EVAPORATION OF BINARY SESSILE DROPS

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ABSTRACT

Evaporation of a binary mixture sessile drop from a solid substrate is a highly dynamic and complex process with flow driven both thermal and solutal Marangoni stresses. Here, we examine the behaviour and stability of volatile wetting ethanol-water drops deposited onto heated substrates using both experimental and modelling approaches. We focus on the case of thin drops and develop a model based on lubrication theory for the evaporation of an axisymmetric binary drop. We derive evolution equations for the film height, the temperature and the concentration field considering that the mixture comprises two ideally mixed volatile components with a surface tension linearly dependent on both temperature and concentration. Our simulations and experiments indicate that concentration gradients give rise to super-spreading and contact line instabilities, not previously seen in pure fluids. Results from our model qualitatively and quantitatively agree with experiments.

INTRODUCTION

Evaporation is a fundamental problem in transport phenomena involving mass and heat transfer. It has a number of applications including drying (of ink for instance) or spray cooling. We are particularly interested in the latter, which through evaporation provides an effective way of cooling high heat loaded articles and parts[1,2]. So far, most of reported investigations either theoretical or experimental, were performed considering the case of pure liquids, predominantly water as the most widely used heat-transfer agent. However, the evaporation of multicomponent (in particular, binary) mixtures with different fugacities and phase transition heats of components allows various scenarios of heat exchange to be implemented so as to either significantly increase or reduce the evaporation rate. According to experimental data[3] on boiling aqueous solutions of butyl and ethyl alcohols, the critical heat flux may under conditions exhibit an almost twofold increase as compared to that in the case of pure water. Currently though, there is still lack of understanding of the highly dynamic and complex flow phenomena that arise in multicomponent evaporative droplets predominantly driven by the simultaneous presence of thermal and solutal Marangoni stresses. For binary mixtures, the component with the higher vapor pressure will usually evaporate faster and thus deplete from the contact line region. In general, different liquids have different surface tensions. Thus, nonuniform evaporation causes surface tension gradients and Marangoni flows.

The goal of the present study is to derive a simple model based on lubrication theory, which will contain the essential physics of the system, and explore the dimensionless parameter space to examine the resultant effects on drop wetting and evaporation. We derive a fully coupled set of equations for the droplet height, temperature and concentration field which is solved using the finite element method. Finally, the predictions of our model will be compared against experimental observations.

THEORETICAL MODEL

We study the behaviour of a small and thin sessile droplet consisting of a mixture of two volatile, miscible liquids A and B. Fluid A is the more volatile component (MVC) in the mixture and fluid B the less volatile component (LVC). The mixture is assumed to be ideal and the drop is considered Newtonian with density $\hat{\rho}$, specific heat capacity $\hat{c}_p$, thermal conductivity $\hat{k}$ and viscosity $\hat{\mu}$. For simplicity, we assume the liquid to be incompressible and the density of components A and B to be equal, $\hat{\rho}_A = \hat{\rho}_B = \hat{\rho}$. This assumption will have a minor impact since we also assume that the drop is sufficiently small as to neglect gravitational effects. The remaining properties vary locally with concentration and are accounted for using the following rule of mixtures

$$\Omega = \Omega_A x_A + \Omega_B(1 - x_A), \text{ where } \Omega = \hat{\mu}, \hat{k} \text{ or } \hat{c}_p. \tag{1}$$

The surface tension, $\hat{\sigma}$, of the binary mixture again depends on both the local concentration of each component and the local temperature, $\hat{T}$, but this time takes the form,

$$\hat{\sigma} = [\hat{\sigma}_{A,r} + \hat{\gamma}_{T,A}(\hat{T} - \hat{T}_r)]x_A + [\hat{\sigma}_{B,r} + \hat{\gamma}_{T,B}(\hat{T} - \hat{T}_r)](1 - x_A), \tag{2}$$

where $\hat{\gamma}_{T,i} = \partial\hat{\sigma}_i/\partial\hat{T}$ is the temperature coefficient of surface tension of component i ($i = A, B$). $\hat{\sigma}_{i,r}$ is the surface tension of component i at reference temperature $\hat{T}_r$. We assume this to be the temperature of the vapour phase, $\hat{T}_r = \hat{T}_g$.
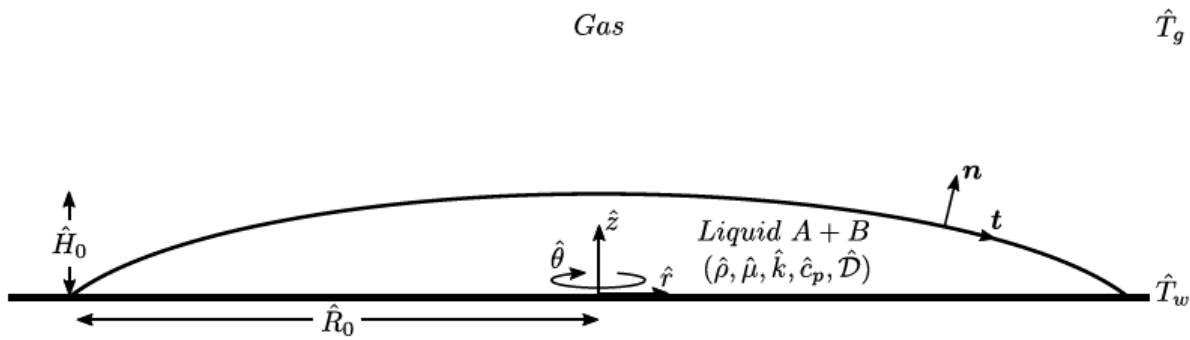

Figure 1 *Drop geometry of initial height $\hat{H}_0$ and radius $\hat{R}_0$ in the cylindrical coordinate frame consisting of miscible components A and B. The drop resides on a heated substrate at temperature $\hat{T}_w$ and the gas temperature is kept constant at $\hat{T}_g$. $\boldsymbol{n}$ and $\boldsymbol{t}$ denote the outward units vectors acting in normal and tangential directions to the interface respectively.*

The drop resides on heated horizontal solid substrate kept at a constant temperature $\hat{T}_w$ and is released into a thin precursor film consisting solely of the LVC. The drop is in contact with the gas phase which has a bulk temperature of $\hat{T}_g$. The velocity of the gas and vapour particles are assumed sufficiently low so that they are negligible. The gas phase has density $\hat{\rho}_g$, viscosity $\hat{\mu}_g$ and thermal conductivity $\hat{k}_g$. These gas-phase properties are assumed to be significantly smaller than their liquid counterparts, such that, $\hat{\rho}_g \ll \hat{\rho}$, $\hat{\mu}_g \ll \hat{\mu}$, $\hat{k}_g \ll \hat{k}$. The same is assumed for the vapour properties. In addition we assume that the total gas phase pressure is sufficiently large that it remains constant with evaporation and changing vapour pressure. Given these assumptions, we may adopt the so-called one-sided model[4] and focus solely on the liquid phase, with the goal to derive a simple model that contains the most important parts of physics that are necessary to reproduce at least qualitatively the behaviour seen in the experiments. The model is expected to be valid in the regime where convection is important (e.g. for a well ventilated environment) and therefore the phase-transition process (i.e., the transfer of molecules across the interface) is the rate limiting step. We consider the drop to be very thin and therefore R_0 greatly exceeds $\hat{H}_0$ (see Fig. 1) so that the drop aspect ratio, $\hat{H}_0/\hat{R}_0 \ll 1$. This assumption permits the use of lubrication theory which we will employ to derive the evolution equations.

For our model, we used a cylindrical coordinate system, $(\hat{r}, \hat{\theta}, \hat{z})$ to model the dynamics and solve for the velocity field, $\hat{\boldsymbol{u}} = (\hat{u}, \hat{v}, \hat{w})$. The LV interface is located at $\hat{z} = \hat{h}(\hat{r}, \hat{\theta}, \hat{t})$ with the solid-liquid

(SL) and solid-vapour (SV) interfaces both being located at $\hat{z} = 0$. The liquid phase is governed by the incompressible momentum, mass, energy and concentration equations. After scaling all equations and discount all terms $O(\varepsilon^2)$, we end up with the following set of equations:

$$\partial u/\partial r + u/r + \partial w/\partial z = 0 \tag{3}$$

$$\varepsilon Re(\partial u/\partial t + u\,\partial u/\partial r + w\,\partial u/\partial z) = -\partial P/\partial r + \partial \tau_{zr}/\partial r \tag{4}$$

$$\partial P/\partial z = 0 \tag{5}$$

$$\varepsilon RePr\big(\partial(c_p T)/\partial t + u\,\partial(c_p T)/\partial r + w\,\partial(c_p T)/\partial z\big) = \partial(k\partial T/\partial z)/\partial z \tag{6}$$

$$Pe(\partial x_A/\partial t + u\,\partial x_A/\partial r + w\,\partial x_A/\partial z) = \partial^2 x_A/\partial z^2 \tag{7}$$

In the above equations the following dimensionless groups arise

$$Re = \hat{\rho}\hat{\gamma}_A \Delta\hat{T}\hat{H}_o/\hat{\mu}_A^2, \quad Pr = \hat{\mu}_A \hat{c}_{p,A}/\hat{k}_A, \quad Pe = \varepsilon^2 \hat{\gamma}_A \Delta\hat{T}\hat{H}_o/\hat{\mu}_A \hat{D}_A \tag{8}$$

Note that the dimensionless concentration has been simplified by assuming that diffusion is rather weak so that $Pe \sim O(1)$.

Along the air-liquid interface the dimensionless normal interfacial stress balances reduces to

$$p = -\frac{\sigma\varepsilon^2}{Ma}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) - \frac{A}{h^3}, \tag{9}$$

where $A = \hat{A}/6\pi\hat{\gamma}_A \Delta\hat{T}\hat{H}_o^2$ is the dimensionless Hamaker constant and $Ma = \hat{\gamma}_A \Delta\hat{T}/\hat{\sigma}_{A,r}$. The final expression for the constitutive relation of total evaporation flux[5].

$$J = \frac{1}{K}\big[x_A(\delta p + T|_h) + (1 - x_A)aM_R^{3/2}(\delta p + \Lambda T|_h)\big], \tag{10}$$

where $K = \hat{k}_A\big(2\pi\hat{R}_g^3\hat{T}_g^5\big)^{\frac{1}{2}}/\hat{H}_o\hat{L}_{v,A}^2\hat{p}_{sat,A}\hat{M}_A^{3/2}$ is the Knudsen number, measuring the importance of kinetic effects at the interface. $\delta = \hat{\gamma}_A\hat{T}_g/\hat{\rho}_l\hat{H}_o\hat{L}_{v,A}$ accounts for the Kelvin effect on phase change. The relative volatility of the mixture is given by $a = \hat{p}_{sat,B}/\hat{p}_{sat,A}$ and $M_R = \hat{M}_B/\hat{M}_A$ is the ratio of molar weights. We partition equation (10) into two separate expressions for the evaporative fluxes of components A and B respectively,

$$J_A = \frac{x_A}{K}(\delta p + T|_h), \tag{11}$$

$$J_A = \frac{(1 - x_A)aM_R^{3/2}}{K}(\delta p + \Lambda T|_h), \tag{12}$$

The dimensionless jump energy and tangential stress balances are given by

$$J_A + J_B\Lambda + k\frac{\partial T}{\partial z} = 0, \tag{13}$$

$$\tau_{rz} = \frac{1}{Ma}\frac{\partial\sigma}{\partial r}, \tag{14}$$

where $\Lambda = \hat{L}_{v,B}/\hat{L}_{v,A}$ is the ratio of latent heats. The kinematic boundary condition in dimensionless form is given by

$$\frac{\partial h}{\partial t} + u\frac{\partial h}{\partial r} - w + E\,J = 0. \tag{15}$$

Under the assumption of weak diffusion, the following boundary condition at the interface is imposed for the concentration field[5]

$$\left.\frac{\partial x_A}{\partial z}\right|_{z=h} = \frac{3PeEh(J_A - x_A J)}{h(JPeEh - 3)} \tag{16}$$

Along the wall we impose typical no-slip, no penetration boundary conditions, constant temperature and zero normal gradient for the concentration field. Finally, the thickness of the precursor layer which consists solely of the least volatile component is given by

$$h_\infty = \left(\frac{A\delta}{\Lambda T_w}\right)^{1/3} \tag{17}$$

These equations are discretized using the finite element method (FEM) applied to a uniform mesh. Fundamentally, solutions to the system of equations are obtained using the Newton-Raphson method.

EXPERIMENTAL SETUP

The experiments conducted aim to provide a source of validation for our one-sided spreading drop model. As an overview of the experiments, drops are deposited on a heated hydrophilic substrate that has been chemically treated to ensure that as close to complete wetting as possible is achieved. The drops spread on the smooth surface and consequently evaporate into the ambient atmosphere. Varying concentrations of ethanol-water mixtures are investigated along with several substrate temperatures. We record from above in an aerial view using an CMOS optical camera (see Fig. 2) to capture the total lifetime from deposition to dry-out. This allows us to track the movement of the contact line as drops spread and retract under evaporation. The apparatus centres around a flexible silicone heating pad (Omega SRFR-4/5-P-230V) providing a heat flux of 0.775 W cm^{-2}. This sits atop an aluminium mechanical scissor lift platform and is held in place with heavy duty white duct (Gorilla) tape. The temperature of the heater is controlled with a PID controller in a feed back loop; the controller maintains the desired set point measured by a thermocouple attached to the heating pad. The droplet is illuminated from the side using a smart phone touch mounted on a large 3 prong clamp as the light source.
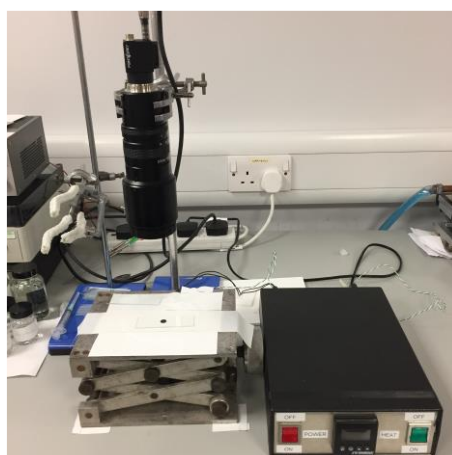

Figure 2. *of the experimental apparatus. The flat drop is recorded from above with a Point grey CMOS camera. The silicon heater is fixed in place below the white tape. Heater temperature is maintained via a PID controller on the right.*

Borosilicate glass microscope slides manufactured by RC Components are used for the substrate. The factory treatment of the glass results in a low equilibrium contact angle for all fluids tested. Finally, the drops are deposited on the substrate manually using a microliter syringe (Hamilton 701N 10 µl) with reading increments of 0.2 µl.
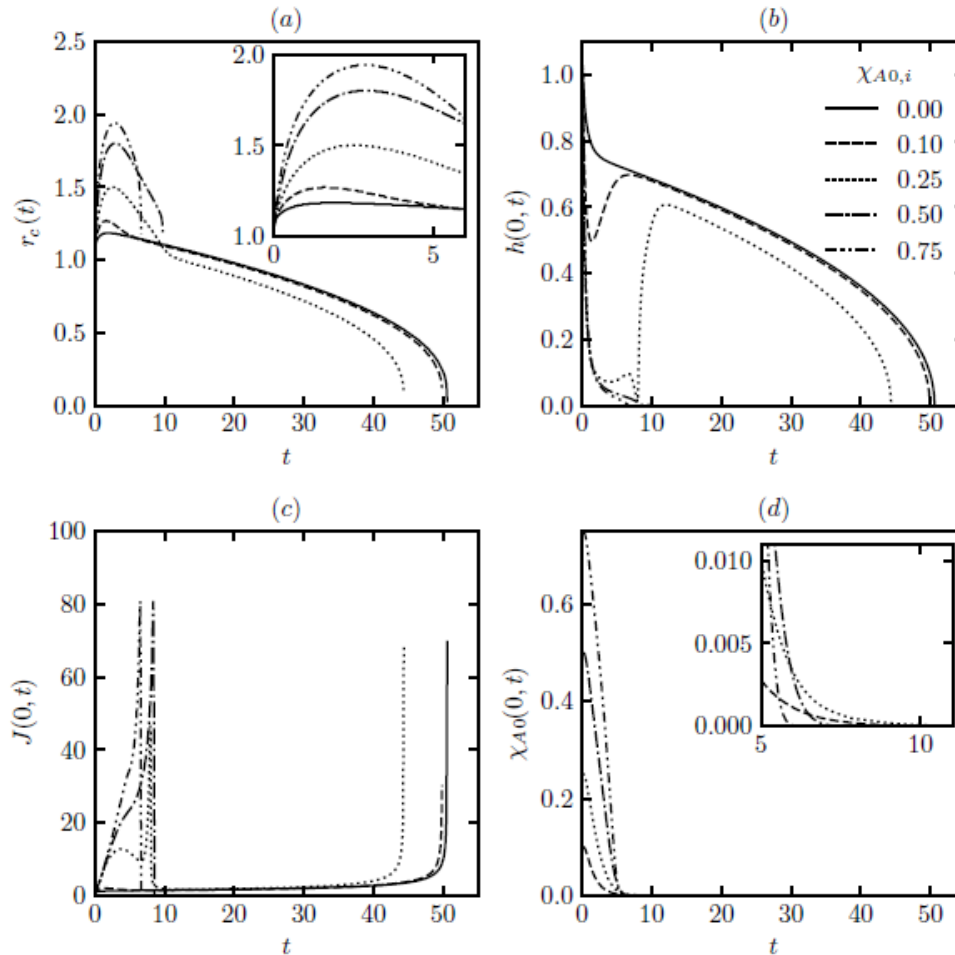
In the study presented below, we consider ethanol-water mixture drops of initial volume of (1.0 $\pm$ 0.2) µl. Mixtures ranging from 11 wt.% to 50 wt.% initial ethanol concentration are considered at three substrate temperatures: 30 °C, 50 °C and 70 °C.

RESULTS AND DISCUSSION

For the purposes of the present study we consider a working mixture of ethanol and water (see Table 1 for corresponding dimensionless parameters). Both liquids are sufficiently volatile on a heated substrate, ethanol being the MVC and possessing a lower surface tension than water.

Table 1. *Dimensioless base parameters for an ethanol-water mixture.*

ε	0.2	δ	10^{-5}	k_R	1
Re	0	A	10^{-4}	μ_R	0.84
Pr	16.1	Pe	20	$c_{p,R}$	1.74
Ma	0.164	σ_R	3.2	M_R	0.39
E	$2.66\ 10^{-4}$	γ_R	1.81	Λ	1
K	$8.85\ 10^{-4}$	a	0.4	$x_{A0,i}$	0-0.75

Figure 3. *Profiles of (a) contact line position, (b) apex height, (c) apex mass flux, and (d) apex mass fraction throughout drop lifetime for varying initial mass fraction of MVC.*

We performed simulations for different concentrations of the binary mixture and present in Figure 3 the position of the contact line, apex height along with the total evaporative flux and mass fraction of ethanol at the apex versus time. The case of pure water sees a modest initial spreading followed by a steady recession. After the initial stages, the height also decreases steadily (see fig. 3b) and evaporation from the apex is modest until the final stages before dry-out (see fig. 3c). Introducing ethanol into the drop, we see that increasing concentration enhances the drop spreading and increases the maximum position of the contact line. In all cases, the enhanced spreading is accompanied with a rapid drop in apex height. Enhanced spreading is driven by the preferential evaporation of ethanol from the contact line. This leaves an ethanol depleted (water rich) region at the contact line with higher surface tension than the bulk drop. Induced by solutal Marangoni stresses, liquid flows towards the freely moving contact line, causing it to spread further outwards. Drop lifetime is considerably reduced as the concentration increases owing both to the increased volatility of the mixture and the decreased drop thickness due to enhanced spreading.
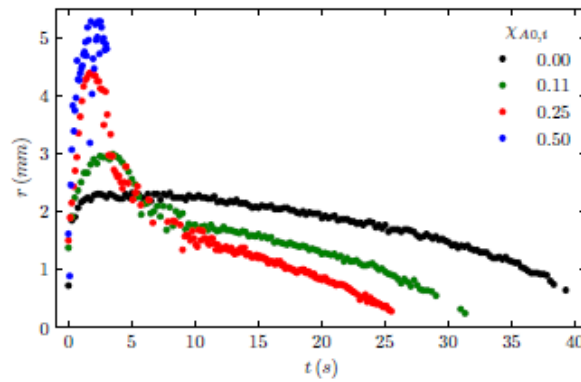
Figure 4. *Drop radius versus time at a constanr substrate temperature of 70 °C for initial ethanol concentrations of 0 wt.% - 0.50 wt.%.*

To verify the predictions of our simulations, we have also conducted an experimental investigation into the spreading and evaporation behaviour of sessile drops comprising various concentrations of ethanol-water mixtures. The drops were deposited on heated borosilicate glass substrates with a hydrophilic coating to encourage spreading. As it is shown in Fig. 4 the experiments are found to be in line with our predictions, and in fact the measured spreading rates closely match those predicted by our simple one-sided model.

CONCLUSIONS

We have developed a one-sided model under the lubrication approximation to study the spreading and subsequent evaporation of volatile binary drops consisting of an ethanol-water type mixture deposited on a heated substrate. The contact line was allowed to move freely with the drops assumed to be very thin such that their radius is much larger than their height. We validated our model against a similar model used to study pure single component drops before examining the effect of increasing initial ethanol mass fraction in a binary ethanol-water drop. We showed that increasing the strength of solutal Marangoni stress gives rise to superspreading. We demonstrated the delicate interplay between solutal effects driving the drop outwards and competing thermal Marangoni stresses encouraging the contact line to contract inward. If the concentration induced surface tension gradient is larger enough, we showed spreading can be so fast that a ridge rich in the LVC can form at the contact line with the drop centre subsequently drying out before it does. We also investigated the effects of other important parameters significantly affecting the behaviour. These included the evaporation rate, thermal Marangoni stress, solutal Marangoni stress, mass diffusion, and inertial effects.

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