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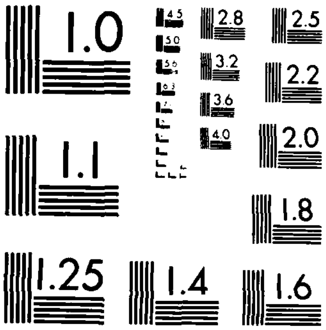

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FOREIGN TECHNOLOGY DIVISION

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KINETICS OF EVAPORATION AND GROWTH OF DROPS OF AQUEOUS SOLUTIONS OF SURFACE ACTIVE SUBSTANCES AT NEGATIVE TEMPERATURES

by

Yu. I. Sokolov

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EDITED TRANSLATION

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В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
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И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*<u>ye</u> initially, after vowels, and after ъ, ь; <u>e</u> elsewhere.
When written as ë in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh^{-1}
cos	cos	ch	cosh	arc ch	cosh^{-1}
tg	tan	th	tanh	arc th	tanh^{-1}
ctg	cot	cth	coth	arc cth	coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

GRAPHICS DISCLAIMER

KINETICS OF EVAPORATION AND GROWTH OF DROPS OF AQUEOUS SOLUTIONS OF SURFACE ACTIVE SUBSTANCES AT NEGATIVE TEMPERATURES

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Thanks to the numerous experiments at the present time it is established that surface-active substances (SAS), both soluble and insoluble, substantially slow the rate of evaporation of water drops. In the case of insoluble SAS the slowing of evaporation comes down to the creation of a mechanical barrier by SAS molecules, preventing the outlet of water molecules from the surface of the drop. In work [1] a formula was theoretically obtained, expressing the rate of quasistationary evaporation of a drop of water, covered with a layer of insoluble SAS:

$$I = \frac{4\pi r^2 (c_0 - c_\infty)}{\frac{c_0}{c_p}\frac{\delta}{D_1} + \frac{1}{\alpha v} + \frac{1}{D}\frac{r^2}{r+\lambda}}, \qquad (1)$$

where r - radius of drop; c_0 and c_∞ - concentration of water vapor near the surface of the drop and at a large distance from it respectively; c_p - concentration of saturated solution in the layer; δ - layer thickness; D and D_1 - diffusion coefficients of molecules of water vapor in air and molecules of water in the layer respectively; α - coefficient of condensation; v - fourth part of average absolute speed of molecules of vapor; λ - length of free path of molecule.

Terms in the denominator of (1) are treated by the authors as partial resistances to evaporation: $\frac{r_0}{r_1}\frac{\delta}{D_1}$ - partial diffusion resistance of layer, $\frac{1}{\alpha v}$ - resistance of molecular flow close to the surface of drop, $\frac{1}{D}\frac{r^2}{r+\lambda}$ - resistance, caused by diffusion of vapor in air.

Since the quantity of molecules of water, leaving the surface of the drop, covered with a layer of insoluble SAS, is sharply reduced, the condensation coefficient for drops with SAS turns out to be $10^2 - 10^3$ times smaller than for drops of water (α=0.036). For example, according to data of [2], the condensation coefficient of water drops, covered with a layer of cetyl alcohol, is $3.5 \cdot 10^{-}$[illegible].

The matter is more complex with the investigation of soluble SAS. Some authors [3, 4] consider that the slowing of the evaporation rate, as in the case of insoluble SAS, is connected with the formation of an adsorption film of molecules of dissolved SAS on the surface of a drop of water. In this case it is assumed that the formation of film occurs with a concentration, starting with which the amount of surface tension, having achieved minimum value, remains constant (for many SAS this is observed already with c=0.1-1% by weight).

Thus, for example, L. F. Leonov and P. S. Prokhorov, having experimentally studied the evaporation of fine drops (r=3-4 microns), consider that the growth of the effect of slowing of the evaporation rate of drops of SAS aqueous solutions with increase of the concentration of solution from 0.01 to 0.1% is connected with the gradual filling of the surface of drops by molecules of SAS [4]. In their opinion, the kinetics of evaporation of fine drops of solutions of SAS with the presence of an adsorption film, as for insoluble SAS, is described by formula (1). However, as experiment has shown, the condensation coefficient of aqueous solutions of SAS is only 2-3 times less than the condensation coefficient of water [5, 6]. Consequently, the mechanism of slowing of the evaporation rate for drops of soluble SAS is different than for drops with insoluble SAS. In the opinion of V. G. Morachevskiy and others [7], the slowing of the evaporation rate is connected with the volumetric properties of aqueous solutions of SAS (up to concentrations, equal to KKM).

Obviously, with such a conception the phenomenon of slowing of evaporation should be considered from the point of view of intermolecular interactions in the system SAS-water. As a result of recent spectroscopic investigations [8] a shift of the absorption band of water is revealed from 5180 to 5173-5170 см^{-1} with the dissolving of very small quantities of SAS in water (c=0.001-0.01% by weight). The shift of the absorption band, in the opinion of the authors, indicates increase of the number and the strength of hydrogen bonds in the solution under the effect of hydrocarbon chains of SAS, which cannot affect the thermodynamic properties of solutions of SAS.

For confirmation of this conclusion it is required to conduct additional investigations, to which this work is dedicated. In it are presented results of experimental investigations of the rates of evaporation and the growth of drops of aqueous solutions of SAS with weight concentrations 0.0001-0.1% at negative temperatures of air.

For conducting the experiments an installation was created, the diagram of which is shown in Fig. 1.

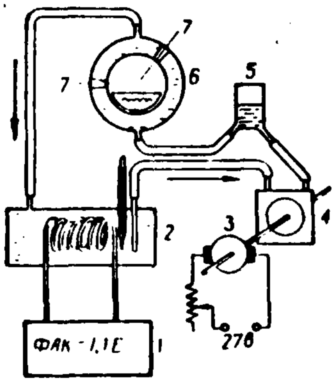


Fig. 1. Diagram of installation (without optical part): 1 - cooling unit, 2 - tank with cooling fluid, 3 - electric motor, 4 - pump, 5 - devibrator, 6 - chamber, 7 - thermistors.

In a brass tank of 9 liter capacity occurs cooling of the liquid, having a low freezing temperature (aqueous solution of ethylene glycol). A coil made of copper tubes, soldered into the tank, serves as the evaporator of the cooling unit FAK-1.1E. The cooled fluid is driven by a pump through rubber tubes into the chamber. The pump is driven by a dc-motor, the speed of rotation of which can be regulated. The temperature in the chamber is set by the operating mode of the cooler and can be changed from +20 to -20°C.

For elimination of vibration from jerks of the fluid being pumped, in the tube between the pump and the chamber a devibrator is installed. It is a metal cylinder, the lower part of which is filled with fluid, and the top part with air. During pumping the air is compressed and the jerks are damped by oscillation of the upper edge of the fluid.

The study of evaporation and growth of the drops is conducted in the chamber, being a cylinder made of organic glass with internal volume 75 $см^3$. The cooling fluid, circulating through the hollow walls of the chamber, provides uniform lowering of the temperature in the internal volume.

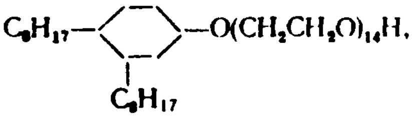
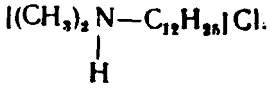
A certain humidity is created in the chamber. For this purpose in the lower part of the chamber is located a container, inside which is located a coil made of thin Nichrome wire. The current passing through the coil heats the distilled water poured into the container, which serves as the source of moisture. The degree of moistening is regulated by the amount of passing current and is measured by the evaporation rate of the water drop.

The investigated drops are suspended on small-scale highly sensitive MTB-60 thermistors, serving as sensors of electrothermometers. The construction of the chamber permits making observations in transmitted or reflected light. For determining the dimensions of drops a KM-6 cathetometer was used.

In our tests on one of the two thermistors was suspended a drop of solution of SAS, on the other - a drop of twice distilled water. The diameter of the drops was 1.0-1.1 mm. The distance between the drops did not exceed their diameter. With the aid of the cathetometer the vertical dimension of the drops was measured. Readings were taken every 2 min for 20 min. The obtained experimental data were subjected to statistical processing with the use of linear regression theory. Computations were made on an M-20 computer.

By the difference between the angular components of straight lines $r^2(\tau)$ (r - radius of drop, τ - time) for drops of water and SAS solution it was possible to quite validly judge the rate of evaporation of the drop of SAS relative to the drop of water.

The temperature and humidity in the chamber during measurements were kept constant. The tests were conducted at temperatures from 0 to -10°C and relative humidity close to 100%.

The rates of evaporation of aqueous solutions of sodium dodecyl sulfate $C_{12}H_{25}SO_4Na$, polyoxyethylated dioctylphenol  potassium stearate $C_{18}H_{35}COOK$ and dimethyl dodecylamine hydrochloride  $[(CH_3)_2\underset{\substack{|\\H}}{N}-C_{12}H_{25}]Cl$.

As a result of the conducted tests it turned out that the solutions of dimethyl dodecylamine hydrochloride, polyoxyethylated dioctylphenyl and sodium dodecyl sulfate with concentrations 0.001 and 0.01% were evaporated slower than drops of water (Fig. 2). Potassium stearate in contrast to the first three SAS slowed the evaporation of water only with 0.1% concentration.

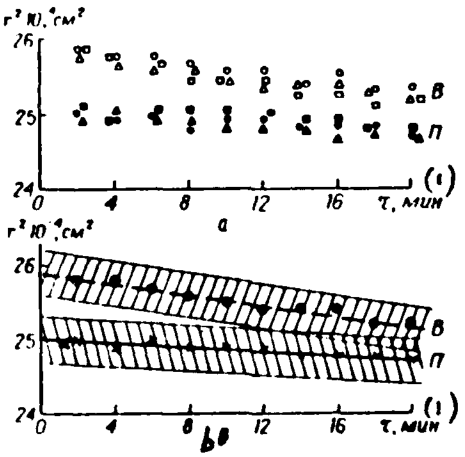


Fig. 2. Evaporation of drops of 0.01% solution of sodium dodecyl sulfate (П) and distilled water (B) at temperature of drops -2°C and relative humidity of air 96%: a - experimental data of three tests. b - results of statistical processing.
Key: (1) min.

Along with tests on the evaporation of drops of SAS and water, of great interest for the correct interpretation of their results was the investigation of the behavior of a drop of solution SAS at the time when the drop of distilled water did not change its size, i.e., with relative humidity 100% with respect to water. For such tests sodium dodecyl sulfate was selected. The obtained results showed that the drops of sodium dodecyl sulfate solutions invariably grew with concentrations of solutions 0.001 and 0.01% (Fig. 3).

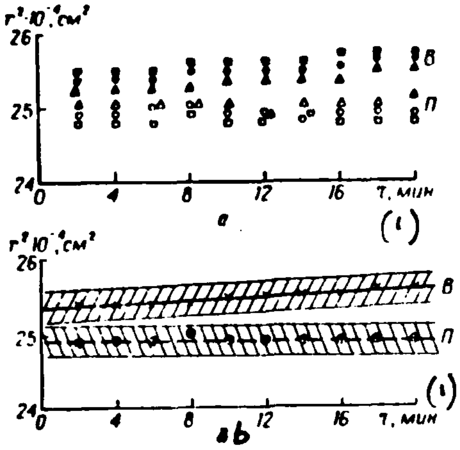


Fig. 3. Growth of a drop of 0.01% solution of sodium dodecyl sulfate (П) and distilled water (B) with temperature of drops -6°C and relative humidity of air 100%: a - experimental data of three tests. b - results of statistical processing.
Key: (1) min.

Taking into account the considerations expressed in [8] and the results of this work, it is possible to make the only possible conclusion about the fact that the cause of slowing of the evaporation rate of drops of solutions of SAS and their growth with humidity equal to 100% is lowering of the equilibrium elasticity of water vapor above their surface. The amount of lowering of vapor pressure, calculated by the evaporation rate and the growth of drops of sodium dodecyl sulfate, is 0.1 mb.

It is interesting to note that with concentration of solution 0.1% no effect of molecules of polyoxyethylated dioctylphenol on the evaporation rate of water appeared, and drops of solutions of sodium dodecyl sulfate and dimethyl dodecylamine hydrochloride were evaporated even more rapidly than drops of water. The effect of increase of the evaporation rate of drops of solutions of SAS, anomalous in its character, was discovered also by other authors. Thus, for example, L. F. Leonov and P. S. Prokhorov observed more rapid evaporation of drops of 0.01% solutions of hexyl alcohol and quartolit in comparison with drops of water [4].

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