THE LIQUID DROPLETS EVAPORATION FOR LOW PRESSURE'S VALUES UNDER LOW-POWER IRRADIATION WITH DIFFERENT FREQUENCIES AT THE OPTICAL RANGE

A.V. BRYTAN, G.M. VERBINSKA, V.M. SYSOEV, V.L. KARBOVSKIY, T.V. CLESHCHONOK

Taras Shevchenko National University of Kyiv, Faculty of Physics
(4b, Prosp. Academician Glushkov, Kyiv 03022, Ukraine; e-mail: `a_britan@ukr.net`*)*

PACS 47.70 Mc, 63.03.Fg

The results of experimental researches concerning the influence of optical radiation with various frequencies (wavelengths of 390, 565, and 625 nm) on the droplet evaporation rate in the atmosphere of dry nitrogen at pressures of 30, 50, and 100 mm Hg and the temperature of a vapor-gas mixture of 20 °C, which were obtained for a number of liquids, are reported. A substantial increase of the evaporation rate for water (up to 25%), nitrobenzene (up to 40%), and iodobenzene (up to 60%) droplets at a constant droplet temperature during the evaporation has been detected. The evaporation rates for ethyl benzene and isoamyl alcohol droplets in the dark regime and under radiation are found invariable within the limits of experimental errors. The red threshold of this effect is observed.

1. Introduction

The evaporation of liquid droplets in a gaseous environment and the inverse process of droplet formation in a medium with oversaturated vapor are of large interest both from the viewpoint of fundamental science and technical applications. Suffice it to recall that water circulates in the nature through the stages of its evaporation from the reservoir surface and the cloud formation owing to the water vapor condensation at condensation centers in the atmosphere. The formation of clouds and fog, as well as the mechanisms of their evolution, is an important issue of the atmosphere physics.

Of special interest are the processes of liquid evaporation and condensation that run in higher layers of the atmosphere under low pressures and optical irradiation which substantially change the rate of those processes. This work is aimed at studying the influence of the mentioned factors on the evaporation rate of suspended liquid droplets 1–2 mm in dimension.

2. Theoretical Part

The specific phase transformation, including the evaporation process, occurs at a certain rate that depends on conditions, under which the phase transition takes place. The simplest case is the evaporation from a liquid surface into vacuum.

If a liquid is in a closed vessel, a saturated vapor is formed over its surface, and a dynamic equilibrium is established, at which the number of molecules leaving the liquid surface is equal to that of molecules going from the vapor back into the liquid. The number of molecules that condense on a unit area of the liquid surface per unit time is expressed by the known formula for the kinetic evaporation regime

$$\frac{dN}{dt} = \alpha\,\Omega\,n\frac{\overline{v}}{4}, \tag{1}$$

where n is the concentration of vapor molecules, α is the so-called condensation coefficient, $\Omega = 4\pi r^2$ is the droplet surface area, and $\overline{v} = \sqrt{\frac{8kT}{\pi m}}$ is the average thermal velocity of vapor molecules.

In many real cases, the evaporation of a liquid occurs in the presence of another (background) gas. Then, molecules that left the liquid cannot go far away from its surface owing to their collisions with molecules of the background gas. Molecules of the evaporating substance diffuse away from the liquid surface. This process is called the diffusion regime of evaporation. The rate of diffusion evaporation of a droplet with radius r is determined by the Maxwell formula [1, 2]

$$I_m = -\frac{dm}{dt} = 4\pi r\, D(C_0 - C_\infty), \tag{2}$$

where I_m is a change of the droplet mass per unit time, D the diffusion coefficient of the liquid vapor in the background gas, C_0 the concentration of the saturated vapor at the droplet temperature, and $C_\infty = C_0\varphi$ the vapor concentration at an infinite distance from the droplet, which is determined by the humidity.

While comparing expressions (1) and (2) in the case where the droplets of the same substance and with a unit dimension are evaporated, one can see that the evaporation in the diffusion regime is determined by the value of diffusion constant, which is of the order of 10^{-5} m^2/s, whereas the evaporation in the kinetic regime is determined by the product $\alpha\frac{\bar{v}}{4}$ of the order of 10^{-1} m/s. Using these data, we can evaluate the ratio between the evaporation rates in both regimes to obtain that the evaporation rate in the diffusion regime is low in comparison with that in the kinetic one. That is why the diffusion rate of the liquid vapor in the background gas governs the droplet evaporation rate.

Supposing droplets to be spheres with density ρ, the evaporation rate can be expressed by the formula

$$-\frac{dS}{dt}=\frac{8\pi D}{\rho}\left(C_0-C_\infty\right), \qquad (3)$$

The experimental values of evaporation rate $\frac{dS}{dt}$, which were obtained in the diffusion regime and under the condition that the pressure in the environment gas is close to the atmospheric one, and those calculated by formula (3) coincide within the limits of experimental errors.

Substantial deviations from the Maxwell theory are observed at low ambient pressures, when droplets evaporate intensively [1]. Those deviations result from the following factors:

1. There exists a macroscopic concentration jump at the droplet surface, which grows at the intense droplet evaporation [1, 3]. There emerges the so-called Δ-layer around a droplet [1]. The layer width is of the order of the mean free path of molecules. The vapor concentration C_1 at the boundary of this Δ-layer is not equal to the concentration C_0 of the saturated vapor near the droplet surface.
2. There appears a flow near the droplet surface. The flow is governed by the dynamics of collisions between molecules of the vapor and the background gas.
3. The temperature of the droplet surface decreases during the establishment of a quasistationary regime at the initial stage of evaporation, and the temperature jump “droplet temperature – ambient temperature” is formed. This jump can sometimes reach tens of degrees.

Therefore, a number of corrections, which take real experimental conditions into account, must be introduced into the Maxwell formula [1]:

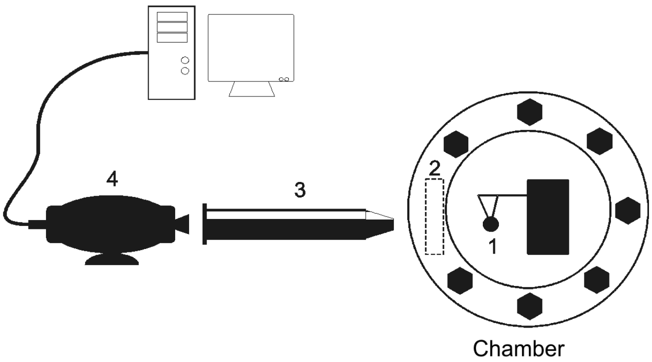

Fig. 1. Scheme of an experimental installation for the measurement of the evaporation rate of liquid droplets

– a correction on the vapor concentration jump at the droplet surface (the Fuks correction), $\left[\frac{D}{ru\alpha}+\frac{r}{r+\Delta}\right]^{-1}$; in the case $\Delta \ll r$, it looks like $\left[\frac{D}{ru\alpha}+1\right]^{-1}$;
– a correction on the Stefan flow, $\left(1+\frac{P_0+P_\infty}{2P}\right)$;
– the account of the temperature dependence of the diffusion coefficient at large $(T_\infty-T_0)$-values, $D=\sqrt{D_0D_\infty}$.

At the intense evaporation, the droplet surface is strongly cooled down. An ordinary temperature sensor located at the droplet center has no time to reply and inserts an error into the T_0-measurement. Therefore, a special electronic system was created, which allowed the droplet temperature to be measured with a required accuracy.

Hence, with regard for all those corrections, the evaporation rate is determined by the formula

$$-\frac{dS}{dt}=\frac{8\pi\sqrt{D_0D_\infty}\left(C_0-C_\infty\right)}{\frac{D}{ru\alpha}+1}\left(1+\frac{P_0+P_\infty}{2P}\right). \qquad (4)$$

With the help of this formula, we approximated the experimental dependences of the droplet evaporation rate $\frac{dS}{dt}$ on the reciprocal pressure. This allowed us to determine the condensation coefficient for the studied liquid.

3. Experimental Part

The evaporation rate was measured on an installation, the scheme of which is exhibited in Fig. 1. Chamber *2* used to study the evaporation of suspended droplet *1* had a form of a horizontally oriented cylinder 20 l in volume. A thermostating liquid was circulating between the double walls of a cylinder. The thermostat kept the temperature in the chamber constant to within ±0.1 °C in the range of 5–40 °C.

In this work, we consider the processes of droplet evaporation under the influence of low-power optical radia-

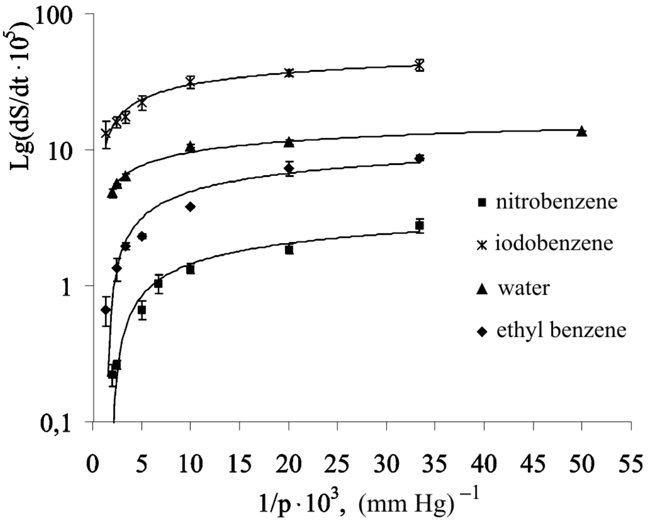

Fig. 2. Dependences of the evaporation rates of nitrobenzene, iodobenzene, water, and ethyl benzene droplets in the atmosphere of dry nitrogen at $T = 20$ °C in the dark regime on the reciprocal pressure

tion. In this case, very important is the measurement of the exact droplet temperature during the droplet evaporation. Therefore, to monitor the droplet temperature, we created a special device composed of a circuit board of temperature-sensitive elements and the circuit board of an analog-to-digital converter supplied with an interface card to connect it to a personal computer. The temperature in the chamber was monitored by a temperature sensor. For this purpose, we used the *p*-*n* junction of a chip transistor. This allowed the inertia of the system for the temperature monitoring to be considerably reduced. The electronic system allowed us to measure the temperature with an accuracy of ±0.03 K. Another similar sensor was used to monitor the droplet temperature. To make a contact with the liquid better, the sensor was also used as the bracket for a droplet. It should be noted that the simultaneous application of the *p*-*n* junction of a chip transistor as a bracket and a temperature sensor allowed us to substantially reduce heat conductivity through the bracket and approach the conditions of free-droplet evaporation much closer in comparison with the traditional technique of temperature measurements with the help of a thermocouple.

For carrying out the measurements of the droplet evaporation rate in a wide range of pressures (from ambient to 3–5 mm Hg), a special vacuum device was connected to the chamber, which allowed us to obtain low pressures in the chamber. The pressure was measured using an U-tube mercury-filled manometer and controlled by an electronic device. A high air-tightness of the chamber allowed us to carry out measurements at a constant pressure within a wide time interval.

Glass windows were hermetically built into an end surface of the chamber, which allowed us to illuminate the chamber and observe the evaporation process.

A suspended droplet was regularly photographed at a certain time interval making use of video camera *4* located outside the vacuum cylinder and supplied with a specially selected objective *3*. For qualitative measurements, it is necessary to establish such an illumination regime that the dark droplet edge be clearly distinguished against a light background. A wire with calibrated thickness was located near the droplet to provide the proper scaling of the photo. Since the temperature and the photos were registered with the help of the same computer, the computer's system clock was used as a time scale. The droplet images were automatically registered in regular time intervals, and the file creation time was identified as the time of image registration.

4. Experimental Results

In our experiments on the evaporation of liquid droplets suspended on a bracket in a chamber with a fixed pressure, we determined the droplet surface area S, the droplet temperature T_k, and the ambient temperature T_∞. The measurements were repeated with a definite time step. The evaporation rate dS/dt was determined from the slope of the linear dependence $S(t)$ of the droplet surface area on the time. Droplets were evaporated in the dry nitrogen atmosphere, so that $C_\infty = 0$ in formula (4).

The evaporation of water, nitrobenzene, iodobenzene, and ethyl benzene droplets was studied both in the dark regime and at the illumination of droplets with laser-diode radiation with the wavelengths $\lambda = 390$, 565, and 625 nm. In the absence of illumination and at the illumination with a wavelength of 390 nm, the droplets of indicated liquids were evaporated in a wide range of pressure: from atmospheric to 30 mm Hg. The droplet evaporation rate under the illumination with $\lambda = 565$ and 625 nm was studied at pressures of 100 and 50 mm Hg, because, as was shown in works [4, 5], the influence of optic radiation on the droplet evaporation rate is the most pronounced just at low ambient pressures.

In Fig. 2, the dependences $\frac{dS}{dt} = f(\frac{1}{p})$ obtained for all indicated liquids in the dark regime are depicted on the logarithmic scale. The evaporation rate grows along the series nitrobenzene → iodobenzene → water → ethyl benzene. The corresponding condensation coefficients

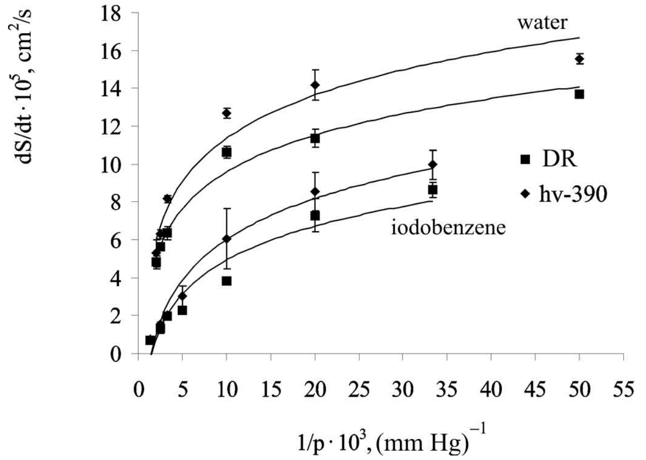

Fig. 3. Dependences of the evaporation rates of water and iodobenzene droplets in the atmosphere of dry nitrogen at $T = 20$ °C on the reciprocal pressure in the dark regime (DR) and at the ultra-violet illumination

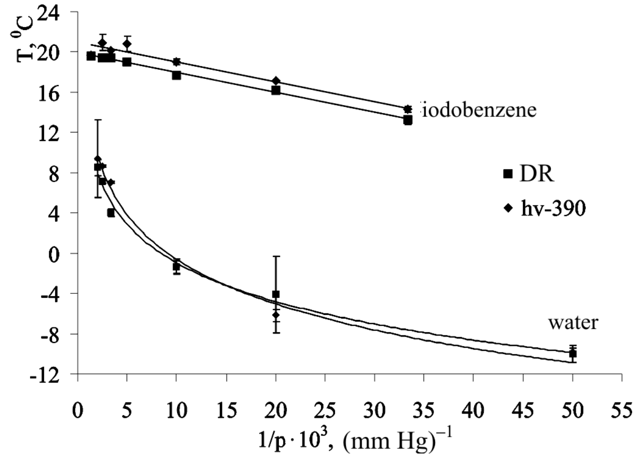

Fig. 4. Dependences of the water and iodobenzene droplet temperatures T_k on the reciprocal pressure during the stationary process of evaporation in the dark regime and at the ultra-violet illumination

calculated by formula (4) are $\alpha = 0.006$ (nitrobenzene), 0.004 (iodobenzene), 0.0017 (water), and 0.001 (ethyl benzene).

A low-power source of radiation (a 3.5-W laser diode) was mounted at a distance of 2.5 cm from the droplet. Therefore, both the droplet and the surrounding vapor-gas environment were illuminated. As Fig. 3 demonstrates, an appreciable increase in the evaporation rate of water and iodobenzene droplets was observed—in comparison with the dark regime–at the illumination of droplets at a wavelength of 390 nm. The growth of the evaporation rate at the illumination was higher at lower environment pressures.

It should be noted that the measurements of the temperature in the course of droplet evaporation testified that the increment of the evaporation rate was not connected with the droplet heating. In Fig. 4, the dependences of the droplet temperature on the reciprocal pressure, $T = f(\frac{1}{p})$, obtained at the illumination of droplets and in the dark regime are depicted. One can see that the temperatures of water and iodobenzene droplets practically did not differ in both regimes. The temperature difference at a specific pressure did not exceed 1–2 °C. At the same time, the evaporation rate of water droplets at the lowest pressures increased by 25% in comparison with that in the dark evaporation regime. For iodobenzene droplets, this increment amounted to 59%.

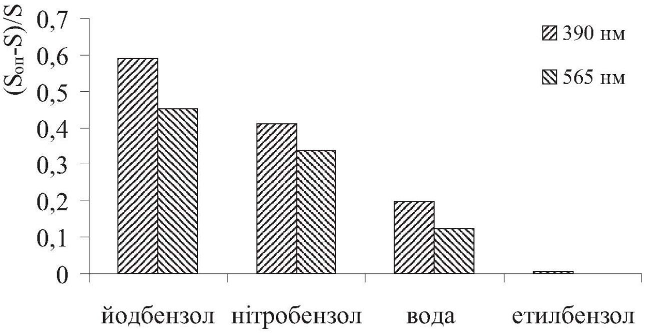

Fig. 5. Relative increase of the evaporation rate, $(S_{\mathrm{ill}} - S)/S$, under the illumination at wavelengths of 390 and 565 nm and a pressure of 100 mm Hg for various liquids

In Fig. 5, a histogram of the relative growth of the evaporation rate under the action of illumination at $\lambda = 390$ and 565 nm in comparison with the dark regime is presented for all liquids concerned. At the illumination with $\lambda = 390$ nm, the evaporation rate grows by 19% for water droplets, by 40% for nitrobenzene ones, and by 59% for benzene iodine ones. At the illumination with $\lambda = 565$ nm, the relative growth of the evaporation rate was 13, 17, and 45%, respectively. The following fact is to be noted: the illumination with a red source with the wavelength $\lambda = 625$ nm did not result in an increase of the evaporation rate for the liquids under investigation. The evaporation rate of ethyl benzene droplets did not change at illumination, in the limits of experimental errors, irrespective of the used source. Similar results were obtained at a pressure of the surrounding gas of 50 mm Hg.

Hence, we have found experimentally the growth of the evaporation rate of water, nitrobenzene, and iodobenzene droplets under the optical illumination at wavelengths of 390 and 565 nm, with the evaporation rate being higher for higher radiation frequencies (shorter wavelengths). At the same time, there is a "red threshold" for this effect ($\lambda \geq 625$ nm), below which the illumination does not result in a change of the evaporation rate.

It is evident that there must be a mechanism of energy absorption and accumulation by molecules of a liquid in the near-surface layer of the droplet, which is responsible for this effect. The radiation absorption by the droplet itself can be neglected, because no droplet heating was detected (see Fig. 4), which can be explained by the low intensity of a light source in this experiment and rather small dimensions of droplets. In accordance with the energy conservation law, the molecules of a liquid, which absorbed some dose of electromagnetic radiation, leave the liquid surface with a velocity that is a little higher than that, which the molecule have under usual evaporation conditions. The concentration of excited molecules depends on the liquid properties, which can explain the difference between the relative evaporation rates for different liquids under the influence of illumination.

The surface tension coefficient of a liquid is equal to the ratio between the work that is spent to overcome surface tension forces and a variation of the surface area, $\sigma = \triangle A/\triangle S$. By applying the known formula for the red threshold of this effect, which is a consequence of the energy conservation law, $h\nu = \triangle A = \sigma\triangle S$, we obtained the value $\triangle S = 7$ nm^2. Let us imagine the process of molecule detachment from the droplet surface as a phenomenon, during which there forms a hemispherical cluster of several molecules on the surface, and the molecule that flies out of the droplet is located on the cluster top. Then, we can evaluate the size of this hemisphere to obtain that the radius of the excited area $r \approx 1$ nm. It should be noted that this estimation is somewhat overrated, because the photon energy is distributed between the molecule's internal degrees of freedom, which makes the matter much more complicated. However, even such a rough estimate gives a value which, by its order of magnitude, corresponds to the radius of a cluster composed of several molecules.

5. Conclusions

1. An increase of the evaporation rate of water, nitrobenzene, and iodobenzene droplets under the action of the optical radiation with wavelengths of 390 and 565 nm was experimentally detected. The largest growth of the evaporation rate was observed at an illumination wavelength of 390 nm and a low ambient pressure (100 mm Hg): by 19% for water, by 40% for nitrobenzene, and by 59% for iodobenzene droplets. The growth of the evaporation rate of ethyl benzene droplets under the same conditions was not detected.

2. The evaporation rate of liquid droplets depends on the illumination frequency. If the frequency of a radiation source becomes lower (the wavelength increases), the relative value of evaporation rate growth diminishes.

3. The presence of the so-called "red threshold" of radiation, below which the illumination does not increase the evaporation rate in the liquids concerned, was experimentally shown.

1. N.A. Fuks, *Evaporation and Growth of Droplets in a Gaseous Medium* (USSR Acad. Sci. Publ. House, Moscow, 1954) (in Russian).
2. L.A. Bulavin, G.M. Verbinska, and V.M. Nuzhnyi, *Kinetics of Liquid Droplet Evaporation in a Vapor-Gas Medium* (Kyiv Univ., Kyiv, 2003) (in Ukrainian).
3. G.M. Verbinska, V.N. Mal'nev, V.M. Nuzhnyi, and O.A. Zagorodnya, Ukr. Fiz. Zh. **48**, 944 (2003).
4. G.M. Verbinska and O.A. Zagorodnya, in *Modern Problems of Molecular Physics* (Kyiv Univ., Kyiv, 2003), p. 169 (in Ukrainian).
5. G.M. Verbinska, O.A. Zagorodnya, and V.M. Mal'nev, Ukr. Fiz. Zh. **48**, 428 (2003).

Received 10.03.11.
Translated from Ukrainian by O.I. Voitenko

ВИПАРОВУВАННЯ КРАПЕЛЬ РІДИН ПРИ НИЗЬКИХ ТИСКАХ ПІД ВПЛИВОМ МАЛОПОТУЖНОГО ОПРОМІНЕННЯ РІЗНОЇ ЧАСТОТИ В ОПТИЧНОМУ ДІАПАЗОНІ

*А.В. Британ, Г.М. Вербінська, В.М. Сисоєв,
В.Л. Карбовський, Т.В. Клещонок*

Резюме

Представлено результати експериментального дослідження впливу опромінення різної частоти (довжини хвиль 390, 565, 625 нм) на швидкість випаровування крапель деяких рідин в атмосфері сухого азоту при тисках 100, 50, 30 мм рт. ст. при температурі парогазової суміші 20 °С. Виявлено суттєве зростання швидкості випаровування крапель води (до 25%), нітробензолу (до 40%) та йодбензолу (до 60%) при незмінній температурі краплини під час її випаровування. Швидкість випаровування крапель етилбензолу та ізоамілового спирту в темновому режимі та за опромінення залишається незмінною в межах похибки експерименту. Встановлено червону границю цього ефекту.