Fluorescence Capillary Photometry for Characterization of Liquid–Liquid Dispersions

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The behavior of droplet swarms in liquid–liquid dispersions, especially found in extraction columns, are analyzed by a new fluorescence measurement technique, which represents an extension to the capillary suction method. The measuring principle developed benefits from detectable-emission light intensity of a fluorescent dye even in a trace concentration. The addition of this nontransferring dye to the dispersed phase enables in situ determination of bivariate drop-size/drop-concentration distributions, which provides important information on droplet history for the evaluation of coalescence and breakup rates. Furthermore, the measuring method represents a new approach for the measurement of droplet-size-dependent residence times in extraction columns.

Introduction

Agitated liquid–liquid dispersions are widely used in various kinds of separation and reaction processes in chemical and production engineering. Due to the large interfacial area available, they provide effective mass transfer between the two immiscible or only partially miscible media.

Drop interaction in liquid–liquid dispersions

The drops in the dispersion continuously undergo breakup and coalescence processes in the more or less turbulent flow field of the contact apparatus, for example, a liquid–liquid extraction column. Therefore the size distribution, starting from its generation at the dispersed-phase distributor, develops in space and time. For dispersed-phase volume fractions below the critical value of the phase inversion and for constant operating conditions in a batch reactor, the size distribution reaches a steady state, which is characterized by a dynamic equilibrium between the breakup and coalescence processes. In a column apparatus, containing constant flow rates of both phases, the time evolution of the size distribution is represented by the change of a certain density function over the column height.

By modifying the size distribution, we can influence the effect of coalescence and breakup on the hydrodynamics of the two-phase mixture, for example, on the effective rising velocity of the droplet swarm, on the drop residence times, and on the holdup profile. These effects are summarized under the general expression forward mixing (Míšek and Rod, 1974).

Furthermore, even in the case of a steady-state size distribution the intensity of the coalescence/redispersion cycles may have a significant effect on mass transfer, due to the enhanced interface renewal processes accompanying the coalescence and breakup events. This connection is often overlooked in discussions concerning droplet interaction in liquid–liquid dispersions, although the reverse effect—the influence of mass transfer and especially mass-transfer direction on coalescence efficiency—is a well-known phenomenon (Davies, 1992; Sawistovski, 1974).

The preceding arguments on the influence of drop interaction processes on column hydrodynamics and mass transfer in liquid–liquid dispersions motivated the current investigation of detecting coalescence events in an agitated dispersion in countercurrent extraction columns. The basic idea is, given a specific liquid–liquid dispersion at fixed operating conditions, to determine whether coalescence is an important factor concerning the evolution of the drop-size distribution and the interfacial mass transfer. That implies a quantification of the coalescence rates. It must be emphasized that in investigating this question it is not sufficient to determine an overall mean coalescence rate. Consequently, a large number of methods that rely on the detection of some mean quantity step response (e.g., Sauter diameter change following a change of agitation intensity; Hancil et al., 1986; Villermaux,

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1981) cannot be used. They are, however, valuable for an overall characterization of the constraints put on the dispersion dynamics by the physicochemical properties of the specific system used. The task of the present study is to evaluate the constraints of the apparatus hydrodynamics on drop interaction. Therefore it will be necessary to determine size-specific rates, to decide whether coalescence events are important in the region of big size classes, where the main amount of the dispersed phase volume is involved.

Description and estimation of drop interaction

The population balance equation is the general framework for analyzing the mixing intensity in the dispersed phase (Hulburt and Katz, 1964; Ramkrishna, 1981). It describes the time evolution of the transient property density functions of the droplet swarm. For our purposes, we are interested in the drop-size distribution transient and, as is discussed later, the drop-concentration distribution transient.

The coalescence and breakup events are represented as rate expressions and are incorporated in the source terms of the population balance equation. Two additional inputs for the population balance in the case of a countercurrent flow application are the size-specific drop-rising velocities or the drop residence time in the agitated column compartment. In the general case of a polydisperse droplet swarm, the appropriate choice of that function introduces one more source of uncertainty. Population-balance-based models require considerable input information for simulation as well as for proper validation of the simulation results, at least, size-specific experimental data.

Applying the drop interaction rates and quantifying the convective transport of the dispersed phase, the population balance can be used as a *simulation tool* to predict the evolution of the drop-size distribution in space and time. There are numerous investigations that are exploring the influence of drop interaction on the dynamics of the drop-size distribution in extraction columns. They solve directly the integrodifferential equation (Kronberger et al., 1994; Casamatta and Vogelpohl, 1985), a stagewise discretization (Jiricny et al., 1979), or use discrete Monte Carlo algorithms as the interval of quiescent method (Bapat et al., 1983) and the Bastinaire point method (Guimarães et al., 1990).

Complementary to the preceding, a second group of investigations extracts the unknown rates of of the coalescence and breakup process by solving the so called *inverse problem* of population balance. These methods are based on measured transient drop-size distributions (Laso et al., 1987; Tobin et al., 1990), or a color reaction between two drop populations marked with two different reactive agents to detect coalescence effects (Hamilton and Pratt, 1984; Garg and Pratt, 1984). A method for measuring tracer gas concentration in gas bubbles was developed by Prince and Blanche (1990) to quantify coalescence in a bubble swarm. Unfortunately the coalescence-rate estimation activities in liquid–liquid dispersions do not represent a coherent picture: While the colorimetric techniques of Hamilton and Pratt (1984) and Garg and Pratt (1984) predict decreasing coalescence rates with increasing drop size, the analysis of the drop-size distribution transients of Ramkrishna and coworkers (Tobin et al., 1990; Wright and Ramkrishna, 1994) indicate the reverse trend. At the current state of knowledge, it is unclear whether these differences are caused by the chemical media and the applied operating conditions of the experiments, or if they result from the specific assumptions in the models used for rate estimation.

The intention with the present measurement technique is to provide drop distribution data that can be used to estimate size-specific coalescence and breakup rates separately. Due to the instantaneous occurrence of coalescence and breakup, detection of the evolution of the size distribution alone is not sufficient. Therefore measurement of a drop concentration as a second independent variable must be implemented. Within this context drop concentration denotes the concentration of an inert, nontransferring tracer. A fluorescence tracer was used in the experimental investigations. In the following we therefore use the term drop concentration instead of fluorophore concentration within droplets. Starting with a drop population that contains a fraction of tracer-marked drops, the detection of concentration changes in the droplet swarm monitors only the coalescence events, since drop breakup does not change the actual fluorophore concentration. The mathematical tools for addressing the associated inverse problems of rate estimation based on bivariate drop distribution data were recently introduced by Ramkrishna and coworkers (Ramkrishna et al., 1995).

Previous concepts for drop-size/drop-concentration measurements

Only two experimental techniques are available for *in situ* measurements of bivariate drop-size/drop-concentration distribution in liquid–liquid dispersions. Both concepts are based on the capillary suction technique, where a representative sample of the dispersion is withdrawn through a glass capillary (Pilhofer and Miller, 1972).

The laser capillary spectrophotometry (LCS) described by Bae and Tavlarides (1989) uses a photometric principle to detect the concentration of a colored organic cobalt complex by laser light absorption. The electrical conductivity capillary (ECC) technique of Hocq et al. (1994) uses electrical conductivity to discriminate between the organic continuous-phase and the aqueous dispersed-phase slugs flowing through the sample capillary. Simultaneously an electrolyte concentration is quantified by the conductivity/concentration relationship. Both methods suffer from certain drawbacks. They are matched to the specific dispersion systems under investigation. The applicability of the conductivity method is restricted to systems, with the dispersed phase being aqueous. The photometric LCS technique requires a comparatively high solute or dye concentration to provide sufficient light absorption for the drop-concentration measurement. It is well known that the physicochemical properties of the specific system have a strong influence on drop interaction, and especially that electrolytes alter the coalescence behavior of dispersions dramatically (Prince and Blanch, 1990; Davies, 1992; Hancil et al., 1986). Furthermore, regarding a specific two-phase system, the interfacial properties exhibit a kind of asymmetry—that is, coalescence efficiency can be shown to be very different for the oil/water (o/w) type dispersion compared to the corresponding water/oil (w/o) type (Kumar, 1996; Pacek and Nienow, 1995). Therefore a concentration detec-

tion method, showing a greater flexibility and adaptability on the chemical media and the chosen dispersion type used, is desirable in order to compare the apparent coalescence behavior. It also should maintain the dispersed phase in a "native" form. This implies that the necessary additives should ideally have a negligible influence on viscosity, interfacial tension, and so forth. The newly developed fluorescence photometric technique is designed to meet this need.

Fluorescence Capillary Photometry

Measurement principle

A small volume of the droplet dispersion is continuously sampled through a glass capillary tube with an optical device attached. Aided by two light beams that cross the capillary perpendicular to the probe-axis tracer concentration in the drops, droplet volume and suction velocity are measured simultaneously. Determination of *fluorophore concentration within droplets* is based on the fluorescence intensity measurement of a fluorescent dye within the drop. A light beam of a specific wavelength excites the tracer, causing it to emit a concentration-proportional light signal. The measurement and storage of the signal height is realized by transforming the fluorescence light intensity signal to an electrical signal by means of a photomultiplier. The transmission light intensity of the excitation light beam shows a series of rectangular pulses caused by the difference of the refractive index between the continuous and the dispersed phase slugs. A drop's time of passage is determined from the width of the corresponding rectangular pulse. A transmission light beam located 2 mm from the first one produces a second pulse signal. The time shift between both signals allows us to calculate the suction velocity and in combination with the time of passage of the drop, the *droplet volume*.

Experimental setup

The experimental setup is shown in Figure 1. A representative sample of the droplet dispersion is sucked through a glass capillary tube by the pressure difference along the tube. In the funnel-shaped entrance the organic droplets are transformed into cylindrical slugs that slide through the capillary on a thin water film and pass across the two staggered light beams transmitted across the capillary. A precision-bored device is mounted on the glass tube surface to provide the exact positioning of the fiber-optic light guides, which transmit the signals nearly without loss and noise pickup. The light beams are separated by 2 mm. The fiber that picks up the fluorescence light is angled 60° from the aperture of the second fiber delivering the excitation light.

Light source 1 is a LED and produces infrared light (HFE4000-15, Honeywell), whereas light beam 2 is produced by a 150-W xenon short arc lamp. The wavelength of light beam 2 is adjustable within the broad spectrum of the arc lamp in order to ensure flexibility in choosing the fluorescence dye and to optimize the excitation wavelength, to meet the specific demands of the liquid system under investigation. A large wavelength difference between the light beams was preferred to ensure a small cross-sensitivity at the photodiodes (HFD3038-002, Honeywell and S1226-18BQ, Hamamatsu) used for detecting the transmission light intensity.

Because of the curved liquid–liquid interphases at the leading and the trailing minisci of the dispersed-phase slugs, the primary transmission light signals obtained are distorted

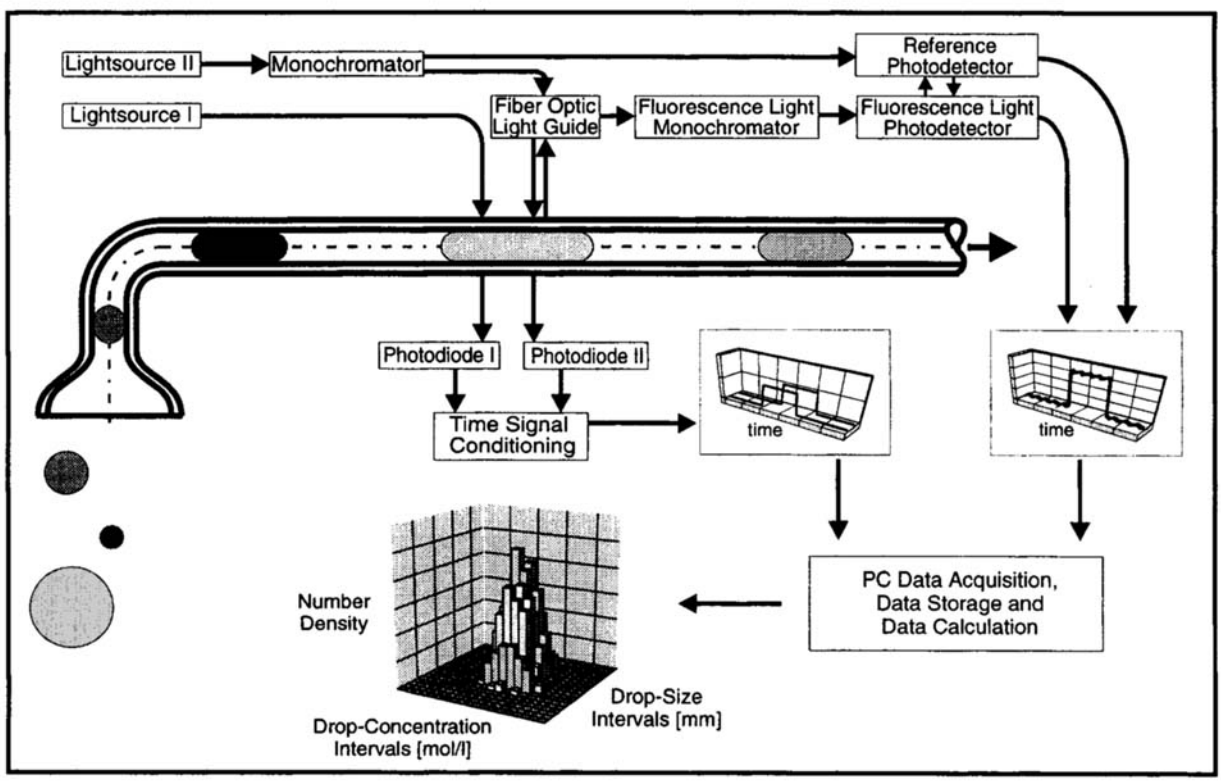

Figure 1. Fluorescence capillary photometric setup.

at the edges by higher frequencies. Therefore the primary signals are transformed into rectangular pulses by introducing a signal validation threshold in the signal conditioning step before acquiring the data with a personal computer.

The fluorescent light emitted by the tracer is sent to a monochromator (concave diffraction grating, Shimadzu; measuring wavelength range 220–650 nm; bandwidth 15 nm) to be separated from the excitation light introduced at the glass capillary by refraction. The beam with the characteristic fluorescent wavelength reaches a photomultiplier (R212, Hamamatsu) that detects the light intensity and sends an analogous electrical signal to the data-acquisition computer. The time constant of the signal amplification circuit lies in the range of 10–100 μs.

A special object-oriented software package (DROPS, written in Borland C++) was developed (Beutner, 1993) to perform the data-acquisition tasks in conjunction with a digital counter/timer board (PC-TIO-10, National Instruments) for the pulse-width measurements and the triggering of the fluorescence-intensity readout via an A/D-converter board (PC-30D, National Instruments). The software consists of an acquisition part and a postprocessing part. It combines drop-size and drop-concentration information and monitors measured and calculated values on-line on the screen.

Having acquired a statistically sufficient number, every drop undergoes an error test procedure and an error correction in case of systematic errors within the postprocessing step. These procedures are important so we can reject drops with diameters less than the capillary diameter, as well as drops following each other at a distance that is less than the separation between the two light beams, which is 2 mm in the actual design. The second feature is mainly associated with the breakup of large drops at the conical capillary entrance in the high suction-velocity range (0.7–1.0 m/s). The error tests are explained in the section on calibration. The frequency distributions of the remaining drops are displayed in a bivariate drop-size/drop-concentration histogram.

Chemicals

An appropriate choice of system for the current investigations is distilled water/kerosine (Shell Sol-T, Donauchem Vienna) because of their physical characteristics, nontoxicity, and cost. For experiments with mass transfer, acetone is used as the third component.

The fluorescent dye is 3-(2-Benzothiazolyl)-7-diethylaminocoumarin (Lambda Fluoreszenztechnologie) with maximum light emission at 468 nm for an excitation wavelength of 428 nm in kerosine. This tracer is:

- Insoluble in water
- Nonreactive
- Detectable in trace concentration
- Negligible surface-active

Calibration

Calibration experiments were performed for capillaries of diameters 1.2 mm, 1.7 mm, and 3.0 mm.

A calibration apparatus that enables drops of constant size and tracer concentration to be generated was constructed. Pressure pulses on the dispersed-phase reservoir connected to a capillary tube cause drops to break off from the tip of the glass tube at a constant frequency. The pulses are caused by the periodic movements of an electronically controlled piston. The exact drop size can be calculated from the volume of the dispersed phase that yields a certain number of drops. The dispersed-phase reservoir can be filled with solutes of different standard tracer concentrations.

Drop-size calibration

In previous publications concerning the capillary suction method it was assumed that the slug diameter was equivalent to the inner diameter of the capillary tube (Bae and Tavlarides, 1989; Hocq et al., 1994). Dispersing the organic phase and drawing off the droplets in a range of 0.2 m/s to 0.7 m/s, the water film between the organic droplet and the capillary wall, illustrated in Figure 2, can no longer be neglected. The volume of each drop is known from the drop generated. We can therefore calculate the length of the corresponding ideal cylindrical slug filling the capillary tube completely without water film. Comparing the ideal and the measured slug length allows us to estimate the apparent film thickness.

The dependence of film thickness s on the suction velocity v is shown in Figure 3 for a capillary of 1.7-mm model. The experimental points represent the whole range of drop sizes that can be measured with this tube. Obviously the influence of drop size on film thickness is negligible compared to the influence of suction velocity.

The conventional equation for the calculation of the droplet diameter, d_d, is

$$d_d = \left(\frac{3}{2} d_c^2 l_s\right)^{1/3}, \tag{1}$$

where d_c is the capillary diameter and l_s is the measured slug length. This is corrected with regard to film thickness s in Eq. 2:

$$d_d = \left[\frac{3}{2}(d_c - 2s)^2 \cdot l_s\right]^{1/3}. \tag{2}$$

Substituting film thickness s by the capillary size-specific correlation $s = f(v)$ (see Figure 3) yields $d_d = f(d_c, l_s, v)$, which becomes Eq. 1 when reducing suction velocity to $v = 0$.

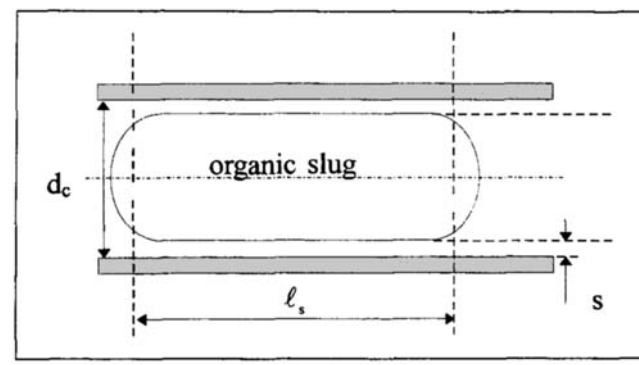

Figure 2. Geometrical dimensions used for drop-size calculation.

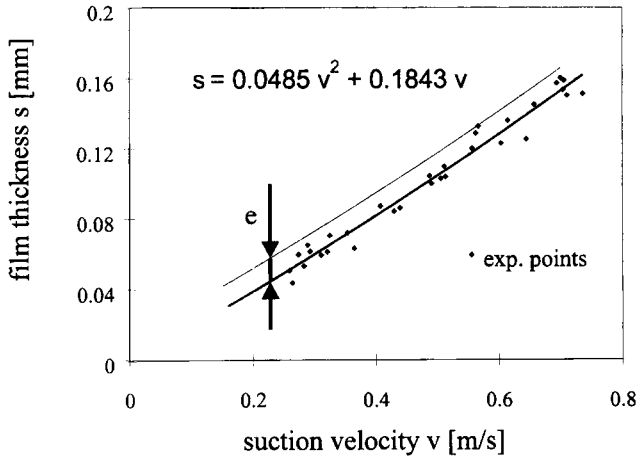

Figure 3. Thickness s of the water film in a capillary of $d_c = 1.7$ mm as a function of the suction velocity; maximum deviation e of the mean film thickness.

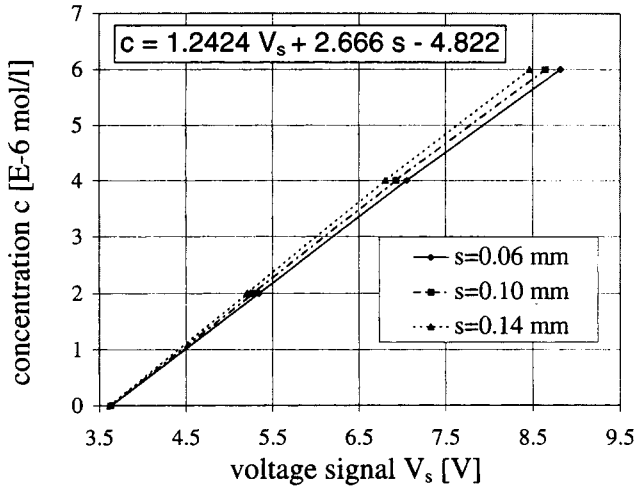

Figure 5. Calibration results concerning fluorophore concentration within drops for capillaries of $d_c = 1.7$ mm.

Without film thickness correction, errors of up to 15% for the drop-size calculation could occur. The calibration results for different-sized capillary tubes show an increase in film thickness at a constant suction velocity with increasing tube diameter.

Drop-concentration calibration

Relating the measured fluorescence voltage values to fluorophore concentration requires knowledge of the following dependencies:

1. Dependence of tracer concentration on the fluorescence voltage signal for different water-film thickness;
2. Rise time of the fluorescence signal and the resulting minimum slug length that is dependent on suction velocity.

The time response of measured fluorescence voltage signals is shown in Figure 4. The drops were drawn off by three different velocities. Each group of curves represents five drops of similar suction velocity. The tracer concentration was 4E-6 mol/L, the capillary diameter was $d_c = 1.7$ mm. A steep rise is shown from 3.5 V to about 7 V, which is followed by stabilizing values. The influence of an increase in film thickness with higher suction velocity on signal height becomes clear. A thicker water film surrounding the drop results in less tracer in the radiated sectional area for a drop of equal concentration, and thus in a lower voltage signal. Detection of this phenomenon illustrates the high precision of the measurements. Furthermore, the coincidence of curves belonging to similar drop velocities prove to be highly reproducible.

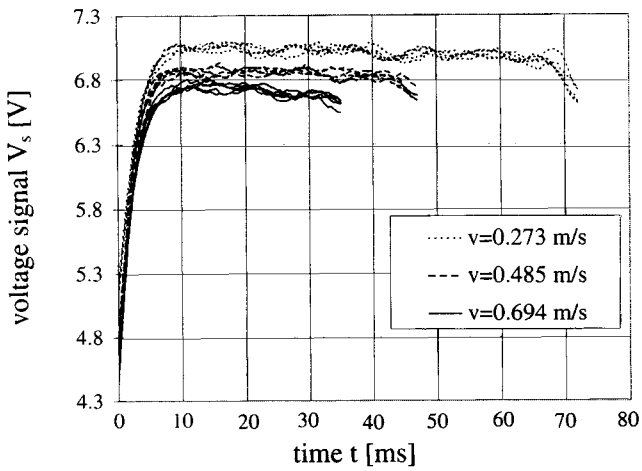

Figure 4. Drop passage signal as a function of suction velocity.

For 1: The results of the calibration experiments with different dye concentrations are shown in Figure 5 for a capillary tube of the 1.7-mm model. The diagram shows approximately linear behavior between the tracer concentration and measured fluorescence voltage signal, depending on the water-film thickness. Knowing the film thickness in Figure 3

$$s = 0.0485v^2 + 0.1843v,$$

the following correlation is used for a 1.7-mm capillary to determine tracer concentration from measured fluorescence and suction velocity values:

$$c = k(1.2424V_s + 0.1293v^2 + 0.4913v - 4.822). \qquad (3)$$

Constant k corrects changes in the excitation light intensity, which can be caused by modifying the optical device. If necessary, constant k can be determined by a measurement test procedure with drops of known concentration.

For 2: The time needed for reaching the signal plateau (see Figure 4) depends exclusively on the response characteristics of the electronic components that form part of the fluorescence detector. The components chosen reconcile rise time and random noise.

The measurement, shown in Figure 4, was performed with a sample frequency of $f = 2{,}000$ Hz, and the voltage plateau is reached after a rise time of less than 10 ms, independent of suction velocity. After cutting off the fluorescence signal rise

Table 1. Measureable Drop Diameter Range for a Suction Velocity of $V = 0.45$ m/s as a Function of the Capillary Diameter

Capillary Diameter (mm)	Measurable Drop Diameter Range (mm)
1.2	2.1–5.8
1.7	2.5–7.0
3.0	3.6–10.1

time and averaging the following twenty fluorescence values, calculation of the drop concentration is possible.

The resulting minimum slug length for getting drop concentration information depends on the suction velocity. With signal rise time $t_r = 10$ ms and suction velocity v, the minimum slug length is $l_{min} = t_r \cdot v$, or l_{min} [mm] $= 10 \cdot v$ [m/s], respectively. For a representative suction velocity of 0.45 m/s and a capillary of 1.7 mm, this corresponds to a minimum drop diameter of $d_{d,min} = 2.49$ mm (cf. Table 1).

Functional Range and Accuracy of Fluorescence Capillary Photometry

The functional range of the capillary-tube suction method depends on the physical properties of the two-phase system investigated, especially the interfacial tension and wetting characteristics. For the kerosine/water system used in the experiments, the following dependencies were found.

Drop-size range

A general limitation of the capillary-tube suction method lies in the measurable drop-size range. The distance between both light barriers and the rise time of the fluorescence signal determine the smallest drop for which size and concentration information is detectable. Droplets forming a slug longer than 100 mm can break into pieces by entering the capillary tube.

In order to ensure applicability to different process conditions, calibration has been performed for capillaries of the diameters and measurement ranges shown in Table 1.

Holdup range

Liquid–liquid dispersions are measurable at a holdup range of 25%, at which a high dispersed-phase fraction promotes high sampling rates. Measurements performed in dispersions of low holdup require longer measurement times for obtaining significant distributions, which is noncritical in the case of a steady-state operation.

Suction velocity range

The suction velocity should not be less than 0.2 m/s because of possible drop breakup in the capillary tube caused by ruptured water-film. Sampling with a velocity higher than 0.7 m/s is possible, but will increase the minimum slug length, l_{min}, and the probability of drop breakup at the conical capillary entrance.

Accuracy of the drop-size measurement

The postprocessing software allows the user to decide an error limit for the deviation of the two light barrier times measured for each droplet. Limiting the acceptable time deviation to 3%, for example, corresponds to a maximum drop diameter error of 1.0%.

Another experimental error, derived from the inequality of the slug diameter and the capillary diameter, is quantified as follows. From the calibration curve (see Figure 3), describing film thickness as a function of suction velocity, the maximum deviation, e, from the mean film thickness is estimated to 0.014 mm. This deviation leads to the maximum relative error, f_f, for calculating the drop volume for large film thickness:

$$f_f = \frac{V_1 - V_2}{V_2},$$

where V_1 denotes the drop volume, calculated with the mean film thickness, and V_2 is the drop volume, calculated with the mean film thickness plus the maximum deviation, e, of the film thickness:

$$f_f = \frac{l_s \cdot \pi/4 \cdot d_1^2}{l_s \cdot \pi/4 \cdot d_2^2} - 1 = \frac{(d_c - 2s)^2}{(d_c - 2s - 2e)^2} - 1 = 4.2\%;$$

This value corresponds to a maximum drop diameter error of 1.4%.

Accuracy of the drop-concentration measurement

The fluorescence measurement procedure is very precise. The standard deviation for measuring the points shown in Figure 4, for example, is between 0.3% ($v = 0.273$ m/s) and 0.9% ($v = 0.694$ m/s).

There is a systematic error in accurately determining film thickness. The maximum deviation from the mean value ($e = 0.014$ mm) leads to an error of 7×10^{-8} mol/L in determination of concentration, or an error of 1% relative to a maximum concentration of 7×10^{-6} mol/L.

Distribution Characteristics

Drop-size distribution can be characterized by the cumulative volume (or mass) distribution or, alternately, by the corresponding drop-number density function. The cumulative volume distribution denotes the amount of drops with a volume smaller than v, such as $F(v,t)$. It is related to the number density by

$$n(v,t) = \frac{\partial F(v,t)}{\partial v}. \tag{4}$$

In practice, we are not interested in the local size distribution. It is common to use volume-averaged instantaneous size distributions, $n_{va}(v,t)$, to represent the dispersion in a given control volume element of the flow domain, or to use cross-sectional time-averaged size distributions, $n_{ta}(v,t)$, to represent the ensemble of drops passing through a specific apparatus cross section in a given time interval. In the case of an extraction column, if an explicit function relating drop size

with the effective drop rise velocity, $u(d)$, exists, the averaged distributions can be given by

$$n_{ta}(v,t) = \frac{n_{va}(v,t)\cdot u(d)}{\int_v n_{va}(v,t)\cdot u(d)\,dv}. \tag{5}$$

If drop rise velocity is assumed to increase with drop size, bigger drops have a higher weight in $n_{ta}(v,t)$ compared with $n_{va}(v,t)$. It is important to note that an experimental method for measuring drop-size distributions necessarily introduces a specific volume and (or) time averaging, and therefore produces a drop-size distribution somewhere in between $n_{va}(v,t)$ and $n_{ta}(v,t)$.

For the capillary suction technique in particular the relation between the holdup in the sample, Φ_s, the suction velocity, and the local holdup in the column, Φ_c, was investigated by Wichterlová et al. (1985). The sample holdup is a function of the suction velocity and approaches the local column holdup if the inverse suction velocity is extrapolated to zero ($v^{-1} \to 0$):

$$\lim_{v^{-1}\to 0} \Phi_s = \Phi_c.$$

The resulting drop-size distribution in the sample is a mixture of $n_{va}(v,t)$ and $n_{ta}(v,t)$. At a high suction velocity, that means for $\Phi_s \to \Phi_c$ the final form of the distribution will approach the static distribution $n_{va}(v,t)$. At low suction velocity the sampled drop distribution will approach the dynamic distribution $n_{ta}(v,t)$.

Analysis of Drop Interaction Rates

Method

Modern hydrodynamic models concerning liquid–liquid extraction processes in columns are based on the drop population balance equation. This procedure requires knowledge of physical parameters, such as, drop-coalescence rates, drop breakup rates, and drop rising velocities, that depend on drop size and cannot, as yet, be quantified satisfactorily.

To obtain more information on drop interaction, pilot-sized column experiments can be conducted in an extraction column of the rotating-disk contactor (RDC) type. The organic inlet stream is split into two streams of equal flow rates, one supplied with the fluorescent dye. An exemplary start distribution is shown in Figure 6. The intensity of the fluorophore concentration equalization process within the droplet swarm is a function of the drop-coalescence rates. Thus, measurements of the bivariate drop-size/drop-concentration distributions along the column height at steady-state operation allows us to use a bivariate hydrodynamic model to extend the experimental data to test different rate formulations. In future investigations we intend to verify the estimated rate parameters by predicting the behavior of the dispersion using different operating conditions.

For the comparison between measured and calculated drop-size/drop concentration distributions the bivariate distribution is described by its moments. If we discretize the stationary bivariate distribution determined at column height, h, into m drop-size classes and n drop-concentration classes, the bivariate moments in discrete form are:

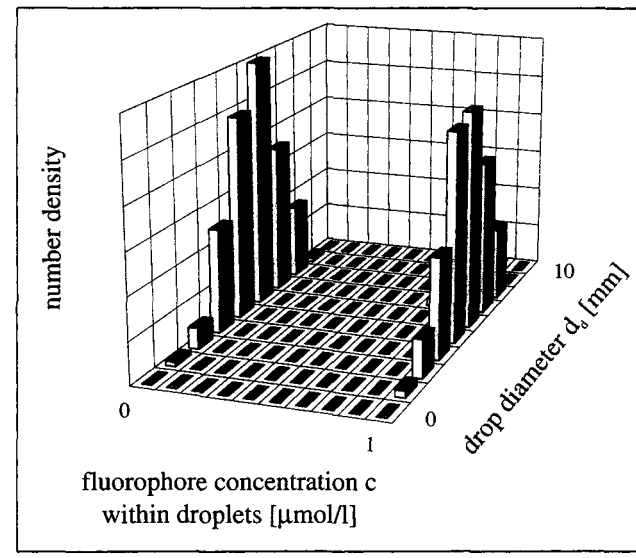

Figure 6. Exemplary bivariate start distribution at the distributor position.

$$\mu_{a,b}(h) = \sum_{j=1}^{n}\sum_{i=1}^{m} \overline{d_{d,i}^{a}}\cdot \overline{c_j^{b}}\cdot N_{i,j}(h),$$

where $\overline{d_{d,i}}$ is the mean drop size in the ith size interval, $\overline{c_j}$ is the mean drop concentration in the jth concentration interval, and $N_{i,j}(h)$ is the number of drops in the ith size interval and jth concentration interval at position h.

The total number of drops included in the distribution is given by the zeroth-order moment

$$\mu_{00}(h) = \sum_{j=1}^{n}\sum_{i=1}^{m} N_{i,j}(h).$$

The ratios of the two first-order moments $\mu_{10}(h)$ and $\mu_{01}(h)$ to the zero moment $\mu_{00}(h)$ define the arithmetic mean drop size $\overline{d_d}(h)$ and the arithmetic mean drop concentration $\bar{c}(h)$ for the bivariate distribution:

$$\overline{d_d}(h) = \frac{\mu_{10}(h)}{\mu_{00}(h)}$$

$$\bar{c}(h) = \frac{\mu_{01}(h)}{\mu_{00}(h)}.$$

The variance of the bivariate distribution relating to drop size $\sigma_d^2(h)$ and the variance relating to drop concentration $\sigma_c^2(h)$ are defined by the central second-order moments $\mu'_{20}(h)$ and $\mu'_{02}(h)$ as follows:

$$\sigma_d^2(h) = \mu'_{20}(h) = \frac{\mu_{20}(h)}{\mu_{00}(h)} - \overline{d_d}(h)^2$$

$$\sigma_c^2(h) = \mu'_{02}(h) = \frac{\mu_{02}(h)}{\mu_{00}(h)} - \bar{c}(h)^2.$$

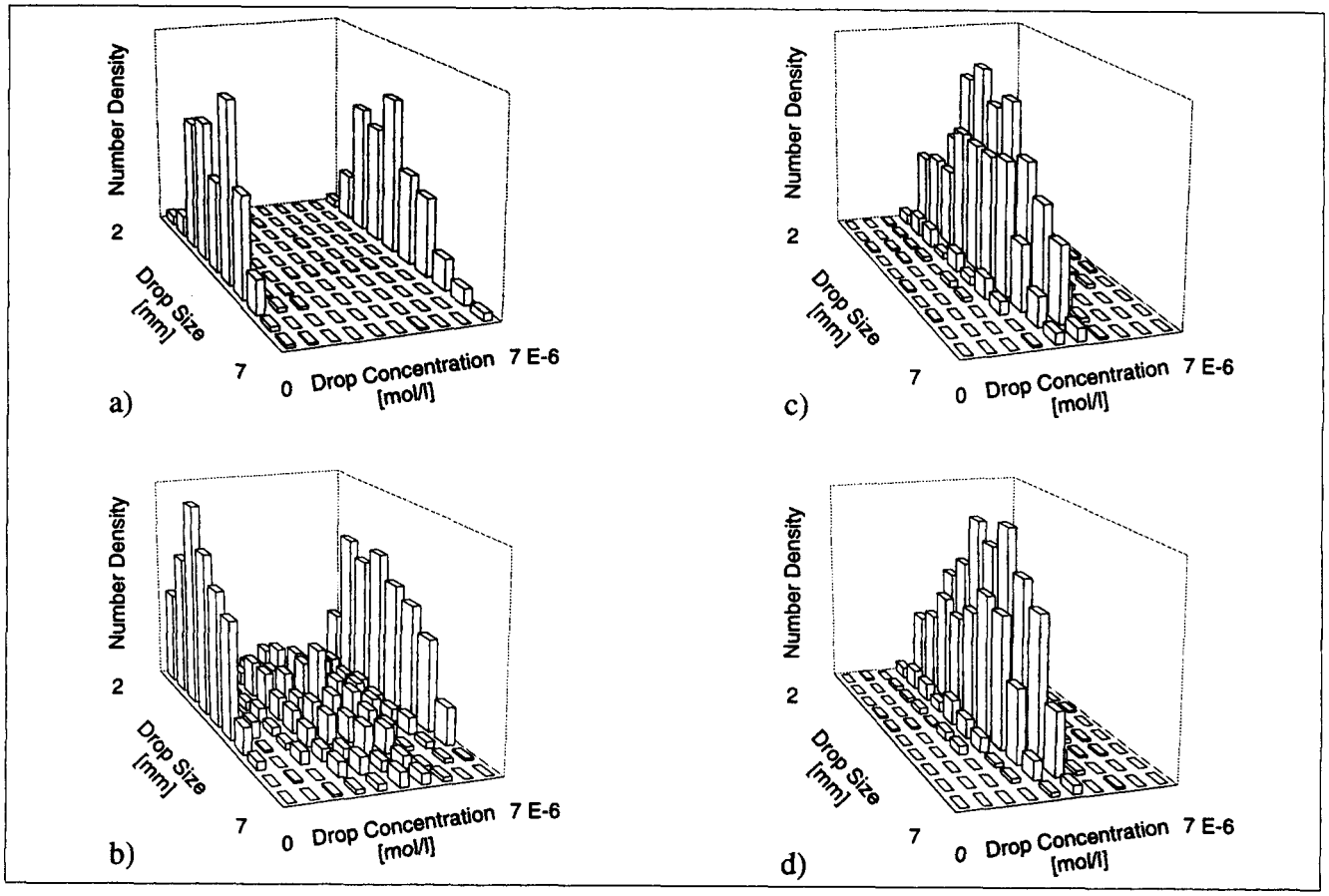

Figure 7. Bivariate drop-size/drop-concentration distributions measured in an RDC at $n = 200$ rpm for the system water (cont.)/kerosine (disp.)/acetone; $V_{water} = 42$ L/h; $V_{kerosine} = 30$ L/h; $V_{kerosine+tracer} = 30$ L/h.

(a) Inlet distribution. (b) Distribution at the column top without mass transfer. (c) Distribution at the column top with 0.5% acetone in the organic phase. (d) Comparison measuring under the same operating conditions as in Figure 7c.

The evolution of the mean drop size, $\overline{d_d}(h)$, with column height, h, gives information about the prevalence of drop coalescence or drop breakup. The decreasing function of the variance $\sigma_c^2(h)$ with column height, h, from the maximum value at $h = 0$ (position of distributor) toward zero for the case of uniform fluorophore concentrated drops indicates the intensity of the coalescence rates.

Column measurements

Investigation of the dynamics of drop interaction requires measurements of the bivariate drop-size/drop concentration distributions along the column height.

Furthermore, modeling the hydrodynamics also requires information on drop-size-specific residence times. The ability to measure two independent characteristics for each droplet that is combined with a nontransferring tracer allows us to determine these times. Applying the measured values to the model instead of theoretical formulations improves the reliability of the simulated droplet swarm behavior.

Bivariate Distributions. Measurements of bivariate drop-size/drop-concentration distributions were performed in an RDC with an inner diameter of 150 mm and an active height of $h_a = 2{,}020$ mm. The results of these measurements are shown in Figure 7.

The inlet stream (kerosine) is split into two streams with equal flow rates ($V = 30$ L/h), one supplied by the fluorescent dye ($c = 7 \times 10^{-6}$ mol/L) and one by the dye-free inlet stream. Both streams are then dispersed by nozzles. Figure 7a shows the measured inlet distribution of the two nozzles. The corresponding drop-size spectra of the drops containing dye and of the dye-free droplets can be seen to be nearly identical.

The bivariate distribution, measured at the top of the column (see Figure 7b), shows only a few drops with intermediate concentration. This indicates low coalescence rates in this process. This behavior is typical of a high-interfacial-tension, two-phase system without mass transfer.

An organic feed phase of 0.5% acetone in kerosine leads to the column-top distribution illustrated in Figure 7c. A considerable amount of interfacial mass transfer occurs under such conditions. Acetone is extracted from the kerosine phase into the water phase while the droplet swarm rises in the column. The impact of the acetone mass transfer on the drop-coalescence rates is quite obvious. High coalescence rates yield the narrow concentration distribution located in the middle of the concentration axis. Because the drop-size distribution in this process is broader than the inlet distribution, but does not show a tendency to larger droplets, the drop breakup rates must be high too.

Besides these qualitative conclusions, which can be easily drawn from the measurement results described earlier, a detailed quantitative analysis of the droplet swarm behavior is the subject of the current investigations. We therefore perform measurements of the bivariate distributions along the column height.

The similarity of distributions obtained for different suction velocities and different capillaries prove good reproducibility of the fluorescence capillary photometry (FCP) technique. As an example, Figures 7c and 7d show distributions of two different measurements performed under the same operating conditions. Each histogram represents about 1,000 drops.

Drop-size-specific Residence Times. Currently drop-size-specific residence times are determined for the case of an extraction process without mass transfer, that is, coalescence and breakup can be neglected, as proved by measurements described earlier. Feeding the column with dispersed-phase droplets of different size classes and producing a step input function of droplet concentration, the response concentration function of each droplet class, measured at the top of the column, leads to a mean residence time for droplets of this size. The quality of drop-size-specific dispersion intensity will be analyzed.

Measurements are performed for different operating conditions, varying flow rates and rotor speed.

Conclusions

Evaluation of drop interaction rates in liquid–liquid dispersions, based on experimental data, requires a measurement technique that gives more information about the droplet swarm behavior than is provided by the evolution of drop-size distributions only. Fluorescence capillary photometry (FCP) takes advantage of the detectability of a fluorescent dye even in trace concentrations of 1 μmol/L to allow the simultaneous measurement of drop size and drop concentration. The influence of the added tracer on drop interaction can therefore be neglected.

The advantage of this nontransferring-dye technique becomes evident when we consider the estimation possibilities for drop coalescence rates, drop breakup rates, and drop-size-specific residence times in two phase flows at steady-state operation, relying on measured bivariate drop distribution data. First measuring results demonstrate the potential of the method. The necessary solution procedures for the associated inverse problems of rate estimation based on bivariate distributions have recently started to become apparent (Ramkrishna et al., 1995).

The FCP technique allows reliable measurements in liquid–liquid dispersions with a dispersed phase fraction of up to 25%. Suction velocities should lie in the range of 0.2 to 0.7 m/s. Meeting the specific demands of the system under investigation, the experimental setup is flexible concerning the capillary diameter, which determines the measurable drop-size range. The possibility of adjusting the measurement device to different excitation and emission wavelengths makes choosing an appropriate fluorescent dye easier. Fiber-optic signal transmission reduces noise and signal loss to a minimum.

The high accuracy of the drop-size and drop-concentration measurement stems from the extensive calibration procedure, which is necessary for two phase flows with dispersed organic phase.

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