_*, diffusion coefficient for molecules in solution, cm²/sec.

LITERATURE CITED

1. F. L. Jackson and F. P. Krause, J. Phys. Chem., No. 11, 2355 (1963).
2. A. E. Afanas'ev, N. I. Gamayunov, and N. V. Churaev, Kolloidn. Zh., 33, No. 11 (1971).
3. P. P. Zolotarev, Dokl. Akad. Nauk SSSR, 168, 83 (1966).
4. V. D. Sobolev, in: Questions in the Physics of Form Formation and Phase Transiton [in Russian], Tulsk. Politekh. Inst., Tula (1970) p. 143.
5. N. V. Churaev, and N. E. Yashchenko, Pochvovedenie, No. 9 (1973).
6. Handbook of Chemistry [in Russian], Vols. 3 and 4, Khimiya, Leningrad (1967).
7. H. Bin-Juine and H. Jen-Chi, Nature, 261, 36 (1976).
8. B. V. Deryagin, S. V. Nerpin, and N. V. Churaev, Kolloidn. Zh., 26, 301 (1964).
9. N. V. Churaev, Inzh.-Fiz. Zh., 19, No. 2 (1970).
10. I. G. Ershova, Z. M. Zorin, and N. V. Churaev, Kolloidn. Zh., 38, 973 (1976).