

Computations and experiments on the evaporation of multi-component droplets

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This paper presents a model of multi-component liquid droplet evaporation in a gaseous environment. The model is built on the well known approach by Abramzon and Sirignano. It treats the liquid phase as real, and the gas phase as ideal. The real liquid behavior has consequences for the vapor pressures of the various components, which arise due to mutual influences of the liquid components on their activities. In order to account for this effect, the vapor pressures of the various components are calculated as functions of the liquid mixture composition and the component activities. The activities of the liquid components are calculated using the UNIFAC method. The computational results are verified by experiments on single droplet evaporation in an acoustic levitator. The set of information about the droplet obtained with these experiments consists of the volume-equivalent droplet diameter, the aspect ratio of its shape, and the coordinates of its center of gravity with respect to some reference point. These data, which are obtained as functions of time, allow for the determination of, e.g., the droplet surface area evolution with time, which is considered in the comparison between computation and experiment. The results from the model agree very well with the experimental data, suggesting that our model correctly captures the physico-chemical phenomena.

1. Introduction

The evaporation of liquid droplets is an essential step in many technical processes like spray drying and fuel injection. Particularly in the latter case, the evaporating liquid may consist of very many components, so that its evaporation behavior is difficult to describe. Considerable efforts have been made in the last few decades to develop a theory for multi-component liquid droplet evaporation. It turned out in many investigations that the behavior of a multi-component liquid mixture cannot be represented by a single component. Also, simple theories cannot explain the behavior of multi-component droplet evaporation. Rather a detailed analysis is required.

Newbold and Amundson described the evaporation behavior of droplets of binary and ternary mixtures [1]. The authors found that the augmentation of diffusive mass transport by Stefan flow from the droplet played an essential role in their model, where it turned out that the transport of one component could be augmented by the transport of another. Abraham and Magi developed a model for multi-component droplet evaporation in sprays, reflecting the volatility of the components in their latent heat of vaporization and the inter-species liquid diffusivity [2]. Law and Law pointed out in their work [3] that a multi-component analog of the classical d^2 -law of droplet evaporation exists, if the extremely slow rate of

liquid-phase diffusion is taken into account, which causes the droplet concentration distributions to attain almost constant values during much of the droplet lifetime. Kneer et al. [4] examined the importance of variable liquid properties in droplet evaporation. They found that large temperature and concentration gradients within the droplet may cause variations in physico-chemical properties during evaporation. Their work emphasized the need to account for non-ideal behavior of both the liquid and the gas phases in order to match the real conditions, and the importance of variable physical properties in the calculation of droplet evaporation rate.

Many investigations in the existing literature rely on Raoult's law for calculating the vapor pressures of the liquid components. It is the objective of the present study to develop a realistic evaporation model for multi-component liquid droplets, which accounts for the real liquid mixture behavior in terms of the activities of the components, rather than making Raoult's simplifications. Our model is based on the nowadays well accepted model by Abramzon and Sirignano [5]. This model includes the effect of Stefan flow on the mass transfer, using the approach of the film theory. The various complications arising in the modeling of the evaporation behavior of a multi-component droplet are discussed in the following section.

2. Development of the evaporation model

The analysis of heat and mass transfer in the gas phase during the evaporation process allows one to determine the instantaneous rate of evaporation \dot{m} and rate of heat transfer \dot{Q}_L into the droplet. The present work is based on the evaporation model developed by Abramzon and Sirignano [5] for droplets of pure liquids. This is a widely accepted and applied theory, which predicts the evaporation and heat transfer rates accurately, even for high transfer rates. In the model, it is assumed that 1) the droplet is spherical all the time, 2) the solubility of air in the liquid is negligible, 3) mass diffusion due to temperature and pressure gradients is negligible, 4) the gas phase is in a quasi-steady state, 5) the droplet evaporates in an inert environment without chemical reactions, and 6) heat transfer due to radiation is negligible. The model accounts for the Stefan flow in the gas phase and describes the transfer rates by modified Nusselt and Sherwood numbers. For applying the model, an infinite conductivity and a rapid mixing model may be used for modeling the liquid phase temperature and mixture composition. Alternatively one could use a conduction and diffusion limit approach for calculating the temperature and mixture component distribution profiles in the droplet.

The gas phase flow over an evaporating droplet with a velocity U is in principle unsteady, due to the temporal evolution of the droplet size d_d . A characteristic time for the flow in the gas phase is $O(d_d/U)$, which is in all practical cases much smaller than the lifetime of the droplet. Hence, the assumption that the gas phase is at a quasi-steady state is justified. The Fourier and Fickian laws are used to describe the conductive heat and diffusional mass transfer in the gas phase, respectively. With the approach of the film theory, Abramzon and Sirignano obtained the evaporation rate \dot{m} of a pure liquid droplet as

$$\dot{m} = 2\pi a (\bar{\rho} \bar{D})_g Sh^* \ln(1 + B_M) \quad , \quad (1)$$

where a is the (time-dependent) radius of the droplet, $\bar{\rho}_g$ and \bar{D}_g the density and binary diffusion coefficient of the gaseous phase, Sh^* a modified Sherwood number, and B_M the Spalding mass transfer number. The modified Sherwood number Sh^* accounts for the effects of a high mass transfer rate, and is defined by the equation

$$Sh^* = 2 + \frac{Sh_0 - 2}{F(B_M)} \quad (2)$$

with the Sherwood number Sh_0 for small mass transfer rate given by the Frössling correlation [6]

$$Sh_0 = 2 + 0.552 Re^{1/2} Sc^{1/3} \quad (3)$$

or a similar correlation found by Ranz and Marshall [7]. The function $F(B)$ reads

$$F(B) = (1 + B)^{0.7} \frac{\ln(1 + B)}{B} \quad (4)$$

The symbol B in this equation may represent the Spalding mass transfer number B_M (as it is the case in Eq. (2)) or the Spalding heat transfer number B_T . The latter will arise later. In Eq. (3), Re and Sc are the Reynolds and Schmidt numbers of the gaseous phase, respectively. In our model, the Reynolds number is calculated for the acoustic streaming flow in the levitator, as given by Lierke [8]. The Spalding mass transfer number is given by the equation

$$B_M = \frac{(Y_{F,s} - Y_{F,\infty})}{(1 - Y_{F,s})} \quad (5)$$

where $Y_{F,s}$ and $Y_{F,\infty}$ are the mass fractions of the fuel vapor at the droplet surface and in the undisturbed ambient medium, respectively.

The transfer of heat from the ambient host medium to the liquid droplet is of importance for providing the energy needed for the evaporation, which takes place at the wet-bulb temperature of the liquid in the ambient medium at given thermodynamic state. The rate Q_L of net heat transfer into the liquid droplet is given by the equation

$$Q_L = \dot{m} \left[\frac{\bar{c}_{p,F} (T_\infty - T_s)}{B_T} - L(T_s) \right] \quad (6)$$

where $L(T_s)$ is the latent heat of evaporation of the liquid at the droplet surface temperature T_s , and $B_T = (1 + B_M)^\phi - 1$ the Spalding heat transfer number, with the exponent ϕ given as

$$\phi = \frac{\bar{c}_{p,F}}{\bar{c}_{p,g}} \frac{Sh^*}{Nu^*} \frac{1}{Le} \quad (7)$$

The bars on the specific heat capacities c_p indicate the average value between the wet-bulb temperature of the droplet and the ambient gas temperature. \bar{Le} is the average Lewis number of the gas mixture. The modified Nusselt number Nu^* is given by an equation analogous to (2), with a function $F(B_T)$ analogous to (4) with $B = B_T$. The temporal evolution of the droplet temperature T_s (for the infinite conductivity approach) is determined by the equation

$$\frac{dT_s}{dt} = \frac{3}{4\pi a^3 \rho_L c_L} Q_L \quad (8)$$

which is used in our computational procedure to determine the droplet temperature as a function of time, since we assume uniform temperature distribution inside the droplet. In the case of application of a conduction limit model, the temperature distribution inside the droplet would have to be computed by solving the related differential equation.

It is the purpose of our work to extend the above model to describe the evaporation behavior of multi-component liquid droplets. In this extended model, we formulate the evaporation rate of the droplet as a sum of component evaporation rates, i.e., by an equation of the form

$$\dot{m} = \sum_{i=1}^N \dot{m}_i = \sum_{i=1}^N \left[2\pi a_{i,D} (\bar{\rho} \bar{D}_i)_g Sh^* \ln(1 + B_{M,i}) \right] \quad (9)$$

where \dot{m}_i is the evaporation rate of liquid component i in the droplet. In this equation $a_{i,D}$ is the volume-equivalent partial radius of component i , corresponding to its volume fraction, given as $a_{i,D} = a(V_i/V)^{1/3}$, and the Spalding mass transfer number $B_{M,i}$ is computed for each component i according to

$$B_{M,i} = \frac{(Y_{i,s} - Y_{i,\infty})}{(1 - Y_{i,s})} . \quad (10)$$

Kastner developed this approach for binary liquid mixtures ($N=2$) and found that using the volume-equivalent partial radius of component i in the mixture is appropriate [9]. The other symbols in Eq. (9) have their usual meanings. The diffusion coefficient of component i is still a binary coefficient, since we consider the gas phase as ideal and therefore ignore effects from vapor components other than i in the gas phase. The rate of heat transfer into the liquid is modeled, by an equation analogous to (6), for all components separately, which means that we do not account for liquid mixing enthalpy. We therefore consider the liquid mixture as ideal in the caloric sense.

For evaluating the above model equations, we treat the liquid mixture as real by accounting for mutual influences of the liquid components on their activities. This behavior has consequences for the actual vapor pressures (and therefore mass fractions) of the various components in the gas phase, which is saturated at the droplet surface. The mass fractions of the components occur in the mass transfer number $B_{M,i}$ and are needed for calculating all gaseous mixture properties, like a reference composition, using the 1/3 rule. The mass fraction Y_i can be computed from the mole fraction x_i , which is calculated using the equation

$$x_i = \frac{p_{vap,i}}{p_m} \gamma_i x_{L,i} . \quad (11)$$

Here $p_{vap,i}$ is the vapor pressure of the *pure* component i , γ_i the activity coefficient of component i in the multi-component liquid mixture, and $x_{L,i}$ the mole fraction of component i in the liquid phase. The whole mixture equilibrium is established under the total mixture pressure p_m , which is the ambient air pressure, composed of the contributions from the vapor pressures of the evaporating liquids and the partial pressures of the air and the water vapour content due to the humidity of the air.

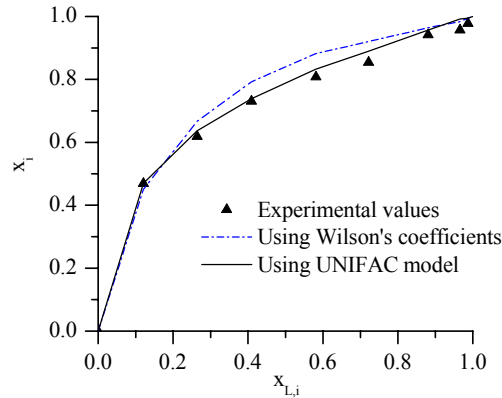


Fig. 1 The equilibrium molar fraction x_i of Methanol in the gas phase as a function of the molar fraction $x_{L,i}$ in the liquid phase for a water/methanol system ($p=1\text{bar}$, $373\text{K} \leq T \leq 338\text{K}$).

For binary mixtures, the activity coefficients may be described using Wilson's coefficients. In the case of multi-component mixtures, however, a different approach is needed. In our model, we use the UNIFAC method [10]. This method allows for the calculation of activity coefficients of many organic compounds, based on their molecular structure. When considering the molecular interactions, the liquid mixture is considered as a solution of the structural units of the molecules, rather than of the molecules themselves. The mathematical equations, which make out the UNIFAC method and are relatively simple, rely on a data base for the molecular behavior of the compounds investigated. An example of data obtained

with the Wilson's coefficients and with the UNIFAC method for a binary mixture is shown in Fig. 1. This example shows that the UNIFAC method represents the measurement data very well. Similar comparisons for multi-component mixtures are more difficult to make since the experimental data are sparse.

In the following section, the experimental procedure is discussed.

3. Experimental Procedure

Computational results obtained from the model described above were verified with experiments. In the experiments, the evaporation behavior of single, multi-component liquid droplets is investigated using an acoustic levitator [11]. The fundamental interest of the levitator lies in the suspension of the droplets without any mechanical contact, making use of the quasi-steady sound-pressure distribution between the transducer and a reflector. This helps in maintaining the thermodynamical properties of the droplet and in ensuring that heat transfer into the droplet takes place only due to the presence of the ambient gaseous medium. Due to this advantage, an acoustic levitator is useful for tracking the life history of a droplet. The acoustic levitator shown in Fig. 2 consists of a transducer, which houses a piezo crystal, and a reflector. The piezo crystal, excited by an electrical signal, moves a stainless steel horn and produces ultrasonic waves at a frequency of 56kHz (wavelength $\sim 6.2\text{mm}$ in air at $T=298.15\text{K}$). The ultrasonic waves produced are made to stand by a flat reflector positioned opposite to the transducer at a distance appropriate to allow for the formation of 5 pressure nodes. This arrangement is placed in an acrylic glass box, where a controlled

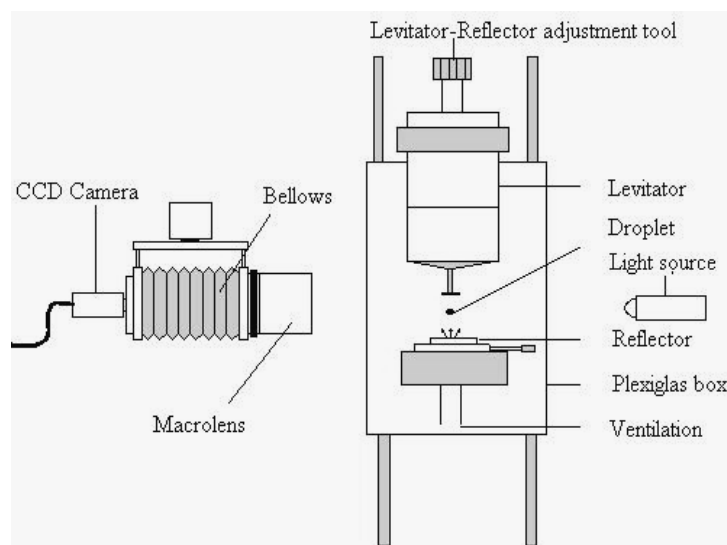


Fig. 2 Set-up with acoustic levitator used for the droplet evaporation experiments.

environment is maintained with a temperature around 298.15K (error $\sim \pm 1\text{K}$), and a relative humidity of 2% (error $\sim \pm 5\%$). The droplet is introduced into the acoustic pressure field with the aid of a micro liter syringe. A known quantity of the liquid to be tested is taken in and introduced into the standing wave, thereby levitating the droplet. The levitated droplet is back lighted by a white light source. A sharp image of the shadow of the ellipsoidal droplet is obtained through a CCD camera, and it is further processed with the image analyzing software OPTIMAS. The set of information about the droplet consists of the volume-equivalent diameter, aspect ratio, and coordinates of the center of gravity of the droplet with respect to some reference point in space. These data are obtained as functions of time through the software. Further information regarding the evolution of the droplet, such as volume, surface decay, and vertical displacement due to mass loss, are processed as

functions of time from these raw data. The interactions of the levitated droplet with the ultrasound field, and the droplet evaporation in the acoustic field are well documented [12].

4. Experimental results and comparison with theory

Experiments were carried out with droplets of liquid mixtures containing more than two components. The accuracy of the measurements was assessed by repeating the experiments and plotting the root mean square fluctuation of the normalized drop surface as an error bar. The evaporation behavior of liquid droplets containing three, four and five liquid components is presented here. The measurement and computational results are given in terms of the normalized droplet surface as functions of time. In Fig. 3a, the results are depicted for a ternary mixture of Methanol, Ethanol and 1-Butanol. Further experiments were carried out for a four-component liquid mixture of Methanol, Ethanol, 1-Butanol and n-Heptane, and the results obtained are compared with computed data in Fig. 3b. Furthermore,

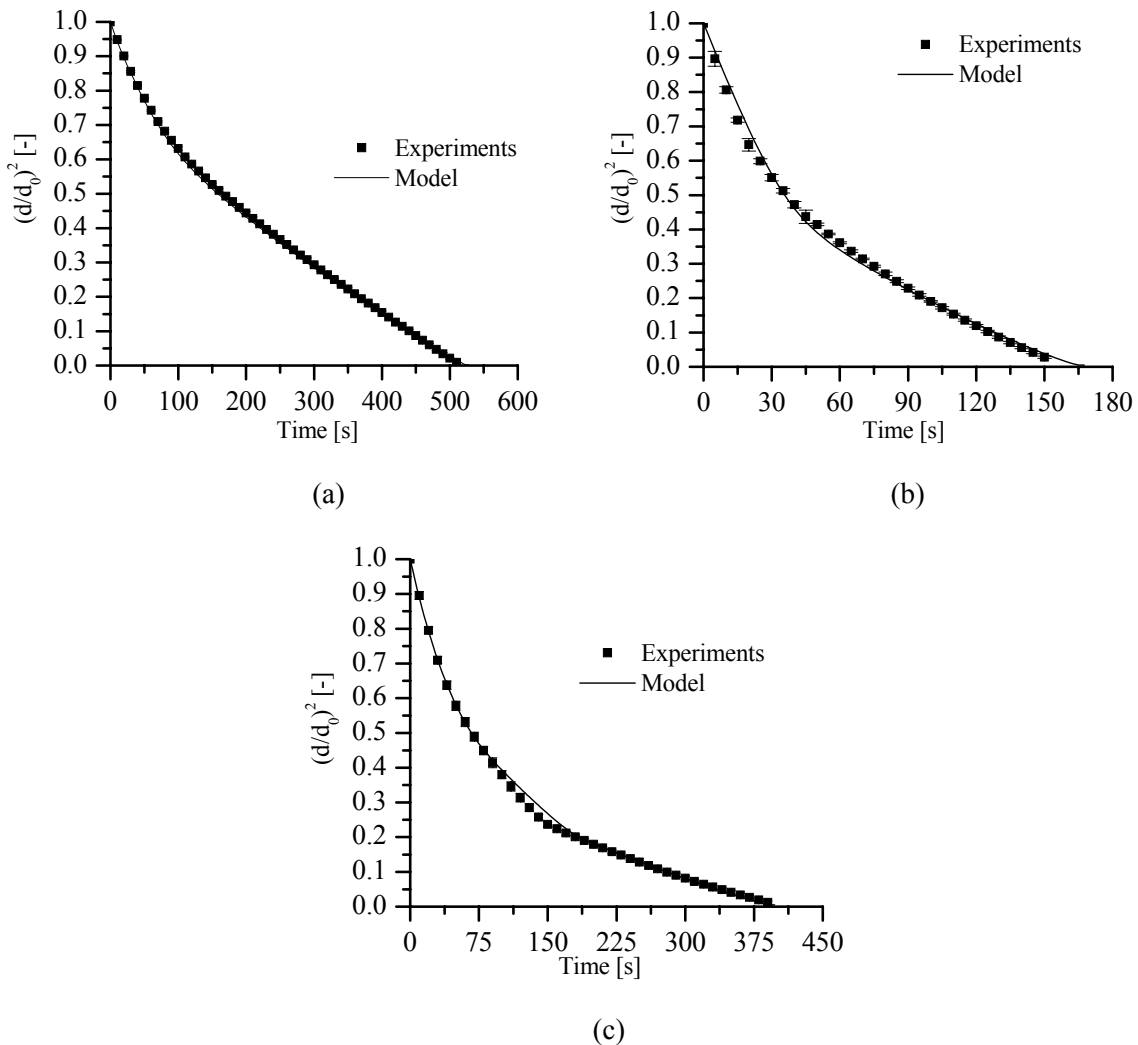


Fig. 3 Evaporation characteristics of droplets of different liquid mixtures as measured and computed. (a) Three components – initial drop size 1.67 mm, initial composition 30% Methanol, 20% Ethanol, 50% 1-Butanol, ~ 5% relative humidity, $T=30^\circ\text{C}$. (b) Four components – initial drop size 1.53 mm, initial composition 25% Methanol, Ethanol, 1-Butanol, n-Heptane, ~ 4% relative humidity, $T=28^\circ\text{C}$. (c) Five components – initial drop size 1.72 mm, initial composition 20% Methanol, Ethanol, 1-Butanol, n-Heptane, n-Decane, ~ 4% relative humidity, $T=31^\circ\text{C}$. Initial mixture compositions in volume percent.

droplets of a five-component mixture of Methanol, Ethanol, 1-Butanol, n-Heptane and n-Decane were investigated. The results from experiment and computation are presented in Fig. 3c. All data reveal very good repeatability of the experiments, and also excellent agreement

between measurement and computation. This is a clear indication for the fact that the model computations account for the physico-chemical phenomena which are relevant for the evaporation process.

Further experiments were carried out by varying the initial composition of the droplets. The details of these experiments for the three-component mixture of Fig. 3a are given in Tab. 1.

Tab. 1 Lifetime of droplets containing Methanol, Ethanol and 1-Butanol. Initial drop size 1.65mm.

Initial volume fraction of Methanol	Initial volume fraction of Ethanol	Initial volume fraction of 1-Butanol	Droplet lifetime	
			Experimental [s]	Calculated [s]
0.10	0.40	0.50	520	517.55
0.20	0.30	0.50	510	515.05
0.30	0.20	0.50	510	515.05

It is found that, for the present three-component liquid system, the lifetime obtained from the experiments and those predicted by the computation match closely. The lifetime of the droplets does not change appreciably with the droplet composition for the range of compositions investigated. This behavior is quite expected, since the volatilities of Methanol and Ethanol (components whose initial volume fractions vary) are quite similar, and the total lifetime is certainly dominated by the content of 1-Butanol. The components also belong to the same homologous series, hence large differences in their properties are not to be expected. Further tests were carried out with another three-component liquid system of Methanol, Ethanol, and n-Decane. From Tab. 2, it is found that the lifetime of the droplets decreases as the initial volume fraction of the volatile component Methanol is increased. Again the measured and computed lifetimes match closely.

Tab. 2 Lifetime of droplets containing Methanol, Ethanol and n-Decane. Initial drop size 1.63mm.

Initial volume fraction of Methanol	Initial volume fraction of Ethanol	Initial volume fraction of n-Decane	Droplet lifetime	
			Experimental [s]	Calculated [s]
0.10	0.50	0.40	450	457.55
0.20	0.50	0.30	380	360.05
0.30	0.50	0.20	310	317.55

Tab. 3 Lifetime of droplets containing Methanol, Ethanol, 1-Butanol, n-Heptane, and n-Decane. Initial drop size 1.62mm.

Initial volume fraction of Methanol	Initial volume fraction of Ethanol	Initial volume fraction of 1-Butanol	Initial volume fraction of n-Heptane	Initial volume fraction of n-Decane	Droplet lifetime	
					Experiment [s]	Calculated [s]
0.30	0.20	0.20	0.15	0.15	360	355.05
0.30	0.30	0.10	0.20	0.10	320	322.55
0.20	0.10	0.10	0.40	0.20	260	250.05

A comparison of the lifetimes of droplets of five-component mixtures with varying initial composition is given in Tab. 3. Though predicting the interaction between the components is difficult, both computation and experiment systematically show that the lifetime of the droplet decreases when the volume fraction of the most volatile component (here n-Heptane)

is increased. This is consistent with the three-component system discussed above. In all measured and computed lifetimes of the droplets of the various liquid mixtures, we see deviations of not more than 5%, which is an excellent agreement.

5. Conclusions

A computational model for the simulation of the evaporation behavior of multi-component liquid droplets is developed and verified experimentally. The model is based on the model of pure liquid droplet evaporation by Abramzon and Sirignano and extends that model to complicated liquid mixtures. The essential effect is the mutual influence of the various components on the activities. Mixing enthalpy is not accounted for. The model is not limited in terms of the number of components in the liquid phase. The verification experiments were carried out with ultrasonically levitated single droplets of multi-component liquids. Computational and experimental results on the decay of the droplet surface with time agree very well, indicating that the model accounts for the relevant physico-chemical phenomena in multi-component liquid evaporation. A maximum deviation in measured and computed lifetimes of the droplets of various multi-component mixtures of 5% occurs, which is an excellent result. From the computed data, rates of evaporation of the various components can be deduced. This kind of information cannot be readily obtained from the levitator data, which consist predominantly in geometrical information. Further work in the field will consist in measuring the time-dependent droplet temperature and comparing it with the computational results.

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