LOW PRESSURE EVAPORATION OF BINARY PICOLITER DROPLET ON SUBSTRATE

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- Fluid: liquid droplet
- Visualization method: digital video, microscope
- Other keywords: binary droplet, metal substrate, free molecular regime, simulation

Introduction
For a number of modern technical applications it is necessary to know data about the evaporation time of picoliter droplets from a metal substrate at a reduced pressure of [1]. In particular, these values help to calculate the high heat fluxes due to the droplet evaporation. The results of our experimental and theoretical study of the evaporation of picoliter water droplet on a substrate were published recently in [2]. It is important to note that our mathematical simulation of the droplet evaporation is based on the free molecular approximation of the processes into the gas phase. The results of the next chapter of our research that is evaporation of water – alcohol picoliter droplet on metal substrate at reduced pressure are presented in this paper.

Experimental results
The original homemade setup is schematically shown in Fig. 1. The droplets were situated on a brass substrate. We use a transparent hood over droplet. Geometrical sizes of the hood are much larger than the droplet base diameter. Minimal pressure under hood was about 20 Torr. Droplets have been created by means of small hole with a diameter of 10 microns. The diameter of the droplet base ranges from 20 to 1000 microns.

In these experiments, we investigated the droplet base diameter of 150 microns. Droplets were an aqueous solution of various concentrations of ethanol. Registrations process took place with the help of a digital optical microscope "Digital Blue" company QXS. The experiments were performed with increasing '60s, as the focus and lighting do not provide a clear image with an increasing of 200x.
Picoliter droplet evaporation was recorded on videorecorder. We started recording when the height of the drop was 10 μm. It is worthy to emphasize that initial shape of droplet strongly dependent on the concentration of ethanol, that is depends on the effective surface tension of solution. It was found that base diameter of the droplet practically does not changed during evaporation and only the contact angle increased. In other words, we observed strong pinning effect. Physics of this phenomenon is very fast evaporation of edge of the droplet on substrate. Fast evaporation is due huge temperature gradient at the interfacial edge, approximately more than 10^6 K/m.

Photographs of the initial shape of droplets of solutions of different concentrations are shown in Fig. 2. The form of the surface of the droplets confirms that the surface tension of the solution decreases with increasing mole fraction of ethanol. Concentrations of ethanol are presented in Table.

![Initial shapes of droplet with different concentration of ethanol with the same diameter](image)

Figure 2 Initial shapes of droplet with different concentration of ethanol with the same diameter

<table>
<thead>
<tr>
<th>Θ (degree)</th>
<th>30</th>
<th>55</th>
<th>75</th>
<th>100</th>
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<tbody>
<tr>
<td>Molar concentration of ethanol, x</td>
<td>1</td>
<td>0.66</td>
<td>0.33</td>
<td>0</td>
</tr>
</tbody>
</table>

Table

Experimental measurements were carried out at a pressure of 60 Torr and the relative air humidity of 55%. The substrate temperature was equal to the air temperature; both ones are equals to 28 °C. The effective rate of droplet evaporation versus its initial composition is shown in Fig. 3.

![Evaporation rate versus the concentration of ethanol](image)

Figure 3. Evaporation rate versus the concentration of ethanol

For relatively low concentrations of ethanol (<40%) experimental results in Fig. 3 are explained by the specific behavior of the saturated ethanol vapor over the solution at temperatures near 20 °C. For such concentrations it is well known that the partial saturated pressure of ethanol vapor over the solution is much smaller than water vapor. As a result, only the evaporation of water vapor affects the rate of evaporation. The lower temperature of evaporation surface the more profound this effect. As can be seen in Fig.3, the rate of evaporation increased significantly with
increasing concentration of ethanol (> 70%). The main reason is increasing the equilibrium value of the partial pressure of saturated ethanol vapor over the solution.

It can be shown by means of qualitative analysis of the equations of hydrodynamics in evaporating picoliter droplet the evaporation time is to 5-10 times larger than the characteristic hydrodynamic time \( \tau \) of the relaxation of hydrodynamic processes. Characteristic time \( \tau \) can be estimated by the expression

\[
\tau = \frac{\rho h^2}{4\pi \mu},
\]

where \( \mu \) is the viscosity, \( \rho \) is the mass density of the liquid. For aqueous droplet with height \( h = 10 \mu m \) \( \tau \) is about \( 10^{-4} \) s.

Therefore quasi-stationary temperature profile and ethanol concentration profiles can be used. Keeping in mind our visualization facts, shown in Fig.2, we developed one-dimensional mathematical model of evaporation of picoliter binary droplets on substrate at reduced pressure. Some additional details are discussed in [2]. Also we introduce the effective height of the droplet, which take into account the initial shape of the droplet and the evaporation surface [2]. It is worth to note that for parabolic approximation of the droplet shape if the maximum height is 10 \( \mu m \) the effective height is about 5 \( \mu m \).

**Simulation results**

Our approximate mathematical model combines three ordinary differential equations: the equation for the change of the number of water molecules in the droplet, the equation for the change of the number of ethanol molecules in the droplet and, finally, the equation for change the temperature of the evaporation surface.

In particular, the equation for the change of the number of water molecules \( N_w \) in the droplet is

\[
\frac{dN_w}{dt} = \frac{1}{\sqrt{2\pi m_w k}} \left[ \frac{p_w}{\sqrt{T}} \frac{p_w(T_s, x)}{\sqrt{T_s}} \right],
\]

where \( k \) is Boltzmann constant, \( p_w \) and \( T \) are, correspondingly, the partial pressure of water vapor and gas temperature in the vacuum chamber (hood), \( T_s \) is temperature of the surface evaporation, \( m_w \) is mass of water molecules, \( p_w(T, x) \) is pressure of saturated water vapor over the solution to molar fraction of ethanol \( x \). Similar equation is used for the describing of the evaporation of ethanol molecules.

Let us introduce the velocity interfacial surface \( v \) of the droplet due to evaporation

\[
\frac{dh}{dt} = v,
\]

It can be easily measured by means of microscope observation and can be calculated if we know \( N_w \) and \( N_e \), droplet diameter and mass density of mixture \( \rho(x) \), which is well known from a handbook.

On the surface of droplet we have the Stefan Boundary condition:

\[
-\lambda(x)\nabla T = vU(x)\rho + F,
\]

here \( \lambda \) is the heat conductivity of the mixture, \( U \) is specific heat of evaporation per mass unit, \( F \) is the term, describing heat exchange of vapors and carrier gas with interface [2]. It is worthy to remind that for calculation \( F \) we use free molecular approximation. We transformed this equation into ordinary differential equation following [2].

For setting the initial conditions and the solving of the system of differential equations we used the time-reversal technique. That is the boundary conditions are given for practically evaporated droplet and then we solve in opposite direction of time. At this approach with good accuracy the temperature of the evaporation surface is equal to the temperature of the substrate at a height of droplet \( h_0 = 10 \) nm or less.
Some results of calculations evaporation of pure droplet of ethanol and water with the initial height 10 micron are shown in Figure 4. We see that evaporation rate of pure ethanol droplet is significantly larger than for pure water. Calculations are made with 55 % humidity, the pressure in chamber was 60 Torr and substrate temperature is the temperature of the gas phase and is 300 K.

From the results of the calculation it is clear that the average rate of evaporation of pure ethanol is 10 times higher than the average rate of evaporation of water droplets. Also our simulation shows that the evaporation rate is not constant during evaporation and increases sharply when the droplet height decreases to about 2 - 3 microns (see Fig. 4). For such height of droplet the temperature gradient inside the droplet provides a sufficiently high energy fluxes for evaporation of the molecules.

It is worthy to note that the surface temperature of evaporating droplets is very important parameter. We cannot measure the surface temperature of picoliter droplet yet. Calculations results gives that temperature of surface ethanol droplet can fall to 255 K, but for pure water droplet it falls only up to 290 K. For this difference in temperature one reason is that water thermal conductivity is much higher compare to ethanol one. The second reason is a higher rate of evaporation of ethanol. Note that in the residual gas atmosphere around the droplet is almost absence of ethanol molecules exist, which further ensures high effective rate of evaporation. It is worthy to note that the contribution of mixing heat is small enough one. The results of the surface temperature droplets of water and ethanol are shown in Fig. 5, calculation is carried out under the same conditions as in Fig. 5. It can be seen that quasy steady state temperature is practically constant and only at the end of evaporation it reach the temperature of substrate. For shorter period of time the temperature of evaporating surface of ethanol droplet has the same features. The temperature profile is linear one in the droplet.

For relatively low concentration of ethanol the temperature of evaporation surface of binary droplet is close to simulation results for pure water droplet. The reason is effect nonlinear dependence of saturated pressure of ethanol vapor over solution described above.

Qualitative estimation of time for reaching of steady state profiles of impurity $\tau_D$ in binary droplets is

$$\tau_D = \frac{h^2}{\pi^2 D}.$$ 

where D is the diffusion coefficient of impurity in the droplet. Thus for $h = 10 \mu m$ we have $\tau_D$ is about $10^2 s$. Similar, characteristic time for reaching steady state temperature profile $\tau_T$ is
\[ \tau_T = \frac{h^2}{\pi \alpha^2}, \]

where \( \alpha^2 \) is the thermal diffusivity of liquids. Thus for \( h = 5 \mu m \) we have \( \tau_T \) is about \( 10^{-4} s \).

**Conclusions**

Experimental and theoretical studies of evaporation of binary picoliter droplet on metal substrate at reduced pressure, about 50 Torr, have been made. Due to visualization of the droplet evaporation it was found that there is a strong pinning effect, which permits to develop one dimensional model of evaporation. Evaporation time of picoliter droplets on brass substrate was measured for different concentration of ethanol and substrate temperatures.

Additionally our qualitative hydrodynamic estimations [3] gives that for picoliter droplets the viscosity effectively suppresses any convective motions inside droplet due to small size.

We hope to use evaporation of binary droplet on substrate for cooling electronics with high heat fluxes [4] for broad range of temperatures of substrates.

**References**


