

Determination of the composition of multicomponent droplets by rainbow refractometry

by

J. Wilms*, N. Roth*, S. Arndt**, B. Weigand*

*Institute of Aerospace Thermodynamics (ITLR), University of Stuttgart
Pfaffenwaldring 31, 70569 Stuttgart, Germany

**Robert Bosch GmbH, FV/SLE2-Sh, Po. Box 106050, 70049 Stuttgart, Germany
E-Mail: jochen.wilms@itlr.uni-stuttgart.de

ABSTRACT

With an experimental setup using optical levitation techniques, the evaporation of multicomponent droplets is investigated. As substances, n-alkanes are used. In a first step, n-alkanes with a low volatility are used so that the temperature and concentration inside the droplet is assumed to be constant. The evolution of the droplet diameter as a function of time is determined from the fringe spacing of the scattered laser light in the forward hemisphere, which is detected by a linear CCD camera. A second linear CCD camera is placed in the backward hemisphere, so that the scattered laser light in the region of the first rainbow is captured. From this light intensity distribution, the refractive index of the droplet is obtained by an evaluation method described in this paper. At first, the evaluation method filters out the ripple frequency by using a discrete Fourier transform. Then the calculated intensity distribution from Airy theory is fitted to the filtered intensity distribution by varying the refractive index. In this way, the refractive index of the droplet is found. From the refractive index, the temperature or the composition of the droplet can be determined. For this reason, the temperature dependency of the refractive index of n-alkanes has been measured with an Abbé refractometer and in order to facilitate the evaluation of the measurements, a general formula of the refractive index for all n-alkanes under investigation and for a selected temperature range has been developed and is presented in this paper. Light intensity distributions have been calculated using Lorenz-Mie theory and have been evaluated using the described method in order to investigate the accuracy of the method. Experimental results are presented for a binary mixture droplet consisting of n-dodecane and n-hexadecane. The experimental results are compared with the numerical results from a uniform temperature model. The temporal evolution of both the droplet diameter and the droplet composition, i.e. the molar fraction of n-dodecane, from the measurements agree very well with the numerical results.

1. INTRODUCTION

At the Institute of Aerospace Thermodynamics (ITLR), the evaporation of single droplets is investigated by an optical levitation technique described by Roth et al. (1995). With this technique, the temporal evolution of the droplet diameter of binary mixture droplets of n-alkanes has been studied at different ambient temperatures (Wilms et al., 2003). In order to obtain more information about the evaporating droplet, such as temperature and composition, rainbow refractometry has been employed. In this paper, the applied method of the rainbow refractometry is described and results for a binary mixture droplet are presented.

2. EXPERIMENTAL SETUP

A second linear CCD camera has been added to the experimental setup described by Wilms et al. (2003). This camera is placed in the backward hemisphere of the scattered light, so that it captures the scattered light in the region of the rainbow. The resulting experimental setup is depicted in Fig. 1. In front of each linear CCD-camera, a cylindrical lens is placed at a distance of one focal length with respect to the sensor of the camera. These lenses serve as Fourier lenses, so that the position of a ray of light on the linear CCD camera is independent from the droplet position and depends only on the light scattering angle.

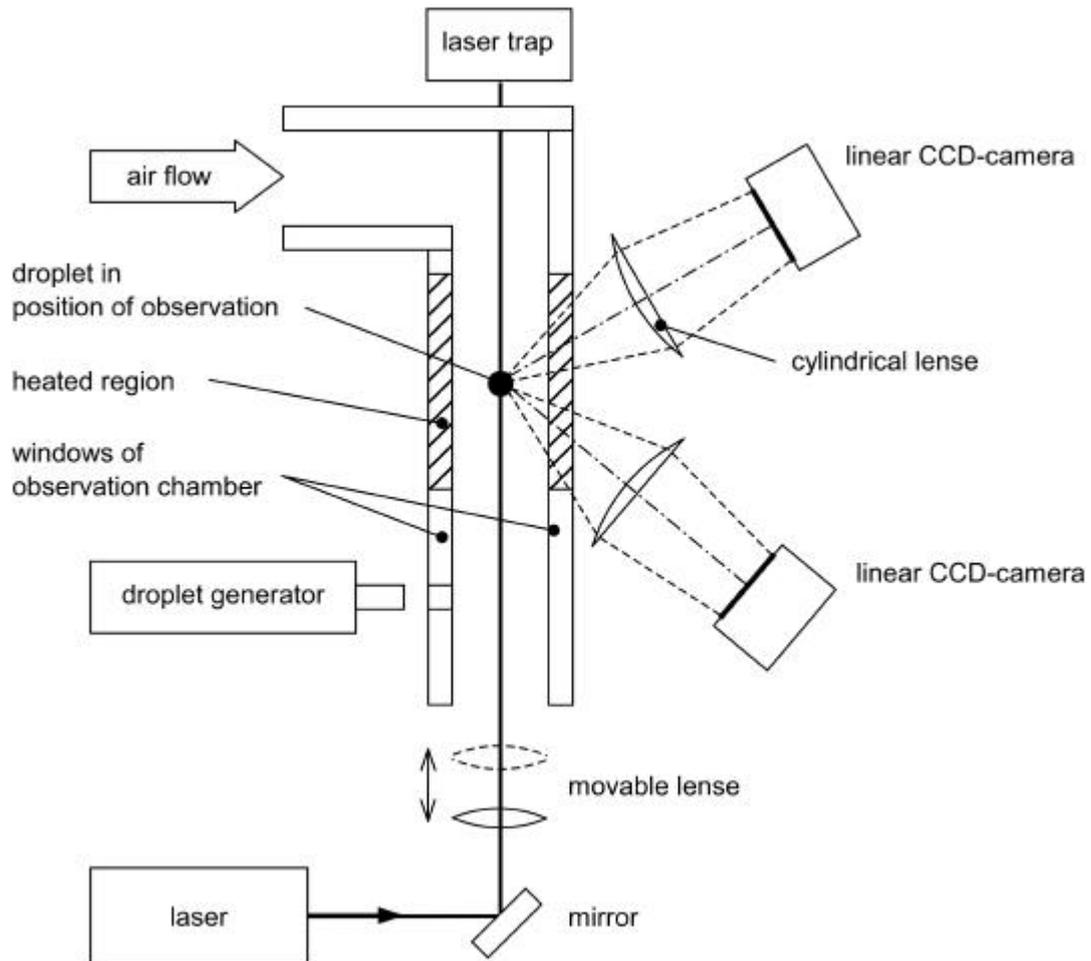


Fig. 1. Schematic view of the experimental setup.

3. MEASUREMENT TECHNIQUE

Rainbow refractometry is a non-intrusive measuring technique to determine the refractive index of droplets as presented by Roth et al. (1988). Since the refractive index is different for different species and depends also on the temperature, information about both the composition and the temperature of a droplet can be obtained by rainbow refractometry. In this study, the focus is on the determination of the composition of droplets consisting of n-alkanes.

3.1 Refractive index of n-alkanes

For the refractive index of n-alkanes, literature values are generally available at room temperature, but only some values at higher temperatures. Therefore, measurements of the refractive index of n-alkanes have been done in order to measure the influence of the temperature on the refractive index. In order to facilitate the evaluation procedure, a general formula for the refractive index covering a range of n-alkanes and a certain temperature range has been sought. The resulting relationship, which is used in this study and yields the real part of the refractive index n for a wavelength of 532 nm reads as follows:

$$n(C, T) = a(C) + b(C)(T - 273.15K)$$

$$\text{with } a(C) = 1.35858 + 0.03414 \ln(C - 3.63) \text{ and } b(C) = -6.073 \cdot 10^{-4} + 7.833 \ln(C + 2.986)$$

In this relationship, T represents the absolute temperature in Kelvin and C the number of carbon atoms of the n-alkane. This relationship is applied in the range $290\text{ K} < T < 350\text{ K}$ and $5 \leq C \leq 16$. The results for the refractive index within these ranges are illustrated in Fig. 2.

The relationship was obtained by measuring the refractive index of some of these n-alkanes at different temperatures with an Abbé-refractometer at a wavelength of 589 nm . The measurements reveal a linear relationship between the refractive index and the temperature in the temperature range under investigation. The data was fitted to a linear relationship by a least squares method. In order to minimize discrepancies with available literature data, the values were fitted to literature values (Lide, 1998) at a temperature of 293.15 K . For the experiments with the droplets, a NDYAG laser is used with a wavelength of 532 nm . Since the refractive index depends also on the wavelength, the results were corrected using relationships and values of the literature (Camin, 1945 and 1955; Forziati 1950) about the dependency of the refractive index on the wavelength for n-alkanes at a temperature of 298.15 K . This correction changed the constant $a(C)$ of the relationship.

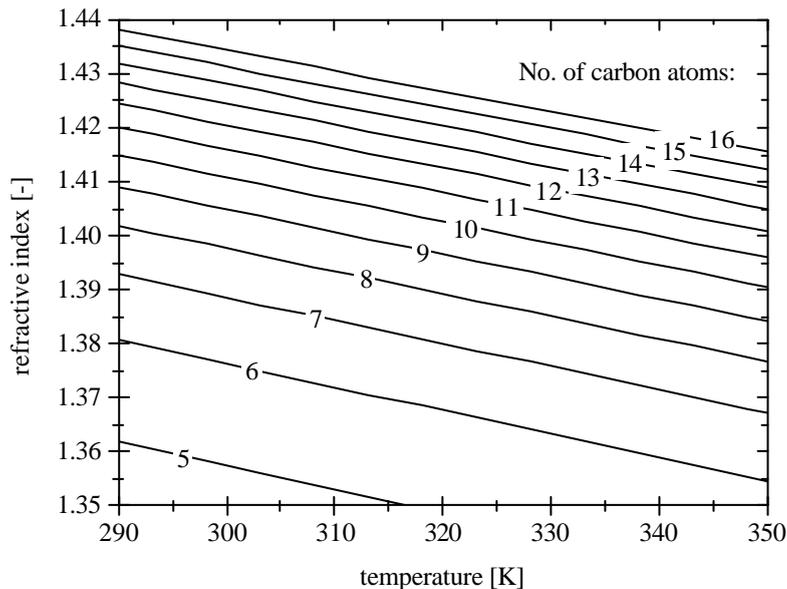


Fig. 2. Refractive index of n-alkanes from n-pentane with 5 carbon atoms till n-hexadecane with 16 carbon atoms for a wavelength of 532 nm .

3.2 Method for the determination of the refractive index from the scattered light in the region of the rainbow

For the determination of the refractive index from the scattered laser light in the region of the rainbow, a method is chosen, which seems to be a sufficiently good compromise between high accuracy and low computation time. For the validation of this method and the examination of its accuracy, calculations of the light intensity distribution in the region of the first rainbow have been performed using Lorenz-Mie theory and have been evaluated by this method.

For the measurements, the droplets are relatively small, i.e. they are in a range of 20 to 60 μm . One advantage of this fact is that due to surface forces problems with non-sphericity do not occur. On the other hand, an interference pattern, which is often called ripple structure, is superimposed on the supernumerary bows of the scattered light intensity in the region of the rainbow. This ripple structure becomes more and more dominant, the smaller the droplet is. The ripple structure can be recognized in the example of a light intensity distribution according to the Lorenz Mie theory, which is depicted in Fig. 3.

In order to avoid a negative effect of the ripple structure, the scattered light intensity is filtered using a discrete Fourier transform and eliminating the intensity amplitude at the ripple frequency. The ripple frequency F_{ripple} [rad^{-1}] can be calculated using the equation of Van Beeck (1997), since the droplet diameter is known by measuring the fringe spacing of the scattered light in the forward hemisphere:

$$F_{ripple} = \frac{d}{2\lambda} \left(\cos t_{rg} + \cos \frac{q_{rg}}{2} \right)$$

$$\text{with } t_{rg} = \arcsin \left(\sqrt{\frac{n^2 - 1}{3}} \right) \text{ and } q_{rg} = 2t_{rg} - 4 \arccos \left(\frac{1}{m} \cos t_{rg} \right)$$

In this equation, d is the droplet diameter, λ the wavelength of the laser, t_{rg} the incidence angle for the geometric rainbow and q_{rg} the geometric rainbow angle.

The effect of the filtering can be seen in Fig. 3, where a curve is depicted which represents the filtered intensity distribution of a calculated intensity distribution according to Lorenz-Mie theory.

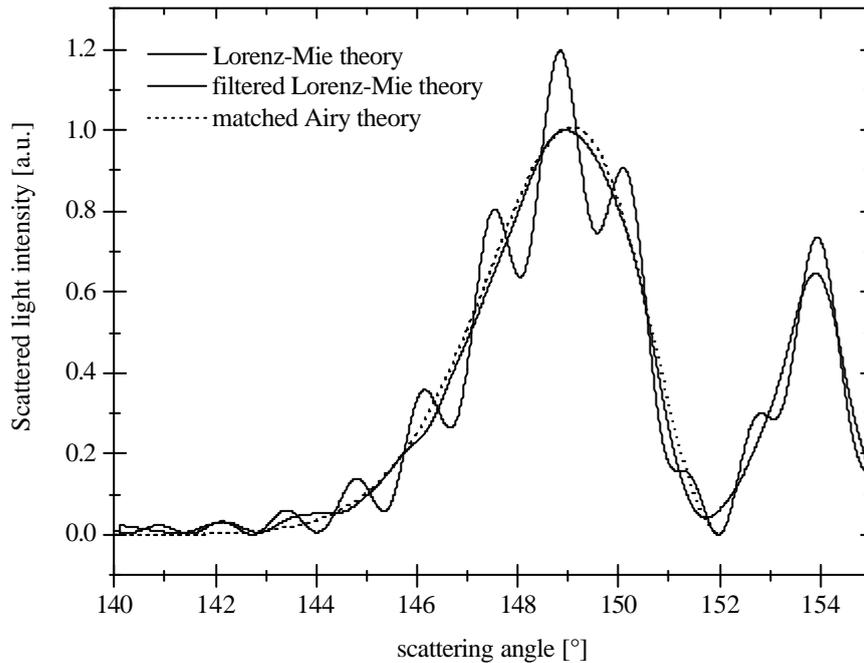


Fig. 3. The scattered light intensity as a function of the scattering angle in the region of the primary rainbow.

In order to find the refractive index, the filtered intensity distribution is then compared to the intensity distribution of the first rainbow according to the Airy theory. For this reason, the rainbow integral, which is also known as the Airy function, has been solved for a range of a non-dimensional parameter z . This non-dimensional parameter z denotes the normalized angular deviation from the geometric rainbow angle (Van Beeck, 1997) and reads

$$z = -(\mathbf{q} - \mathbf{q}_{rg}) \left(\frac{16d^2}{hI^2} \right)^{1/3} \text{ with } h = \frac{1}{\tan \mathbf{t}_{rg} \sin^2 \mathbf{t}_{rg}}.$$

From this data, the light intensity distribution as a function of the scattering angle \mathbf{q} according to Airy theory can be derived, if the refractive index n is known. Thus, the refractive index is found by varying the refractive index and iteratively optimizing the result of a cross correlation of the filtered intensity distribution of the measurement with the intensity distribution according to Airy theory. For the cross correlation, only the main bow of the rainbow pattern is taken into account, which means that the values are cut off at the first minimum at $z = 2.4955$. The reason is, that for larger z the Airy theory becomes inaccurate, i.e. there is more and more angular deviation of the intensity distribution according to Airy theory from the real intensity distribution, which can also be seen by a comparison to the intensity distribution predicted by the Lorenz-Mie theory, especially in the case of small droplets (Van Beeck, 1997). As initial value for the iterative approach to the refractive index, the relationship of Walker (1974) for the rainbow angle \mathbf{q}_{ra} based on Airy theory is used:

$$\mathbf{q}_{ra} = \mathbf{q}_{rg} + \frac{1.0845}{\sin \mathbf{t}_{rg}} \left(\frac{I^2 \cos \mathbf{t}_{rg}}{16d^2} \right)^{1/3}$$

In order to evaluate the accuracy of this method, the scattered light intensities of droplets with different size and with different refractive indices have been calculated using Lorenz Mie theory and have been evaluated by this method. The results for the refractive indices are depicted in Fig. 4. In all cases, conditions comparable to the experimental setup have been chosen with regard to the angular resolution and range of the images of the linear CCD camera. Therefore the angular range is always 15° and the angular resolution is 0.01° . This means that for each droplet 1500 intensity values were calculated and hence the angular resolution is even lower than for the experimental setup, since the CCD-camera has 1728 Pixels. The droplet size has been varied in steps of $0.05 \text{ }\mu\text{m}$ covering the main experimental range of the diameter from $20 \text{ }\mu\text{m}$ until $60 \text{ }\mu\text{m}$. The range of the refractive indices has been chosen in order to include the usual refractive indices of the n-alkanes during the experiments. Calculations have been performed for a refractive index from 1.36 until 1.44 in steps of 0.2.

In Fig. 4 it can be seen that the mean value of the refractive index is very close to the original value. This impression is confirmed by the results presented in Fig. 5, where the difference between the mean value and the original value is plotted. In this respect it is interesting to note that a deviation of $\Delta n = 0.0004$ corresponds to about 1 K for n-alkanes. In order to distinguish between two n-alkanes, a minimum $\Delta n = 0.0029$ is necessary for the case of n-pentadecane and n-hexadecane, whose refractive indices are closest next to each other of all n-alkanes under investigation.

The small underestimation of the refractive index agrees very well with observations of Van Beeck (1997) when results of Lorenz Mie theory and Airy theory are compared with each other. The fluctuations around the mean refractive index are due to morphology dependent resonances. Using this method, the fluctuations become larger the smaller the droplet and the lower the refractive index is. For a single measurement of the refractive index they can increase considerably the measuring error, but they don't have an important effect on the mean value.

After the evaluation of the scattered light intensity with this method and finding the refractive index, the equations of paragraph 3.1 for the refractive index can be used to determine the temperature in the case of a monocomponent droplet or the droplet composition in the case of a binary droplet if the droplet temperature is known.

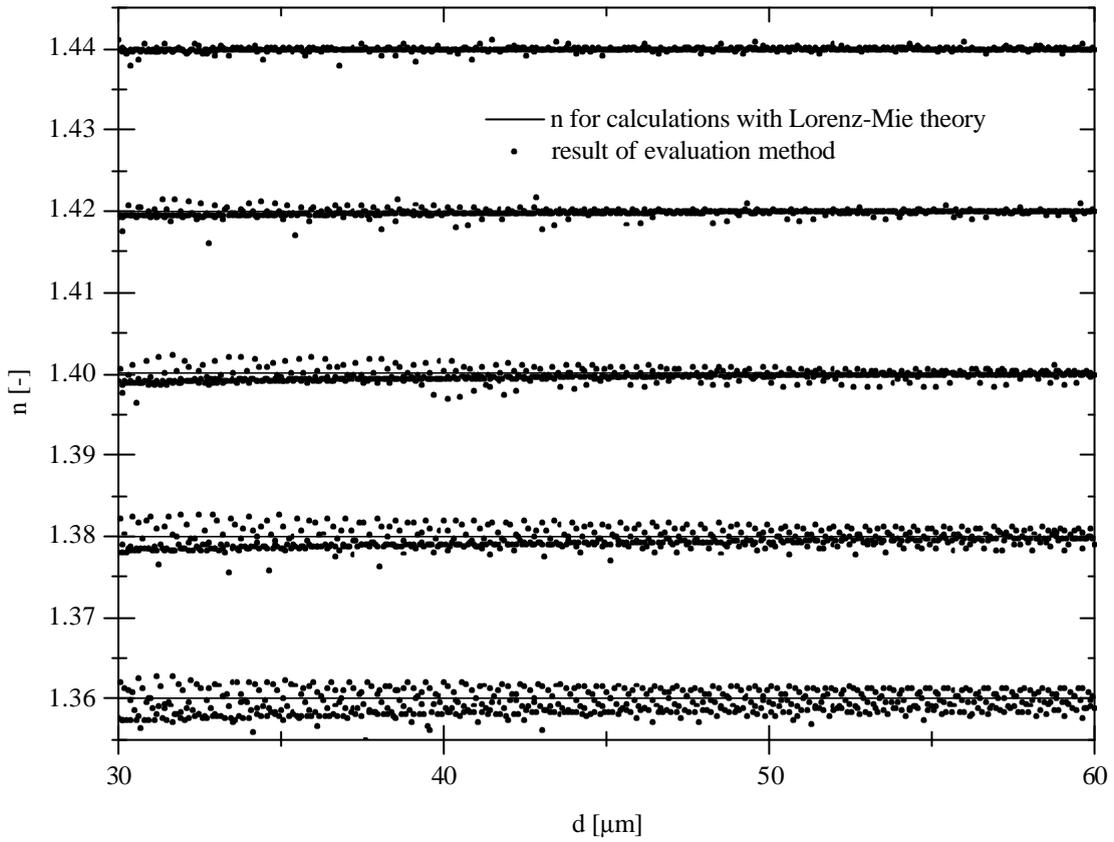


Fig. 4. Results of the refractive index for droplets with different size and different refractive indices.

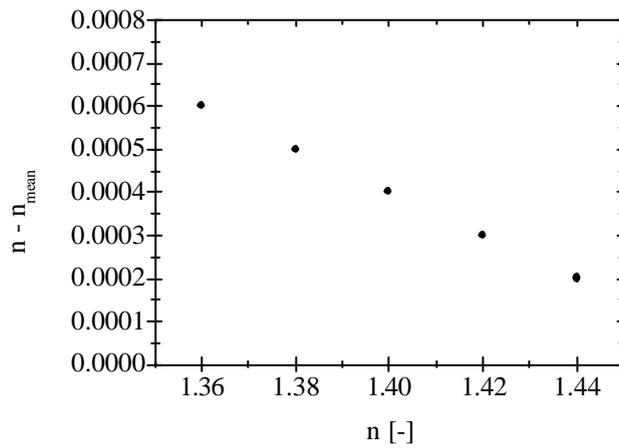


Fig. 5. Deviation of the mean result for the refractive index from the given refractive index for the Lorenz-Mie calculations.

4. RESULTS AND DISCUSSION

Binary droplets have been investigated experimentally in order to demonstrate the applicability of the evaluation method for the rainbow refractometry. In Fig. 5, the evaporation of a droplet of n-hexadecane and n-dodecane is depicted. The initial volume fraction of n-dodecane is 60%, which means that the initial molar fraction is 66%. The droplet diameter has been determined by evaluating the fringe spacing of the scattered light intensity in the forward hemisphere, which has been measured by the CCD-camera at different points in time. Extrapolation of the data to the point in time $t = 0s$ results in an initial droplet diameter of 59.23 μm .

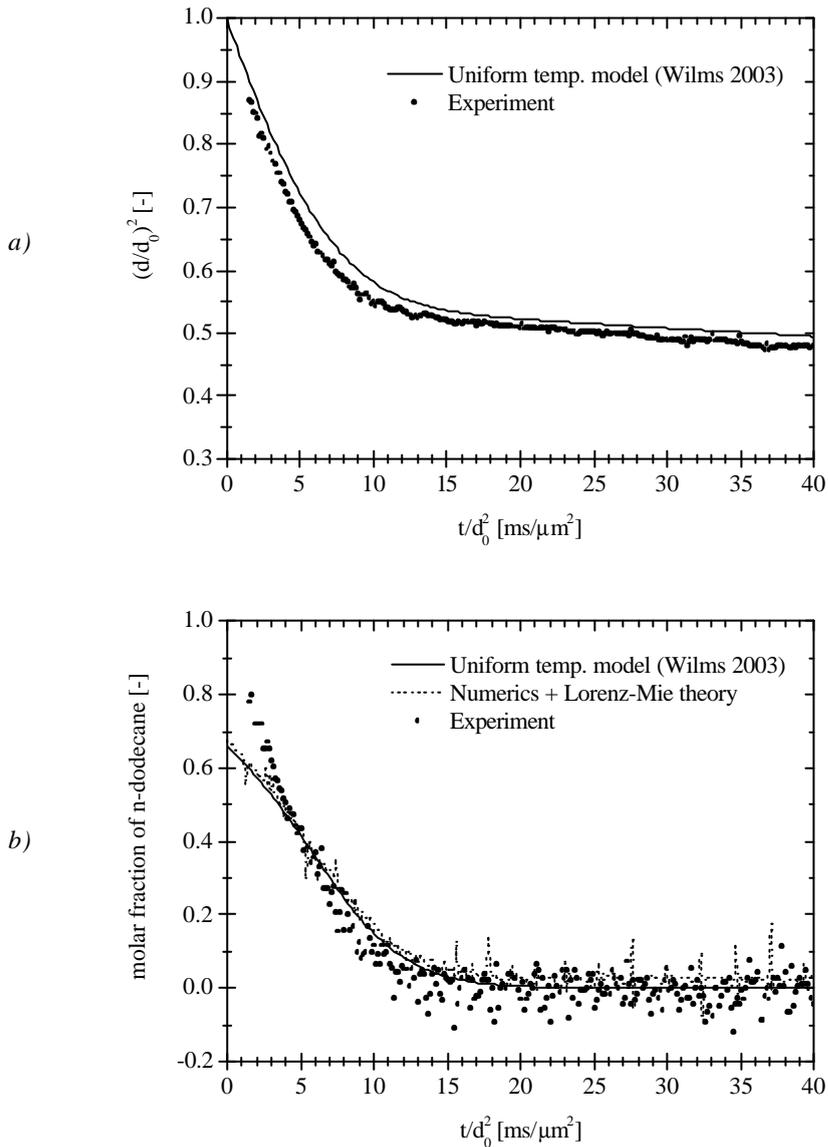


Fig. 6. Evaporation of a binary droplet of n-hexadecane and n-dodecane with an initial molar fraction of 66% n-dodecane, with an initial droplet diameter of 59.23 μm and at an ambient temperature of 302.5 K

a) Nondimensional droplet surface

b) Molar fraction of n-dodecane

The images of the other CCD-camera in the region of the rainbow have been evaluated with the method described in paragraph 3.2. In a first step, the images were evaluated as if the droplet consists solely of n-hexadecane. Since the

droplet really consists of only n-hexadecane after a certain point in time, the droplet temperature, which is assumed to remain constant during the evaporation process, has been determined by using the equations of paragraph 3.1 for the refractive index. The resulting droplet temperature is 302.5 K. With this temperature, the images have been evaluated in order to find the droplet composition during the evaluation. The result, i.e. the molar fraction of n-dodecane is depicted in Fig. 5b).

In Fig. 5, the experimental results are compared with numerical results of a uniform temperature model (Wilms 2003). Experimental and numerical results agree very well with each other, both for the nondimensional droplet surface and for the molar fraction of n-dodecane. The deviation of the experimental results for the molar fraction from the numerical solution at the beginning of the evaporation might be due to concentration gradients inside the droplet. The experimental results for the molar fraction are much more dispersive than the results for the nondimensional droplet surface. By using the described evaluation method for the rainbow refractometry this is unavoidable as can be seen from the results of the evaluation of the calculated light intensity using Lorenz-Mie theory.

5. CONCLUSIONS

The described method for the evaluation of scattered light intensity distributions from rainbow refractometry is a fast and accurate method for the determination of the refractive index. The employment of this method to scattered light intensity distributions calculated by using Lorenz-Mie theory demonstrates that this method is sufficiently accurate to determine the composition of binary droplets consisting of n-alkanes. The experimental results of the molar fraction for a binary droplet consisting of n-hexadecane and n-dodecane show good agreement with numerical results of a uniform temperature model.

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