Evaporation of micro droplet of mixture of two liquids with different volatile

Abstract

We study evaporation of humid 2EG micro droplet observing logistic (sigmoid) evolution of evaporation rate (time derivative of surface are) showing phase transition like behavior from evaporation rate connected with more volatile liquid to level connected with less volatile liquid evaporation. The initial and final rates depends on initial composition of liquid and in the case of water on humidity of atmosphere. For evaporation of humid 2EG droplet to humid atmosphere we observed mainly exponential decay of evaporation rate connected with water evaporation. Evaporation of droplet of 2EG with small contain of water to dry atmosphere showed dependence of evaporation rate on initial radius of droplet what seems to be connected with diffusion of water through droplet.

Introduction.

Evaporation of micro droplet is one of fundamental phenomena appearing in wide area of science and technology. It spreads from physics of climate to physics of sprays and printers as well as to physics of combustions inside fuel engines. Although the principles of evaporation are known since centuries details still attract attention. Additionally basic questions about evaporation seems to not be fully answered. Let's mention the influence of the droplet surface phenomena and surface thermodynamics in respect to volume behavior. Especially physics of surface, surly different from volume seems to be of primordial importance for physics of evaporation. The problem of droplet of suspensions with different behavior of volume and surface and interaction between them can give important contribution to physics of evaporation. Additionally the experimental data seems to follow very simple rules let's mention e.g. the a^2 law –the linear dependence of surface area on time during evaporation. Oppositely for modeling and theoretical description one needs nonlinear very complex and multi functional and several parameters studies.

In this paper we study on the basis of our experiment the influence of solution of two liquids on evaporation trying to approach problems connected with influence on evaporation surface versus volume phenomena. We suggest the simple modeling of droplet evaporation rate using logistic function, suggesting phase transition model when droplet can be considered as composed from two components.

Experimental methods.

We studied evaporation of the single droplets, levitating in an electrodynamic quadrupole trap [15-19]. The trap was kept in a climatic chamber with stabilized temperature and humidity. Droplets were injected into the trap with the droplet-on-demand injector [20, 21],

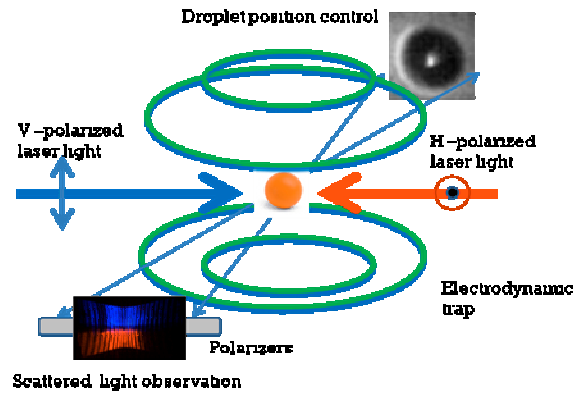Schematic view of the experimental setup is presented in Fig. 1.

Fig.1. Outline of experimental set-up

We used suspension of diethylene glycol (2EG) pure and with tetra ethylene glycol (3EG) (1:5) or glycerol (1:10). As 2EG we use 2EG with ca 2% of water ("pure"2EG), 2EG with ca. 5 % of water and 2EG with ca. 20% of water. Humidity of atmosphere was kept constant on the level of 2% or ca.40% in one experiment.

We measured intensities of scattered light using Mie theory [Bohren] to find radius evolution of evaporating droplets [scaterometry].

Evaporation of microdroplet of one humid liquid (2EG).

When we studied evaporation of suspensions and solutions very important problem appeared. It was everywhere present contain of water and bigger or smaller but almost never 0 humidity of trap atmosphere.

Therefore we decided to study an influence of contain of water and humidity of atmosphere on evaporation of droplet of liquid. Let's have a look on few general properties of such system first.

The equation governing evolution of droplet of humid (containing water $l1$) liquid (named $l2$ or 2EG as it was in the experiment) in humid atmosphere can be written in the form of rates of two streams evaporating from droplet surface -water and 2EG:

$$aa' = (aa')_{l1} + (aa')_{l2} =$$

$$D_{l1}^g \rho_{sat}^{l1} \left\{ H - \exp\left(\alpha \frac{2\gamma}{a} - \frac{\beta_{l1}}{\rho} \right) \right\} - D_{l2}^g \cdot \rho_{sat}^{l2} \exp\left(\alpha \frac{2\gamma}{a} - \beta_{l2}\rho \right)$$

$$\frac{\rho_{in}^{l1}}{\rho_{in}^{l2}} = \rho = \frac{\rho_{in}^{l1}}{1 - \rho_{in}^{l2}}$$

ρ_{in}^{l1} and ρ_{in}^{l2l} are water ($l1$) and 2EG ($l2$) mass fractions in the droplet,

H is the humidity of atmosphere surrounding droplet $H = \dfrac{\rho_\infty^{l1}}{\rho_{sat}^{l1}}$.

Usually for droplets of bigger than micrometer $\exp\left(\alpha \frac{2\gamma}{a} \right) \ll 1$. This property allows to stop evaporation when

$$H = \frac{D_{sl}^g \cdot \rho_{sat}^{l2}}{D_w^g \rho_{sat}^{l1}} \exp(-\beta_{l2}\rho) + \exp\left(-\frac{\beta_{l1}}{\rho} \right)$$

Wet atmosphere (H>0) always slow down evaporation of both liquids. Generally the presence of the second liquid is slowing down evaporation rate of the first one as well.

This is not possible to solve the equation of evaporation in different manner than numerically. But numerical simulation could be done only if one knows all developing in

time processes .Generally these processes are different at the surface and inside the droplet. This limits possibility of numerical approaches as well. So to learn more about drying of this system we made experiment.

Experiment - evaporation of microdroplet of humid 2EG.

The experimental evolutions of evaporation rate of the collection of droplet evaporating in diverse conditions are shown in the Fig.2.

The three kinds of evolution can be distinguished:
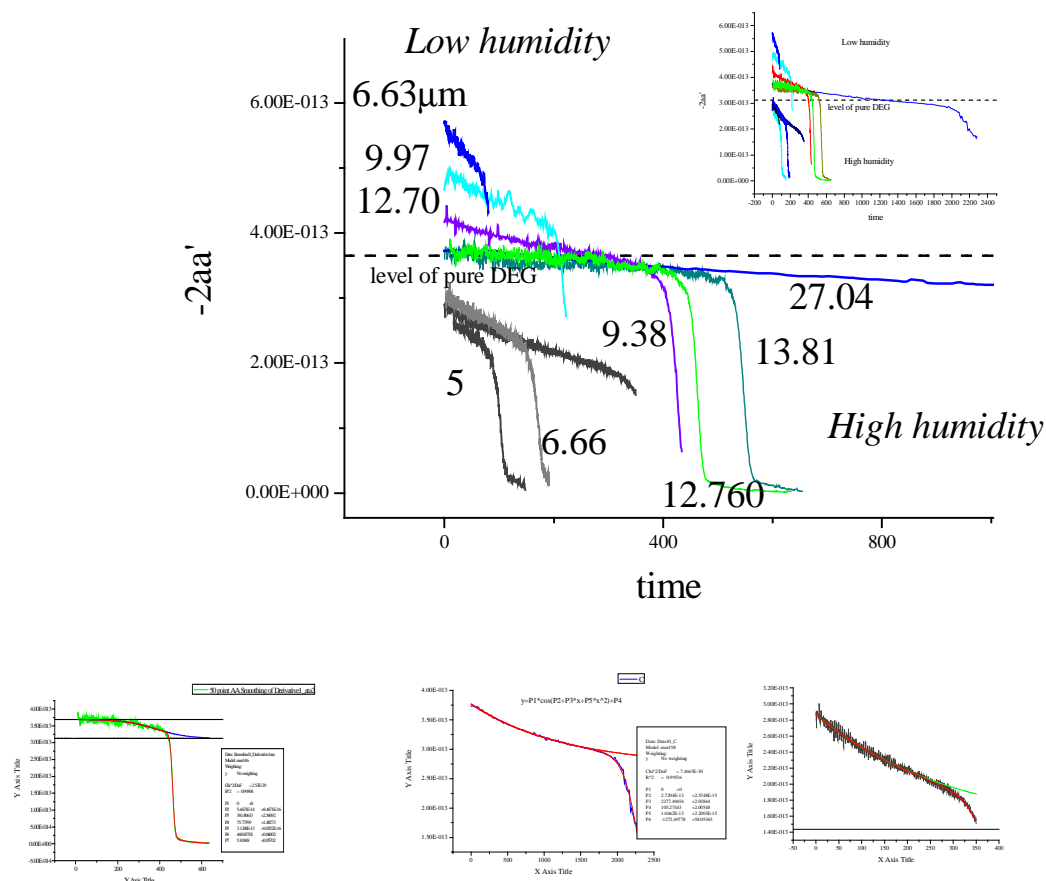
a) Very low humidity of droplet (1-2%) and dry atmosphere (1-2%)–green and dark green evolution in Fig. The evaporation rate is slowly decreasing until final downturn due to a less volatile liquid fraction (impurities-ca.0.1%). Evaporation can be approximated with

two sigmoid (logistic) curves (lower left panel Fig A). One is connected with residual water evaporation the second with residual impurities.

b) Low humidity of droplet 6-7% and dry atmosphere (1-2%), blue, cyan and violet curves. The droplet evaporation rates decay exponentially due to water evaporation rate (increased by 2EG evaporation rate) than evaporation following sigmoid (logistic) dependence ends due to residual impurities. The evaporation rate is initial droplet size dependent. The initial (t=0) evaporation rate is growing with decrease of initial radius indicating Laplace pressure dependence [Fig].

c) Wet droplet (20% of water) and considerable humidity of atmosphere (ca 40%) (gray and black curves)

The evaporating rate is smaller than one of pure 2EG and decreases with time until final downturn. The evaporation rate decreases exponentially due to water evaporation and ends with the sigmoid dependence due to residual impurities. The initial value of evaporation rates seems to do not depend on the initial droplet radius.

The presence of humid atmosphere evidently slow down droplet evaporation   decreasing evaporation rate of both component –water and 2EG.

Exponential and logistic evolution of evaporation rate.

Amazing and very general behavior suggesting phase transitions of evaporation rate – exponential or logistic -can be understood considering flux of vapor from droplet. The change of droplet mass due to the evaporation is given by integral of density of flux over surface of droplet [Prupacher p.504]:

$$\frac{dm}{dt} = -D^g \cdot \int_{S_{l1}} \frac{(\rho_v(\infty) - \rho_v(a))}{a} dS = -\frac{S_{l1}}{a}(\rho_v(\infty) - \rho_v(a))$$

When one is dealing with droplet of suspension or solution the surface S_{l1} is connected with evaporating liquid and it can be considered as smaller than total surface of droplet by the factor described e.g. by the eq. This is obvious for solid suspension when dispersed solid phase cover part of droplet surface but we use here this property for surface of not pure liquid when the first one is much more volatile and the second one can be approached as non volatile at first. Therefore from equ. we obtain evaporation rate proportional to S:

$$a\frac{da}{dt} = -D^g \cdot \int_{S_{l1}} \frac{(\rho_v(\infty) - \rho_v(a))}{a} dS = -D^g \frac{S_{l1}}{4\pi a^2}(\rho_v(\infty) - \rho_v(a))$$

Let's remember that

$$4\pi a^2 = S_{l1} + S_{l2}$$

Where S_{l2} is due to non (slower) evaporating liquid.

Equ. can be transformed into a nonlinear eq. of evolution of S_{l1}:

$$\frac{dS_{l1}}{dt} = -\Omega \frac{S_{l1}}{S_{l1} + S_{l2}}$$

For not too big ratio S_{l1}/S_{l2} this equ. transforms into solvable nonlinear Bernouli type differential equation when evolution of less volatile component is negligible i.e. S_{l2} is kept constant: :

$$\frac{dS_{l1}}{dt} = -\Omega \frac{S_{l1}}{S_{l1} + S_{l2}} \approx -\Omega \frac{S_{l1}}{S_{l2}}(1 - \frac{S_{l1}}{S_{l2}})$$

Logistic, sigmoid function is the solution of this equ. It transforms into exponential decay for still smaller S_{l1}/S_{l2} ratio.

The logistic/exponential behavior of evaporation rate does not make possible to interpret another exponential behavior -radius a dependent evolution of the water evaporation rate [Fig.]. This property seems to be connected with internal diffusion of water inside droplet of solution rather than with surface evolution.

Modeling

To model the influence of the droplet volume on evaporation of solution of two liquids with different volatile we separate once more evaporation on two processes – quick evaporation of more volatile liquid followed with slow of the second.

As the first approximation we will assume that only one liquid is evaporating, i.e. the first liquid (usually water) serves as a solvent of the second. The second is serving as medium slowing down evaporation of the first one only.

Let's stress that the density of vapor of l_1 near the surface is [Prupacher] (see equ.):

$$\rho_v(a) = \rho_s \exp(-\rho_{l2} / \rho_{in}(a))$$

Where ρ_{l2} is $l2$ mass fraction. To determine $\rho_v(a)$ one should calculate mass fraction of $l1$ at the surface inside droplet $\rho_{in}(a)$. We do it using mass flux conservation at the surface.

For simplicity we postpone subscript l1 describing more volatile liquid, conserving however l2 for the less volatile.

Once ore we use most general statement for droplet evaporation i.e. that the change of droplet mass is proportional to droplet radius and the difference of vapor density near the surface and far from it, with speed of diffusion D as coefficient of proportionality [Prupacher p.]:

$$\frac{dm}{dt} = 4\pi \cdot a \cdot D^g \cdot (\rho_v(\infty) - \rho_v(a))$$

Equ is serving to describe transport of mass out of droplet. The flux of mass dm/dt through droplet is governed by a similar equation to diffusion through atmosphere but with additional term:

$$\frac{dm}{dt} = 4\pi \cdot a \cdot \left[D^{pm}\left(\rho_{in} - \rho_{in}(a)\right) + Dl/a \right]$$

ρ_{in} is mean density in droplet volume.

Dl is term describing transport of more volatile liquid through less volatile one analog to term described with Darcy law for transport of liquid in a porous materials. This term is inversely proportional to droplet radius due to the Laplace pressure.

The conservation of fluxes inside and outside droplet surface is used to replace density of vapor near the surface ρ_a by the density inside the droplet ρ_{in} :

$$-D^g a(\rho_v(\infty) - \rho_v(a)) = D^{pm} a\left(\rho_{in} - \rho_{in}(a)\right) + Dl$$

Now one need to express density of vapor near the surface (outside) with mass fraction near the surface (inside). We do t using Raoult's law:

$$\rho_v(a) = W\rho_{in}(a)$$

Finally density of vapor near the surface is:

$$\rho_{in}(a) = \frac{D^{pm}\rho_{in} + Dl/a - D^g \rho_v(\infty)}{D^{pm} + D^g W}$$

With

$$\rho_{in} = \frac{M_{l1}}{M_{l1} + M_{sl2}} = \frac{M_{l1}}{M}$$

Therefore for small contain of ll and dry atmosphere ($\rho_v(\infty)$ =0) aa' is radius dependent like in experiment:

$$aa' = -D^g \rho_v(a) = -\rho_s \exp(\frac{-\left(D^{pm} + D^g W\right)\rho_{l2}a}{Dl})$$

Conclusions

The evaporation rate of two component liquid micro droplet have logistic time behavior showing phase transition like behavior when the more volatile liquid ends to leave droplet. This very general behavior can be understood as due to fact that for evaporation is responsible state of the surface of droplet. This state is determined by bulk properties – diffusion through droplet- limiting surface contain of more volatile liquids. This can lead to profound modification of physics of evaporation especially when any kind of surface layer is created– due to the contain or physical or thermodynamical properties. In this paper we studied specific cases of humid 2EG droplet evaporation showing influence of intra droplet diffusion influencing evaporation rate but always showing character logistic character of phase transitions. For low atmosphere humidity logistic behavior transforms into exponential decay of evaporation rate.

Pruppacher

Pruppacher H R and Klett J D 1997 *Microphysics of Clouds and Precipitation* (Dordrecht: Kluwer)

Scatterometry

Combining weighting and scatterometry: Application to a levitated droplet of suspension