

# Evaporation dynamics and Marangoni number estimation for sessile picoliter liquid drop of binary mixture solution

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**Abstract.** We propose the evaporation model of picoliter sessile drop of binary solvent mixture (with infinitely soluble in each other components) based on Hu and Larson solution for single solvent sessile drop and Raoult law for saturated vapor density of components of binary mixture in wide range of undimensional molar binary concentration of the components. Concentration Marangoni number estimation for such a system is also considered for prediction of liquid flows structure for further applications in dissipative particle dynamics in binary mixture evaporating drop.

## 1 Introduction

The evaporating picoliter liquid sessile drop of axis-symmetric shape is an interesting object of theoretical and experimental investigations due to its important fundamental and practice applications. The evaporation of sessile drop of binary solvent mixture deposited by inkjet device on a flat substrate is considered. In case of picoliter drop, the typical thermal Marangoni number is small ( $M_{aT} < 10$ ), and thermocapillary convection can be neglected, unlike of the concentration driven convection.

The thermal Marangoni number is determined by  $M_{aT} = -\frac{c_V \Delta T H}{\nu \kappa} \frac{d\sigma}{dT}$ , where  $c_V$  is a specific heat

of liquid,  $\nu$  is a kinematic viscosity,  $\kappa$  is a thermal conductivity,  $\frac{d\sigma}{dT}$  is the rate of the change of the

surface tension with the temperature,  $\Delta T$  is the temperature difference between the substrate plane and the apex of the drop, and  $h$  is a drop height. To obtain the value of  $\Delta T$  we have been supposed

[1] the estimation  $\Delta T \propto \frac{\Delta H \rho_s D h}{\kappa R} (1 - \chi)$ , where  $\Delta H$  denotes an enthalpy (heat) of evaporation,

$\rho_s$  is a saturated vapor mass density,  $D$  is diffusion coefficient of vapor in the surrounding air,  $\chi$  is relative asymptotic value of the vapor concentration in the atmosphere (relative humidity of air in case of considering the water evaporation), and  $R$  is a drop radius. Analogously, concentration Marangoni

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number can be estimated by expression  $Ma_c = \frac{\Delta c H}{D_L \eta} \left| \frac{\partial \sigma}{\partial c} \right|$ , where  $\Delta c$  is normalized (relative) concentration difference of mixture component between the substrate plane and the apex,  $\eta$  is characteristic dynamical viscosity coefficient in liquid,  $\sigma$  is surface tension,  $D_L$  is a diffusion coefficient of water molecules in liquid mixture solution,  $n_{s0}$  and  $n_{L0}$  are concentrations of saturate water vapor and liquid vapor respectively,  $H$  is a height of the drop. Our estimation has shown that the value of  $Ma_c$  reaches more than  $10^4$  even for a picoliter binary mixture droplet, and the Marangoni instability really takes place. Recently, the concentration Marangoni driven migration of particles in such a system was experimentally investigated [2]. There was shown that the polystyrene nanoparticles were moved by toroidal vortex flow acted inside a drop, and the direction of this flow depends on solvent components types (ethanol/water, isopropanol/water, metoxypropanol/water), ratio of mixture, particle size and environmental conditions.

To estimate Marangoni number, we have developed novel evaporation model of picoliter sessile drop of binary solvent mixture (with infinitely soluble in each other components) based on Hu and Larson [3] solution for single solvent sessile drop and Raoult law for saturated vapor density of components of binary mixture in wide range of undimensional molar binary concentration of the components. The application of this model also includes the boundary conditions determination for Marangoni flows calculation to use in computer dissipative particle dynamics in picoliter drop of binary solvent mixture [1].

## 2 Model

Let's consider the sessile droplet of binary mixture solution with infinite mutual solubility of components in mixture at given external conditions.

There are two characteristic times in this system: drop evaporation time,  $t_e \propto \frac{L^2 n_L}{D(n_s - n_\infty)}$ , and

relaxation time,  $t_r \propto \frac{L^2}{D_L}$ , where  $L$  is characteristic size of drop;  $D, D_L$  are the diffusion coefficient of

molecule in air and in liquid respectively. Obviously, non-depending on  $L$  ratio  $\frac{t_r}{t_e} = \frac{D(n_s - n_\infty)}{D_L n_L}$

( $n_s, n_L, n_\infty$  are the concentrations of saturated vapor, liquid and vapor far from the drop respectively) is the criterion of concentration relaxation rate into drop. If  $\frac{t_r}{t_e} \ll 1$  then  $c = const$  inside the liquid drop is

good assumption, due to there is fast relaxation of concentration of binary components in the liquid drop of solution. With account of these approximations we obtain the next equations of evaporation dynamics

$$\frac{d\phi}{dt} = -\frac{2\phi(1+\cos\phi)^2}{\pi R^2 \sin\phi} [K_1(c-h) + K_2(1-h)], \quad (1)$$

$$\frac{dc}{dt} = \frac{2\phi \sin^2 \phi}{\pi R^2 \left( \frac{2}{3} - \cos\phi + \frac{\cos^3 \phi}{3} \right)} [K_1(c-h)(c-1) + K_2 c(1-c)], \quad (2)$$

where  $\phi$  is contact angle of the droplet,  $h$  is relative humidity (if the first component of mixture is water, as we mean here),  $c$  is the undimensional water concentration, so that  $(1-c)$

is a concentration of the second component of the mixture,  $K_1 = 2D_1 \frac{n_{S10}}{n_{L10}}$ ,  $K_2 = 2D_2 \frac{n_{S20}}{n_{L20}}$ .

To estimate the Marangoni number in such a system, we obtain the next equation

$$Ma_c = \frac{w(h-\bar{c})H}{D_L \eta} \left| \frac{\partial \sigma}{\partial c} \right|, \quad (3)$$

where  $w = \frac{Dn_{S0}}{D_L n_{L0}}$ ,  $w \ll 1$  ( $D_L$  is a diffusion coefficient of water molecules in liquid

mixture solution,  $n_{S0}$  and  $n_{L0}$  are concentrations of saturate water vapor and liquid vapor respectively,  $H$  is a height of the drop.

### 3 Results

Let us consider the water/mthoxipropanol binary mixture solution sessile drop (Table 1) with initial mix molar proportion of 50% by mass deposited onto glass. The initial parameters of drop are: contact angle  $\phi = 30^\circ$ , radius of contact line,  $R=50$   $\mu\text{m}$ ; volume calculated from given  $\phi$  and  $R$  by formula

$$V = \pi \left( \frac{R}{\sin \phi} \right)^3 \left( \frac{2}{3} - \cos \phi + \frac{\cos^3 \phi}{3} \right) \text{ is } 1308 \text{ } \mu\text{m}^3.$$

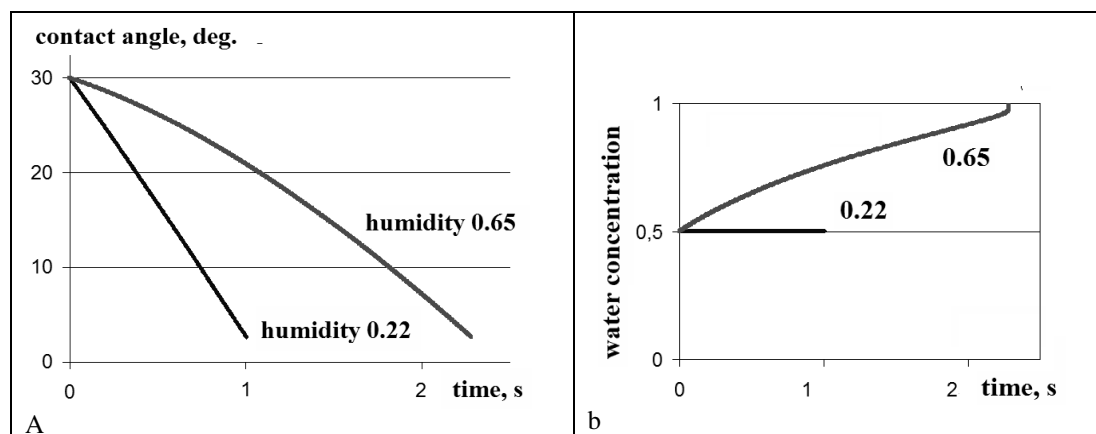
**Table 1.** Parameters of individual components of binary mixture at 20°C

Fluid	$\rho / \text{kgm}^{-3}$	$P / \text{kPa}$	$n_S / \text{m}^{-3}$	$n_L / \text{m}^{-3}$	$D / \text{m}^2\text{c}^{-1}$	$K / \text{m}^2\text{c}^{-1}$	$D_L \text{m}^2\text{c}^{-1}$	$\eta / \text{Pa s}$
Water, H <sub>2</sub> O	1000	2.3	$5.7 \cdot 10^{23}$	$3.3 \cdot 10^{28}$	$2.5 \cdot 10^{-5}$	$8.6 \cdot 10^{-10}$	$2.5 \cdot 10^{-9}$	$10^{-3}$
Methoxypropanol, MP, C <sub>4</sub> O <sub>2</sub> H <sub>10</sub>	920	1.2	$3.0 \cdot 10^{23}$	$6.2 \cdot 10^{27}$	$0.5 \cdot 10^{-5}$	$4.8 \cdot 10^{-10}$	$0.5 \cdot 10^{-9}$	$1.9 \cdot 10^{-3}$

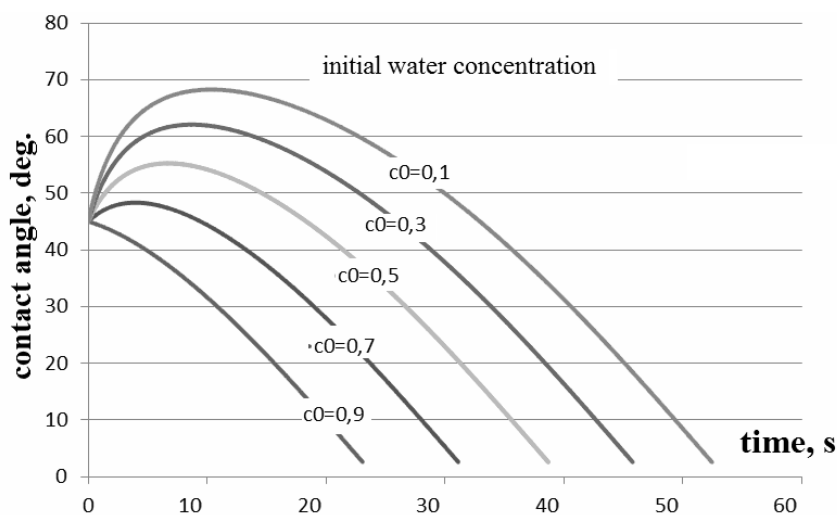
The calculation results obtaining by formulas (1)-(2) are shown at the Fig.1. Evaporation of water-metoxipropanol binary mixture drop with pinned radius of 0.05 mm, initial contact angle 45° and relative humidity 0.9 is shown at Fig. 2.

From these results (Fig.3) it is clear that it is possible that when a drop of a binary solution will initially increase in size if  $K_1(c-h) + K_2(1-c) < 0$ .

It is interesting to compare the theoretical model results with experimental data. However, as far as we know, the experimental data on the dynamics of evaporation of the picoliter binary solvent mixture droplet are not currently available.



**Figure 1.** a – contact angle evolution during evaporation of water-MP droplet (initial molar concentration is 0.5) with pinning, b – water undimensional concentration evolution in the same case.



**Figure 2.** Evaporation of water-metoxipropanol binary mixture drop with pinned radius of 0.05 mm, initial contact angle 45° and relative humidity 0.9 (calculation result).

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