



## Evaporation Dynamics of Microdroplets Coated with Nonvolatile Liquid Layers

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Evaporation dynamics of layered droplets is of interest in many natural and industrial processes. The presence of a layer, which acts as a diffusional barrier to the transfer of a species from the core droplet to the gas phase, gives rise to a number of rate-controlling mechanisms. To examine evaporation dynamics of volatile core droplets coated with layers of nonvolatile components we have conducted experiments on single layered droplets suspended in an electrodynamic balance under vapour-free atmospheres, and determined the core and outer radii of a droplet as functions of time using a resonance based light scattering technique. A theoretical analysis is presented to explain the observed evaporation characteristics of layered droplets of various systems.

### 1. Introduction

Numerous atmospheric and industrial processes such as organic-coated aerosols in atmosphere, spray drying, droplet combustion, and agricultural sprays involve evaporation of layered droplet. Although, an immiscible layer covering a flat surface of a volatile liquid normally retards evaporation of the volatile liquid (Adamson and Gast, 1997), evaporation of a volatile core droplet coated with a nonvolatile liquid is strongly influenced by the gas-layer interfacial area, by the dynamic and by the thermodynamic parameters of the system, and exhibits markedly different behaviour. For example, it has been observed that the evaporation rate of a core glycerol droplet coated with a diethyl phthalate (DOP) layer increases with increasing layer thickness (Ray et al., 1991). In addition, it has been shown that blended polymer microparticles of various morphologies can be produced by evaporating homogeneous solution droplets containing two immiscible polymers dissolved in a common solvent (Rajagopalan et al. 2011). Even though factors that control evaporation characteristics of layered droplets are not well understood, only a few studies experimentally examined layered droplet evaporation, mostly through surfactant layers (Rubel and Gentry, 1984; Taflin et al. 1988), while Bharat and Ray (1992) have presented a mathematical model with numerical parametric studies for unsteady state evaporation of core droplets coated with immiscible layers. In this study we have examined a number of immiscible systems to determine evaporation behaviour of volatile core droplets coated with layers of nonvolatile components, and developed a model based on diffusional transport to explain observed evaporation characteristics.

### 2. Theory

To develop a model for evaporation of a layered droplet, we consider a stationary layer droplet of two partially miscible components A and B that is exposed to a stagnant vapour-free gas phase containing a non-transferring species C (e.g., air). The physical situation schematically depicted in Figure 1 involves a core droplet that is enriched with component A, while the shell phase with B. Component A is significantly more volatile than B; thus, evaporation of B can be neglected during the evaporation of the core. Even though the densities and the molecular weights of the two components may differ significantly, the miscibility limit of A in B is so small that the physical properties, such the total molar concentration, density and diffusion coefficient, in the shell phase remain nearly constant. In addition, the droplet evaporates

relatively slowly, and consequently a pseudo-steady state model under an isothermal condition can be used to describe the present situation. Under these conditions, the composition distributions are given by:

$$x_A^I(r) = x_{Am}^I = 1 - x_{Bm}^I \quad \text{for } 0 \leq r \leq a_c \quad (1)$$

$$x_A^{II} = x_{Am}^{II} + \frac{\left(\frac{1}{a_c} - \frac{1}{r}\right)}{\left(\frac{1}{a_c} - \frac{1}{a}\right)}(x_{As}^{II} - x_{Am}^{II}) \quad \text{for } a_c \leq r \leq a \quad (2)$$

$$y_A = \frac{\gamma_{As}^{II} x_{As}^{II} P_A^0}{P_t} \left(\frac{a}{r}\right) \quad \text{for } a \leq r < \infty \quad (3)$$

where  $x_A^I$ ,  $x_A^{II}$  and  $y_A$  denote compositions of the core, shell and gas phases, respectively,  $P_t$  is the total pressure in the surrounding gas phase,  $P_A^0$  is the vapour pressure of A at the droplet temperature  $T$ , and  $\gamma_{As}^{II}$  is the activity coefficient at the composition,  $x_{As}^{II}$ , in the shell phase at the droplet-gas interface at  $r = a$ . The miscibility limits of B in A,  $x_{Bm}^I$ , and A in B,  $x_{Am}^{II}$ , are related through the equilibrium conditions:

$$\gamma_{jm}^I x_{jm}^I = \gamma_{jm}^{II} x_{jm}^{II} \quad \text{for } j = A \text{ or } B \quad (4)$$

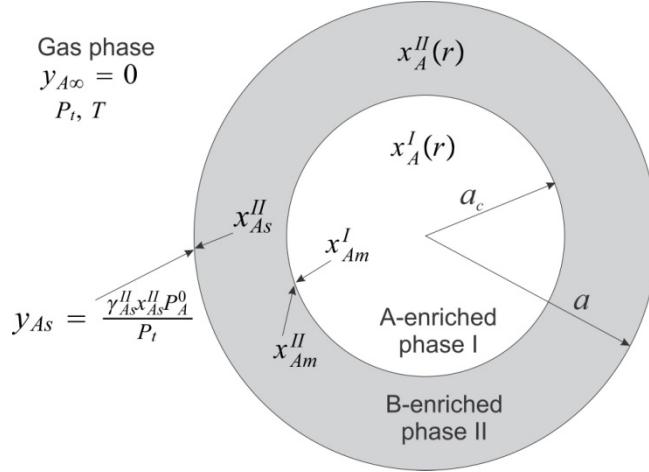


Figure 1: Schematic description of core, shell and gas phases during evaporation of a layered droplet

The droplet surface composition,  $x_{As}^{II}$ , can be determined from the continuity equation at the droplet-gas interface at  $r = a$ ,

$$D_{AL}^H C_L^H \frac{dx_A^{II}}{dr} \Big|_{r=a} = \frac{D_{AG} P_t}{RT} \frac{dy_A}{dr} \Big|_{r=a} \quad (5)$$

where  $D_{AL}^H$  and  $D_{AG}$  are the diffusion coefficients of A in the shell and gas phases, respectively, and  $C_L^H$  is the total molar concentration in the shell phase. Substitution of Eqs. (2) and (3) in Eq. (5) yields:

$$x_{As}^{II} = x_{Am}^{II} - \beta \gamma_{As}^{II} x_{As}^{II} \frac{y}{1-y} \quad (6)$$

where  $\beta = D_{AG} P_A^0 / D_{AL}^H C_L^H RT$ , and  $y = (a - a_c)/a$ , is the reduced shell thickness. A material balance at the core-shell yields

$$(C_L^I x_{Am}^I - C_L^{II} x_{Am}^{II}) \frac{da_c}{dt} = D_{AL}^H C_L^H \frac{dx_A^{II}}{dr} \Big|_{r=a_c} \quad (7)$$

Using Eqs. (2), (6) and (7) we obtain a relation for the core radius

$$a_c \frac{da_c}{dt} = - \left( \frac{D_{AG} P_A^0 M_A}{\lambda \rho_A R T} \right) \frac{\gamma_{As}^{II} x_{As}^{II}}{1-y} \quad (8)$$

where  $\lambda = (M_A/\rho_A)/(C_L^I x_{Am}^I - C_L^{II} x_{Am}^{II})$ ; which for low miscibility limits approaches unity. Since the amount of B remains constant in the droplet, a balance on the droplet under the assumption of ideal mixing (i.e., mixing of A and B causes no volume change) gives

$$a^3 - \lambda a_c^3 = a_0^3 - \lambda a_{c0}^3 = B \quad (9)$$

where B is a constant related to the initial radii,  $a_0$ , and  $a_{c0}$ .

To examine the effect of the layer thickness on the evaporation rate of a core droplet we differentiate Eq. (8) with respect to the reduced layer thickness  $y$ , to obtain the change in the core evaporation rate with thickness

$$\frac{d}{dy} \left( a_c \frac{da_c}{dt} \right) = \frac{\gamma_{As}^{II} x_{As}^{II} [1 - \beta u(x_{As}^{II})]}{\lambda(1-y)[1-y+\beta y u(x_{As}^{II})]} \left( a \frac{da}{dt} \right)_0 \quad (10)$$

where

$$u(x_A) = \frac{d(\gamma_A x_A)}{dx_A}, \quad u(0) = \gamma_A^\infty \quad (11)$$

$\gamma_A^\infty$  is the activity coefficient at infinite dilution, and the evaporation rate of a droplet of pure A is given by

$$\left( a \frac{da}{dt} \right)_0 = - \left( \frac{D_{AG} P_A^0 M_A}{\rho_A R T} \right) \quad (12)$$

In the B enriched phase (i.e.,  $0 \leq x_{As}^{II} \ll x_{Am}^{II}$ ), function  $u(x_A)$ , in general, has the following characteristics: (i) it is always positive,  $u(x_A^{II}) > 0$ ; (ii) it decreases as  $x_A^{II}$  increases, that is,  $u(0) = \gamma_A^\infty \gg u(x_A^{II}) \geq u(x_{Am}^{II})$ . Since  $u(x_A^{II}) > 0$ , Eq. (10) reveals that the evaporation rate increases with increasing layer thickness,  $y$ , if  $\beta u(x_{As}^{II}) < 1$ , and decreases when  $\beta u(x_{As}^{II}) > 1$ . On the basis of these properties, we can now examine the effect of layer thickness on the evaporation rate. For a thin layer, as  $y \rightarrow 0$ , Eq. (6) shows that  $x_{As}^{II} \rightarrow x_{Am}^{II}$ . As the layer thickness increases to the limit  $y \rightarrow 1$ ,  $x_{As}^{II} \rightarrow 0$ . Since the condition,  $\beta u(x_{As}^{II}) < 1$ , is satisfied when  $\beta u(0) < 1$ , in the limit  $y \rightarrow 1$ , the core evaporation rate monotonically increases with increasing layer thickness. Similarly, since the condition,  $\beta u(x_{As}^{II}) > 1$ , is satisfied when  $\beta u(x_{Am}^{II}) > 1$  in the limit  $y \rightarrow 0$ , the core evaporation rate monotonically decreases with increasing layer thickness. In between these two situations, we have a situation where the core evaporation rate increases in the thin layer limit, that is,  $\beta u(x_{Am}^{II}) < 1$  as  $y \rightarrow 0$ , but decreases in the thick layer limit, that is,  $\beta u(0) > 1$  as  $y \rightarrow 1$ . In such a situation, the core evaporation rate as a function of the layer thickness,  $y$ , attains a maximum at a layer thickness  $y$  which can be obtained from Eq. (6) from the droplet surface composition  $x_{As}^{II}$ , determined from the conditions,  $\beta u(x_{As}^{II}) = 1$ . This analysis shows that the evaporation rate of a core droplet covered with an immiscible layer may increase, decrease or show a maximum with increasing layer thickness, depending on the physical properties of the system involved. We will use the results to interpret experimental data.

### 3. Experimental section

Experiments were conducted in an electrodynamic balance (EDB), where single charged droplets were suspended in a vapour-free atmosphere. Tu (2000) has provided details of the experimental system. An EDB is mounted inside a modified temperature-controlled thermal diffusion cloud chamber. A polarized He-Ne laser beam is used to illuminate a suspended droplet, and two photomultiplier tubes (PMTs) are used to detect light scattered by the droplet in the planes parallel and perpendicular to the polarization plane of the incident light. Core droplets of di- and tri-ethylene glycols (DEG and TEG), diethyl-phthalate (DEP), and dimethylphthalate (DMP) coated, respectively, with dioctyl phthalate (DOP), dibutyl phthalate

(DBP), and squalane were investigated in this study. A homogeneous solution was prepared by dissolving two immiscible components in a highly volatile common solvent, such as ethanol, and droplets were generated from the solution. With the evaporation of the volatile solvent from a suspended droplet, two phases separated to form a layered droplet. The initial core volume fraction of the layered droplet was controlled by varying the mixing ratio of the two components in the parental solution used to generate the droplet. In a typical experiment, charged solution droplets were generated by electrical atomization, and a droplet was suspended in the EDB by manipulation of the ac and dc potentials applied to the electrodes of EDB. The common solvent was allowed to evaporate till the formation of a layered droplet. After the phase separation, light scattering intensities from the droplet as functions of time were recorded through the PMTs. The environment surrounding the droplet was maintained vapour-free at 25.3 °C and 1 atm. Resonances (i.e., peaks) observed in the experimental scattering intensity versus time data were interpreted using elastic light scattering theory for coated spheres (Aden and Kerker, 1951) to obtain outer and core radii of the droplet as functions of time (Ray and Nandakumar, 1995; Tu and Ray, 2006).

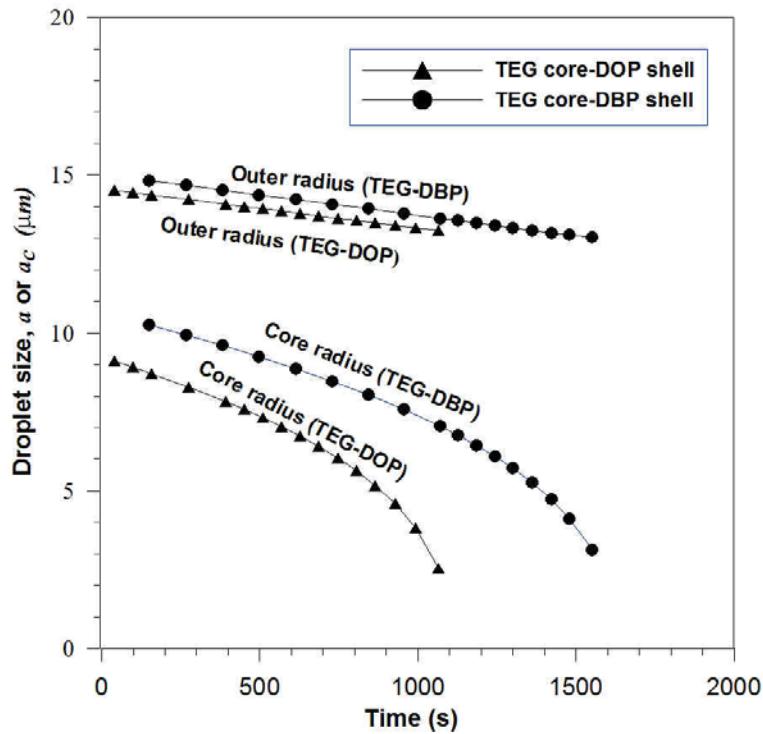


Figure 2: Outer and core radii vs. time data for evaporating TEG droplets coated with of DBP and DOP.

#### 4. Results and discussions

Resonances observed in light scattering intensity versus time spectra have been used to determine outer and core radii of an evaporating layer droplet. Figure 2 shows typical data from TEG core droplets coated with layers of DOP and DBP. Both DOP and DBP layers have similar effects on evaporation of TEG cores, and the core radius of a droplet, as expected, changes faster than the outer radius. To examine the effect of a layer on the evaporation, we have determined the core,  $a_c(da_c/dt)$ , and overall,  $a(da/dt)$ , evaporation rates as functions of reduced layer thickness,  $y = (a - a_c)/a$ , from the droplet radii versus time data. The results from two TEG droplets coated with DOP layers are presented in Figure 3, where the calculated evaporation rates are normalized with respect to the evaporation rate of a pure TEG droplets. The results are highly reproducible and show that for the same reduced shell thickness the core and overall evaporation rates of the two droplets are almost identical, although they differed significantly in their initial dimensions. The overall evaporation rate is always less than the core evaporation rate, and the difference between the these two rates increases with increasing layer thickness, since they differ by a multiple of  $(1 - y)/\lambda$ , as can be seen from Eq. (9). For TEG-DOP system, the results show that the core evaporation rate increases as the layer thickness increases, and this suggests that the condition  $\beta u(0) = \beta\gamma_A^\infty < 1$ , is satisfied by this system. In addition, the rate approaches 1 in the limit  $y \rightarrow 0$ , indicating that the activity of A,  $\gamma_{Am}^{II}x_{Am}^{II}$ , is nearly unity at the miscibility limit.

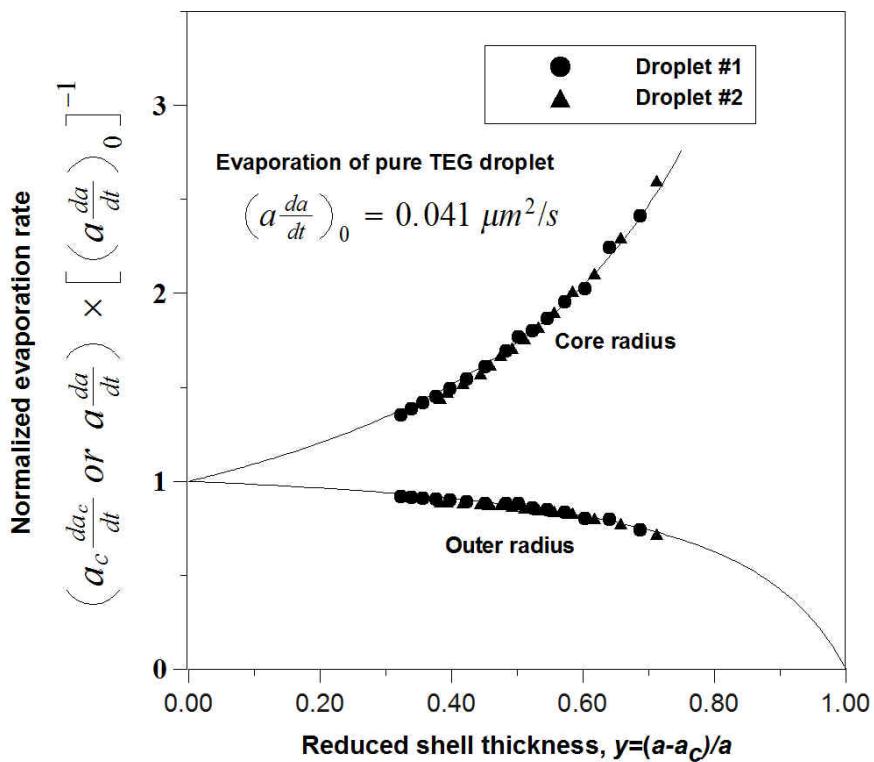


Figure 3: Measured core and overall evaporation rates of two TEG core droplets coated with DOP layers

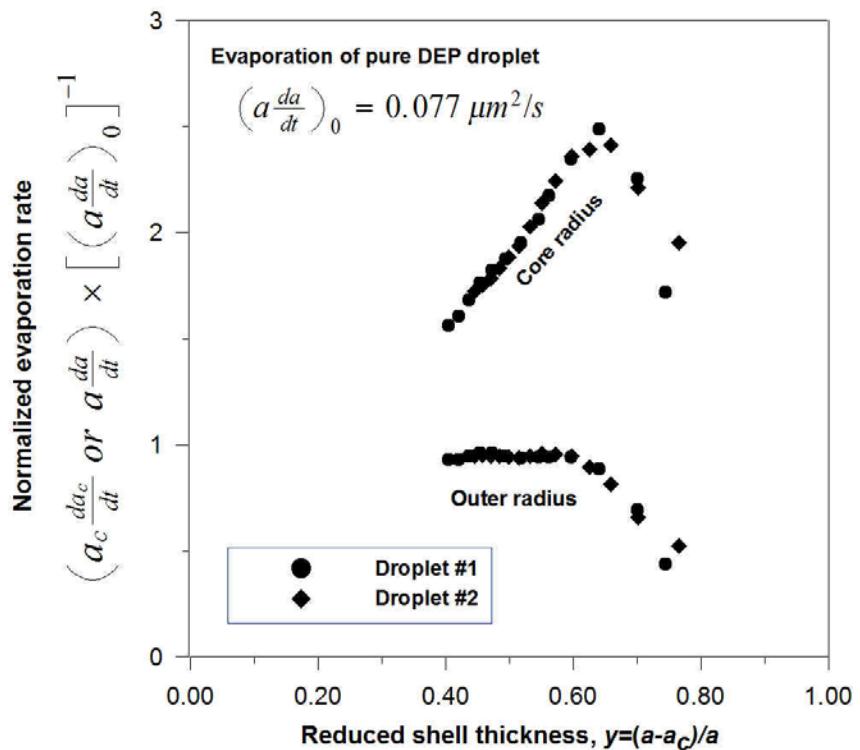


Figure 4: Measured core and overall evaporation rates of two DEP core droplets coated with squalane layers

The experimental results on TEG droplets coated with DBP layers also exhibit nearly the same characteristics as those coated with DOP layers. The results obtained from droplets of all the systems,

except for DEP-squalane, examined also show that the core evaporation rate monotonically increases with increasing layer thickness. Figure 4 shows results from DEP droplets coated with squalane layers. For this system, the core evaporation rate increases to a maximum at about  $y=0.65$ , and then decreases as shell thickness increases. The presence of a maximum indicates that DEP-squalane system satisfy the criterion:  $\beta u(x_{Am}^H) < 1$ , and  $\beta\gamma_A^\infty > 1$ . Of the systems examined in this study, none of the droplets exhibited a reduction in the core evaporation rate for thin layers. The condition for such a behaviour requires that  $\beta u(x_{Am}^H) > 1$ , and can only be achieved with core droplets containing more volatile compound (i.e., higher value of  $\beta$ ) than the ones studied here.

## 5. Conclusions

We have theoretically and experimentally examined evaporation characteristics of layered droplets consisting of volatile cores and nonvolatile shells. The theoretical analysis shows that the core evaporation rate depends on two competing effects: diffusion through the layer, and evaporation from the outer surface of the droplet. As the layer thickness increases the outer surface area available for evaporation increases, while the surface composition decreases due the diffusional resistance. The former effect tends to enhance, while the latter tends to retard the core evaporation rate. The level of retardation depends on the thermodynamics of the immiscible system involved. These interactions can cause the evaporation rate of a core droplet covered with an immiscible layer to increase, decrease or exhibit a maximum with increasing layer thickness. The experimental results obtained from droplets of various partially miscible systems show that for some systems the core evaporation rate increases, while for other systems the rate exhibits a maximum with increasing layer thickness. Because of the relatively low volatility of the core compounds involved in the study, a monotonic decrease in the core evaporation rate with increasing layer thickness was not observed.

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