

Influence of composition and ambient temperature on the evaporation rate of binary mixture droplets

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In this study, the evaporation process of binary mixture droplets consisting of n-hexadecane with n-decane, n-dodecane or n-tetradecane with different initial volume fractions and subjected to ambient temperatures between 302 K and 324 K are investigated. Experimental data for the evolution of the non-dimensional droplet diameter as a function of time from Mie scattering of optically levitated droplets is presented. Results from numerical simulations of a simple model of diffusion-controlled evaporation agree very well with the experimental data. An analytical solution for a rapid estimation of the evaporation behaviour is proposed and also agrees very well with the experimental data.

1. Introduction

Research on fuel evaporation is very important with respect to fuel economy and emission reduction in modern gasoline and diesel engines. Since gasoline and diesel fuel consist of more than 200 different hydrocarbon species, evaporation is strongly affected by the broad variety of different fuel volatility. Therefore, there is a vital interest in accurate modeling of multicomponent droplet evaporation for the purpose of numerical simulations.

In this study, the evaporation process of the droplets is mainly controlled by the diffusion of the evaporated species in the gas phase. In the literature, reviews in this field are given by Law [1] and Sirignano [2].

The experimental method of optical levitation allows detailed studies of slow evaporation processes with minimal external influences. Binary mixtures consisting of n-tetradecane and n-hexadecane droplets and vaporizing at room temperature have been studied by Gartung et al. [3]. Subsequently, the experimental setup was improved to allow faster image acquisition and a variable ambient temperature. The influence of temperature on the evaporation of pure n-hexadecane droplets was examined by Wilms et al. [4].

In this study, binary mixtures of different composition and exposed to different ambient temperatures are investigated. For the binary mixtures, combinations of n-hexadecane with n-decane, n-dodecane or n-tetradecane are studied. The ambient temperature varied between 302 K and 324 K. The surrounding air is nearly stagnant.

2. Experimental setup

For the experimental investigations, the droplets were levitated optically and the droplet diameter was measured continuously with a certain time interval during the evaporation process by evaluating interference fringes of the far-field of the laser light scattered in the forward hemisphere [5].

A schematic view of the experimental setup is depicted in Fig. 1. A laser beam of a NdYag laser is directed vertically upwards into the observation chamber using a mirror. The droplet is originated by a droplet on demand generator and is levitated closely below the observation position. In this position, the ambient temperature is very low. By means of the movable lens, the focus of the laser beam is moved upwards to bring the droplet in the observation position. In this position the droplet can be exposed to a higher ambient temperature, since the walls of the observation chamber can be heated up. During the evaporation process, the droplet is subjected to a slow downwards directed air stream to avoid vapor accumulation within the observation chamber.

The cylindrical lens between the droplet and the linear CCD-array is placed one focal length in front of the linear CCD-array and thus serves as a Fourier lens. In this way, the position of a ray of light on the linear CCD-array is independent from the droplet position and depends only on the light scattering angle.

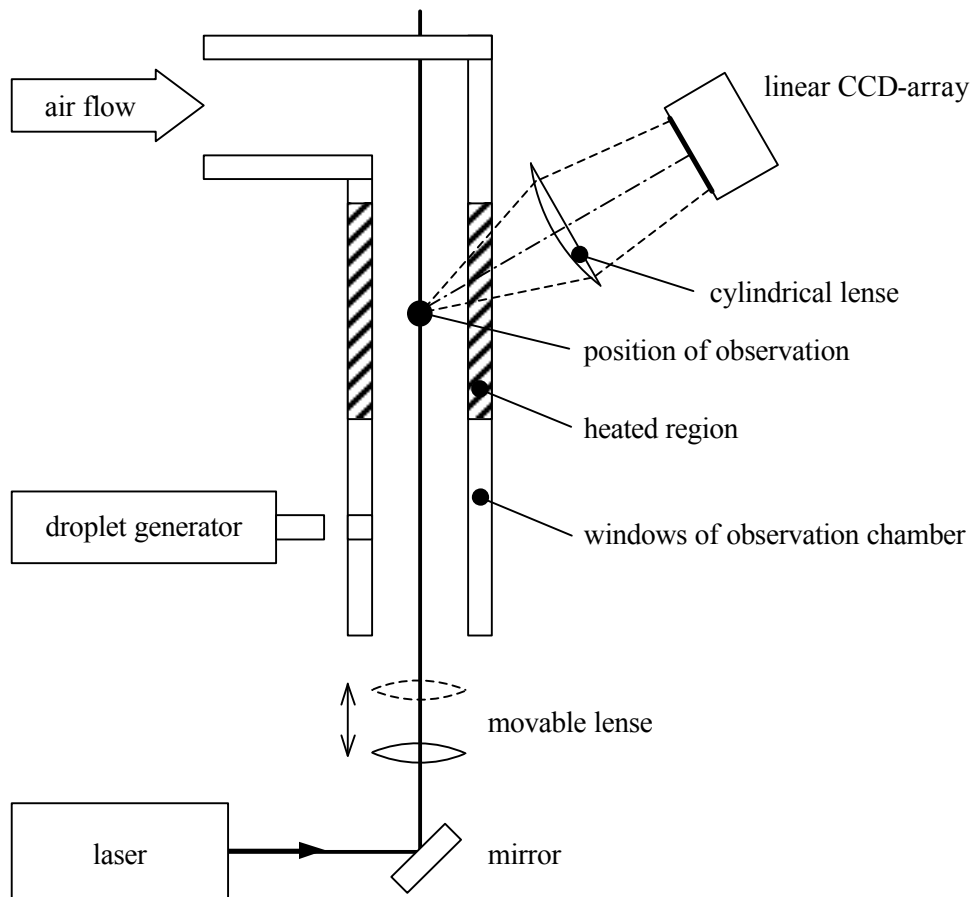


Figure 1: Experimental setup

The initial droplet size was up to about $60\text{ }\mu\text{m}$ in diameter. A maximum power of 5.5 W of the laser was necessary for optical levitation. In general, the droplet size evolution was

monitored down to a droplet diameter of about 10 μm . In this regime, surface tension effects due to the surface curvature can be neglected. According to the Kelvin-Helmholtz-Law, the increase of vaporization pressure due to the surface curvature is less than 0.01 % for droplets with a diameter of 20 μm .

3. Model for numerical simulation

For the substances of this work and the conditions to which the droplets are subjected to, the assumptions hold, that the evaporation process is diffusion-controlled by the diffusion of the evaporated liquid into the surrounding air. By applying Fick's law as well as the continuity equation to the gas phase surrounding the droplet, the treatment of a monocomponent droplet yields the following equation for the molar flux J_i :

$$J_i = \frac{2D_{im}p_i}{dR^{mol}T} \quad (1)$$

In Eq. (1), the index i denotes the droplet liquid, D_{im} the diffusion coefficient of the liquid i in the mixture m consisting of air and the vaporized liquid, p_i the vapor pressure of the liquid on the droplet surface, d the droplet diameter, R^{mol} the molar gas constant and T the temperature which is assumed to be uniform in space and time.

A mass balance of the droplet requires that

$$J_i = -\frac{1}{\rho d^2} \frac{d}{dt} \left(\rho^{mol} \frac{\rho}{6} d^3 \right), \quad (2)$$

where ρ^{mol} is the liquid molar density. Eqs. (1) and (2) lead to the well-known D²-law [1]

$$\mathbf{x} = \left(\frac{d}{d_0} \right)^2 = 1 - \frac{8D_{im}p_i}{\rho^{mol}R^{mol}T} \frac{t}{d_0^2} = 1 - K \frac{t}{d_0^2}, \quad (3)$$

where d_0 denotes the initial droplet diameter and \mathbf{x} represents the non-dimensional droplet surface. If \mathbf{x} is plotted against t/d_0^2 , a straight line is obtained where K represents the evaporation rate constant

For the numerical simulation of the evaporation process of binary droplets, a model developed originally by Ravindran and Davis [6] was used. For each species, the vaporization pressure and hence the molar flux according to Eq. (1) is reduced by its molar fraction according to Raoult's law. In Eq. (2), ρ^{mol} represents the molar density of the mixture which is assumed to be homogeneous. These assumptions result in the following equations describing the temporal decrease of the non-dimensional droplet surface \mathbf{x} and the temporal drop of the molar fraction x_1 of the high volatile component:

$$\frac{d\mathbf{x}}{dt} = \frac{8a_2V_2^{mol}}{d_0^2} \cdot \left[\left(1 - \frac{\mathbf{m}}{\mathbf{b}} \right) x_1 - 1 \right], \quad (4)$$

$$\frac{dx_1}{dt} = \frac{12a_2V_2^{mol}}{d_0^2} \cdot \frac{1}{\mathbf{x}} \cdot \left(1 - \frac{1}{\mathbf{b}}\right) \cdot [(1 - \mathbf{m})x_1^3 + (\mathbf{m} - 2)x_1^2 + x_1]. \quad (5)$$

Index 1 denotes the high volatile component, index 2 represents the low volatile component, i.e. n-hexadecane in this paper. The coefficient $a_i = D_{im}p_i/(R^{mol}T)$ comprises the temperatur T , the molar gas constant R^{mol} , the vaporization pressure p_i as well as the diffusion coefficient D_{im} of the component i in the mixture m consisting of air and the vaporized liquid droplet spezie. V_i^{mol} denotes the molar volume in the liquid phase. $\mathbf{b} = a_2/a_1$ and $\mathbf{m} = V_1^{mol}/V_2^{mol}$ are non-dimensional species constants.

4. Analytical solution

For a rapid estimation of the evaporation behaviour, an analytical solution has been developed based on Eqs. (4) and (5) and following the ideas of Glushkov [7]. Dividing Eq. (4) by Eq. (5) and integrating by separating the variables results in a solution for $\mathbf{x}(x_1)$:

$$\mathbf{x}(x_1) = \left[\left(\frac{x_1}{x_{1,0}} \right)^{\frac{\mathbf{b}}{1-\mathbf{b}}} \left(\frac{1-x_{1,0}}{1-x_1} \right)^{\frac{1}{1-\mathbf{b}}} \left(\frac{x_1 - \frac{1}{1-\mathbf{m}}}{x_{1,0} - \frac{1}{1-\mathbf{m}}} \right)^{\frac{2}{3}} \right] \quad (6)$$

If Eq. (6) is compared to the solution of Glushkov for $\mathbf{x}(x_1)$, it can be seen that an additional factor, i.e. the factor with \mathbf{m} considering droplet density variations, appears in Eq. (6). In order to conclude the analytical solution, $t(x_1)$ was determined. Therefore, the derivative of Eq. (6) with respect to x_1 was introduced into Eq. (4), where the left hand side was extended to $d\mathbf{x}/dt = (d\mathbf{x}/dx_1) \cdot (dx_1/dt)$. For this purpose, Eq. (6) was simplified by dropping the before mentioned factor containing \mathbf{m} . This simplification and the following approximations show only little influence on the results of the analytical solution for the substances of this work and the conditions to which they are subjected to. In order to obtain a closed-form solution, approximations were introduced concerning \mathbf{b} . For the here examined liquid mixtures, the maximum value for \mathbf{b} is $\mathbf{b} \sim 0.09$ in the case of a mixture of hexadecane with tetradecane. Therefore, the assumption $1-\mathbf{b} \sim 1$ was introduced, and since \mathbf{m} adopts a minimum value of $\mathbf{m} \sim 0.67$ for a mixture of hexadecane with decane, also $\mathbf{m}-\mathbf{b} \sim \mathbf{m}$ was applied. The following result was obtained for $t(x_1)$:

$$t(x_1) = \frac{\mathbf{x}'_0}{h_0} \frac{\mathbf{b}}{\mathbf{m}} \left[\left(\frac{1}{1-x_{1,0}} \right)^{\frac{2}{3}} - \left(\frac{1}{1-x_1} \right)^{\frac{2}{3}} + \frac{2}{3} \ln \left(\frac{(1-x_{1,0})^{\frac{1}{3}} - 1}{(1-x_1)^{\frac{1}{3}} - 1} \right) + \frac{1}{3} \ln \left(\frac{(1-x_1)^{\frac{2}{3}} + (1-x_1)^{\frac{1}{3}} + 1}{(1-x_{1,0})^{\frac{2}{3}} + (1-x_{1,0})^{\frac{1}{3}} + 1} \right) \right. \\ \left. + \frac{2}{\sqrt{3}} \operatorname{atan} \left(\frac{2(1-x_1)^{\frac{1}{3}} + 1}{\sqrt{3}} \right) - \frac{2}{\sqrt{3}} \operatorname{atan} \left(\frac{2(1-x_{1,0})^{\frac{1}{3}} + 1}{\sqrt{3}} \right) \right] \quad (7)$$

Eqs. (6) and (7) allow to determine $\mathbf{x}(t)$ for selected values of x_1 . At very small values of x_1 the solution is continued with Eq. (3), where the evaporation rate is calculated for the pure substance with lower volatility.

5. Results

All results are plotted in the same manner, i.e. the non-dimensional droplet diameter $(d/d_0)^2$ is plotted as a function of t/d_0^2 . As was stated earlier, according to Eq. (3) a linear behaviour is obtained for monocomponent droplets, where the negative slope of this curve represents the evaporation rate. In the case of two-component droplet evaporation, the evaporation rate is a function of time and droplet composition.

5.1 Variation of volume fraction of binary droplets

In Fig. 2 the non-dimensional droplet diameter $(d/d_0)^2$ as a function of t/d_0^2 for droplets of n-hexadecane and n-tetradecane mixtures at an ambient temperature of 304 K is depicted for different initial compositions.

At the beginning of the evaporation process, the evaporation rate as slope of these curves is for mixtures in between the limiting values for droplets of pure n-hexadecane and pure n-tetradecane. Since n-tetradecane is the more volatile component of the mixture, a transition phase occurs after which the evaporation rate is the same as for pure n-hexadecane.

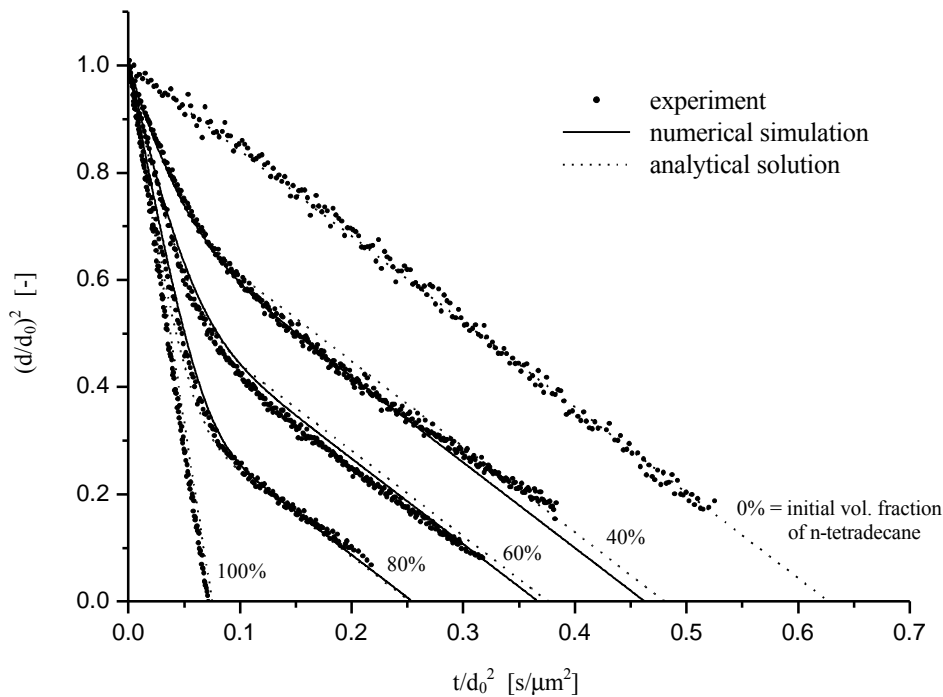


Figure 2: Binary droplets of n-hexadecane and n-tetradecane mixtures at an ambient temperature of 304 K.

In Fig. 2, experimental data is collected from several droplets. The comparison of the experimental results with the numerical simulations demonstrates that the assumptions made for the description of the evaporation process hold since experimental data and numerical

results agree very well. Small deviations between these curves are either due to the fact that for the experiments, the ambient temperature is not exactly 304 K, or that for the numerical simulations, there are uncertainties of the values of the fluid properties taken from the literature.

The analytical solution also agrees quite well with the experimental data.

5.2 Variation of ambient temperature

For binary droplets with an initial volume fraction of 60% n-tetradecane and 40% n-hexadecane, the ambient temperature is varied in Fig. 3. The numerical simulation and the analytical solution still agree very well with each other, whereas there is increasing discrepancy with the experimental data at higher temperatures. This might again be caused by uncertainties of the fluid property values taken from the literature.

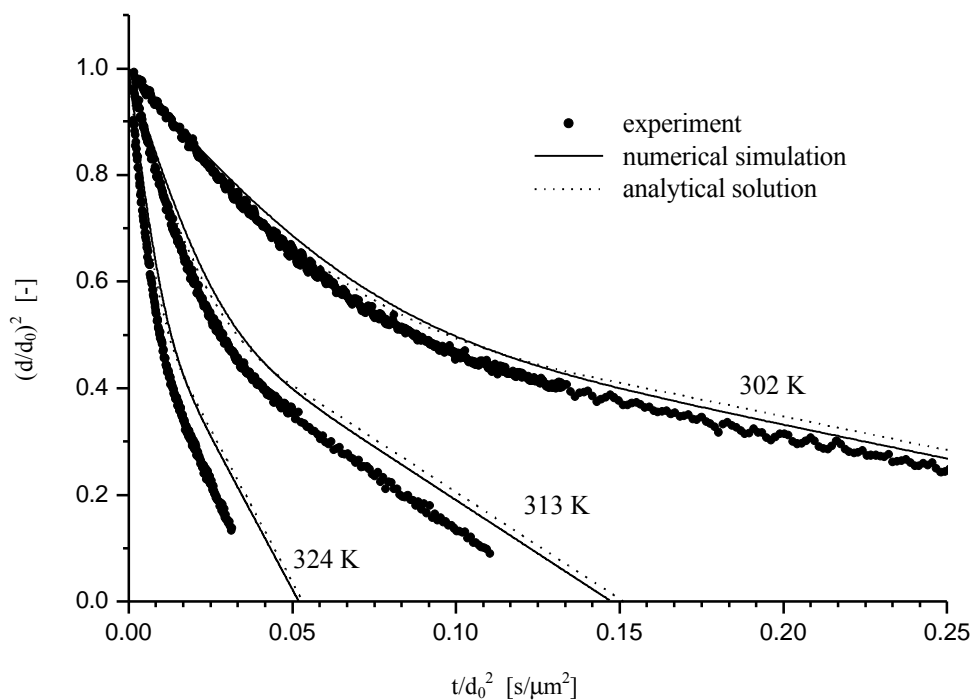


Figure 3: Binary droplets with an initial volume fraction of 60% n-tetradecane and 40 % n-hexadecane at different ambient temperatures.

5.3 Variation of substances

For binary droplets with an initial volume fraction of 60% n-hexadecane, the substance of the high volatile component was varied at approximately the same ambient temperature. Fig. 2 contains the curves with n-tetradecane as high volatile component, whereas in Fig. 4 experimental data with more volatile components such as n-dodecane and n-decane is represented.

As can be seen in Fig. 4, experimental data agrees very well with numerical simulations. The analytical solution also agrees quite well but deviates more and more from the experimental data the more volatile the second component is. This is due to the simplifying assumptions made for the derivation of the analytical solution.

However, the general agreement between the numerical, analytical and experimental results is very good.

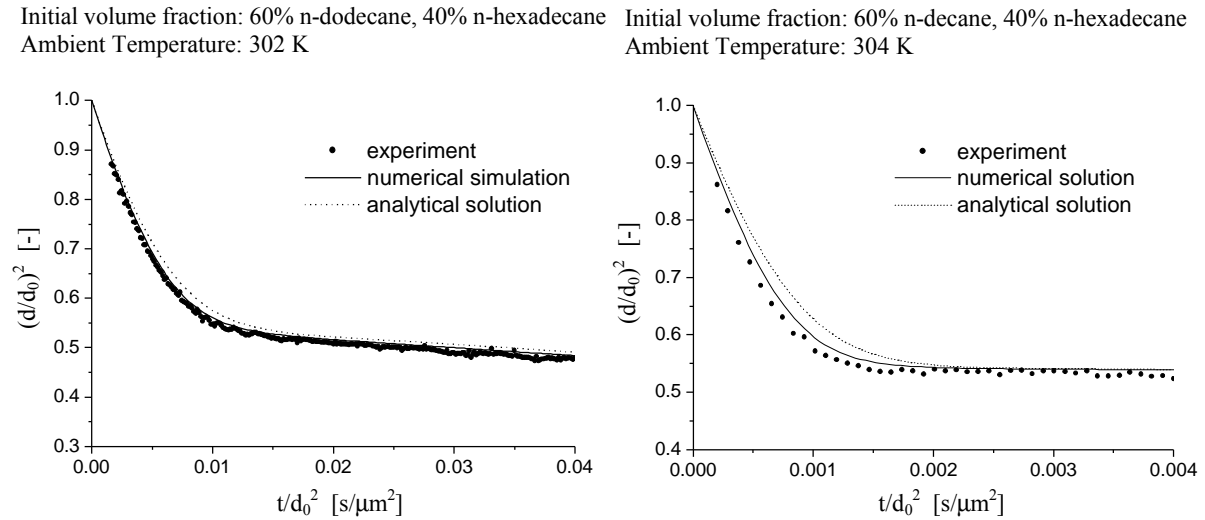


Figure 4: Binary droplets of n-hexadecane with different substances at approximately the same ambient temperature

6. Conclusion

For the here studied substances and the ambient temperatures the droplets are subjected to, the experimental data agrees very well with numerical simulations for diffusion-controlled evaporation. The proposed approximate analytical solution agrees also very well with the experimental data and allows quick estimations of evaporation processes of droplets within the studied regime.

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7. References

- [1] Law C K 1982 *Prog. Energy Combust. Sci.* **8** 171-201
- [2] Sirignano W A 1983 *Prog. Energy Combust. Sci.* **9** 291-332
- [3] Gartung K, Arndt S, Roth N and Weigand B 2000 *16th Int. Conf. on Liquid Atomization and Spray Systems Darmstadt*
- [4] Wilms J, Gartung K, Arndt S, Roth N and Weigand B 2001 *17th Annual Conf. on Liquid Atomization and Spray Systems Zürich*
- [5] König G, Anders K and Frohn A 1986 *J. Aerosol Sci.* **17** 157-167 1986
- [6] Ravindran P and Davis E J 1982 *J. of Colloid and Interface Science* **85** no.1 238-248
- [7] Glushkov V E, Todes O M and Fedoseev V A 1970 *Colloid J. of the USSR* **32** no.5 566-570