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Error estimation, validity and best practice guidelines for quantifying coalescence frequency during emulsification using the step-down technique

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Abstract

Coalescence during emulsification has a significant effect on the outcome of the process, especially for the high volume fractions of disperse phase common in food and pharmaceutical processing. Controlling emulsification requires that the extent of coalescence during different conditions can be quantified. The step-down technique is the most commonly used method for measuring coalescence frequency during emulsification. However, the validity of the method has been questioned. No in-depth theoretical validation or best practice guidelines have been provided for the step-down technique, or for any of the suggested alternative methods.

This contribution derives error estimates for three non-idealities present in every step-down experiment: i) limited sampling rate, ii) non-instantaneous step-down and iii) residual fragmentation after the step. It is concluded that all three factors give rise to systematic errors in estimating coalescence rate. However, by carefully choosing experimental settings, the errors can be kept small. The method, thus, remains suitable for many conditions. Best practice guidelines for applying the method are given, both generally, and more specifically for stirred tank oil-in-water emulsification.

1. Introduction

Emulsification can be understood as the outcome of simultaneously acting fragmentation of larger drops and (re)coalescence of insufficiently stabilized drops. Turbulent emulsification is a phenomenon of fundamental interest for colloidal scientists. Moreover, turbulent emulsification takes place in many applications of chemical processing engineering, e.g., when producing emulsion foods such as mayonnaise or homogenized milk, and when creating topical emulsions in pharmaceutical or cosmetics processing. The coalescence taking place during emulsification often plays a major role in determining the final emulsion drop size, and hence the final emulsion properties [1].

Emulsification in general [2], and coalescence in particular [1, 3], have attracted much research attention. This has substantially increased our general understanding of the underlying mechanism behind coalescence, and our understanding of which factors that can be adjusted to increase or decrease the extent of coalescence taking place during turbulent emulsification [1]. However, despite substantial research efforts, there is still no generally accepted method for quantitatively predicting the coalescence taking place in technically relevant emulsification processes. It could be argued that this lack of understanding is due to a lack of valid standardized methods for quantifying the extent of coalescence.

Measuring the extent of turbulent coalescence as a function of operating condition, emulsifier and phase properties offers a significant challenge. Coalescence occurs simultaneously with fragmentation and needs to be decoupled from it to allow for accurate quantification. Several methods for estimating the extent of coalescence during emulsification have been suggested, see Håkansson [4] for a recent review. The step-down technique first suggested by Howarth [5] is the most widely used method [6, 7, 8, 9, 10, 11]. The technique is easy to implement in any emulsification process, regardless of scale, and does not require special equipment or specialty chemicals with high cost or environmental impact.

The technique is based on the premise that for an emulsion that has been treated for a sufficiently long time to achieve a steady-state drop size distribution (DSD), and is then suddenly subjected to a substantially lower turbulence intensity (a turbulence intensity step-down), the drops will be too small to have a significant breakup probability at the new turbulence intensity just after the step. Thus, the initial evolution of the DSD will be determined solely by coalescence with no impact of fragmentation. During this brief period of fragmentation-free conditions, the coalescence (number) frequency at the turbulence intensity after the step, $\omega_N^{(1)}$, is directly related to the relative change in the number density of drops [5].

$$\omega_N^{(1)} = -\frac{1}{N(0)} \frac{dN}{dt}\bigg|_{t=0} \tag{1}$$

where N is the total number density of emulsion drops and $t = 0$ marks the time of the intensity step-down. Eq. (1) was later reformulated in terms of an average drop diameter, D, and the volume fraction of disperse phase, ϕ_D:

$$N = \frac{6\phi_D}{\pi D^3} \tag{2}$$

and thus Eq. (1) is equivalent to [6]

$$\omega_N^{(1)} = \frac{3}{D(0)} \frac{dD}{dt}\bigg|_{t=0} \tag{3}$$

Most investigators [5, 6, 7, 8, 9] have used the step-down technique to study coalescence in stirred tank turbulent emulsification. A schematic representation of the typical experimental procedure applied to a stirred tank system can be seen in Fig. 1. The impeller is first operated at a high speed, N_0^*, until the drop diameter reaches a steady-state (see the lower pane in Fig. 1). When the impeller speed is suddenly decreased (to N_1^*) the drop size increases due to coalescence. The drop diameter is measured and a finite difference method is used to provide an estimate of the coalescence frequency at the time of the step-down [6]
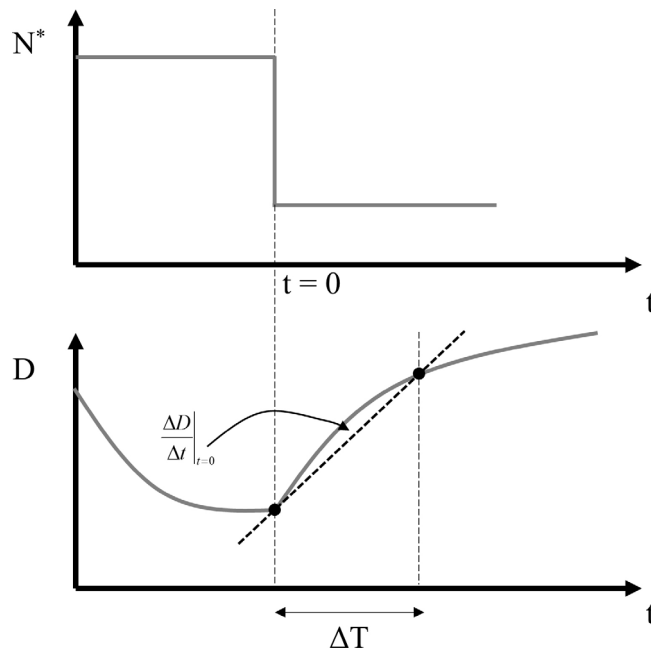

Fig. 1. Illustration of the step-down technique applied to a stirred tank. Upper pane: Impeller speed (N^*) as a function of time (t). Lower pane: Drop diameter (D) as a function of time.

$$\hat{\omega}_N^{(1)} = \frac{3}{D_{t=0}} \frac{\Delta D}{\Delta t}\bigg|_{t=0} \tag{4}$$

Although commonly used, little is known on the validity of this method. Moreover, there is a general lack of validation studies for the methods proposed for determining coalescence extent during emulsification, and it has been suggested that this is one of the reasons why the methods have not been used more extensively [4]. The first step towards evaluating or establishing any coalescence rate technique as a reliable standard method is to determine major sources of errors and find under what conditions it provides valid estimations. For the step-down technique, three sources of error are of primary interest and demand special attention:

i. The initial rate of increase of drop diameter is estimated based on a finite number of measurements of drop diameter, see Fig. 1. Sampling times are often large, of order magnitude minutes, [8, 10]. This could introduce systematic errors in the coalescence frequency estimation.

ii. The intensity step-down is not instant, a small time is generally needed to adjust the intensity (i.e. changing the impeller speed) and for the new hydrodynamic conditions to develop. During this period the coalescence frequency is somewhat larger than $\omega_N^{(1)}$, which can result in a systematic error in the estimation.

iii. The step-down must be sufficiently large in order to ensure fragmentation-free conditions after the step. Arguing from the perspective of DSD width and scaling of maximum drop size versus turbulence intensity, Tobin et al. [12] and Wright et al. [13] suggested.

$$\frac{N_0^*}{N_1^*} > \left(\frac{D_{\max}}{D_{\min}}\right)^{5/6} \tag{5}$$

where D_{max} (D_{min}) is the maximum (minimum) diameter in the DSD established before the step. This has been used as a rule-of-thumb in proceeding investigations. However, the generality of this condition and how it relates to systematic errors requires further elucidation.

The objective of this contribution is to (1) quantify the systematic error from each of the three above-mentioned non-idealities, so as to enable evaluation of the validity of the step-down technique as a function of experimental conditions, and (2) offer a list of concrete best-practice guidelines in implementing the technique, including the space of permissible operating conditions for which the method is valid for estimating coalescence frequencies. This study is part of a larger attempt to establish a set of best-practice procedures for measuring coalescence during emulsification in order to further increase our general understanding and control of emulsification processes.

2. Methodology

In order to estimate the errors associated with the abovementioned non-idealities of a step-down technique experiment, a theoretical analysis of the emulsification process is undertaken. The step-down technique coalescence frequency estimation, $\hat{\omega}_N^{(1)}$ of Eq. (4), is expressed as a function of the true coalescence frequency $\omega_N^{(1)}$ when imposing the non-idealities.

The evolution of a drop size distribution under simultaneous fragmentation and coalescence can be described by the population balance model (PBM). From the PBM, the total number of drops per unit volume at time t is [14, 15]

$$\frac{dN}{dt} = -\frac{1}{2}\int\limits_{v=0}^{\infty}\int\limits_{u=0}^{\infty}\beta(u,v)n(u,t)n(v,t)dudv + (m-1)\int\limits_{u=0}^{\infty}n(u,t)g(u)du \qquad (6)$$

where $\beta(u,v)$ is the coalescence rate, $g(v)$ is the fragmentation rate, m is the number of fragments created in each breakup event and u,v represent drop volume. Eq. (6) can be reformulated by introducing the coalescence (number) frequency and the fragmentation frequency, $\Omega_N^{(1)}$:

$$\frac{dN}{dt} = -\omega_N^{(1)}N + (m-1)\Omega_N^{(1)}N \qquad (7)$$

where the coalescence number frequency is

$$\omega_N = \frac{1}{2}\int\limits_{v=0}^{\infty}\int\limits_{u=0}^{\infty}\beta(u,v)n(u,t)n(v,t)dudv \qquad (8)$$

and the fragmentation number frequency is

$$\Omega_N = \int\limits_{u=0}^{\infty}n(u,t)g(u)du \qquad (9)$$

The combination of the general expressions in Eqs. (6)–(9) with the estimation in Eq. (4) is used here to estimate the errors for each of the three abovementioned non-idealities.

2.1. The emulsification model system

It is possible to derive general expressions for the error in estimating coalescence frequencies without making assumptions about the emulsification system or about the specific form of the PBM kernels in Eqs. (8)–(9). However, in order to translate the theoretical expressions to practical best-practice guidelines and for comparing the error estimates to the previously suggested rule-of-thumb, a specific system must be considered. In this study the turbine impeller in baffled tank system described by Coulaloglou and Tavlarides [16, 17] was chosen as a relevant example. This general emulsification setup with an oil-in-water emulsion in a stirred tank is similar to the one used in several step-down technique experiments

[5, 6, 7, 8, 9]. Moreover, a set of specific kernels are readily available [17]:

$$g(v) = 0.40v^{-2/9}D_i^{2/3}\frac{N^*}{1+\phi_D}\exp\left(\frac{-0.08\sigma(1+\phi_D)^2}{\rho_D v^{5/9}D_i^{4/3}N^{*2}}\right) \tag{10a}$$

$$\beta(v,u) = 2.8\cdot10^{-6}D_i^{2/3}\frac{N^*}{1+\phi_D}\left(v^{2/3}+u^{2/3}\right)\sqrt{v^{2/9}+u^{2/9}} \tag{10b}$$

$$\exp\left(-1.83\cdot10^9\frac{\mu_c\rho_c D_i^2}{\sigma^2}\frac{N^{*3}}{(1+\varphi_D)^3}\left(\frac{v^{1/3}u^{1/3}}{v^{1/3}+u^{1/3}}\right)^4\right)$$

$$m(v,u) \equiv 2 \tag{10c}$$

The total tank volume of the example system from Coulaloglou and Tavlarides [16, 17] is 12 L and the impeller diameter, D_i, is 10 cm. The continuous phase is distilled water (with density, $\rho_C = 998$ kg/m³, and viscosity, $\mu_C = 1.0$ mPa s) and the disperse phase is a mix $(63\% - 37\%)$ of kerosene and dicholorobenzene (with density, $\rho_D = 972$ kg/m³, and viscosity, $\mu_D = 1.3$ mPa s [16]). No emulsifier was added to their experiments, and an interfacial tension, σ, of 43 mN/m was reported [16].

2.2. Numerical settings

In order to evaluate the mean drop diameter, Eq. (7) needs to be integrated over time. For this a variable order method based on the numerical differentiation formula was used–*ode15s* in MATLAB 2015a (MathWorks, Natick, MA). In order to convert the kernels in Eq. (10) to fragmentation and coalescence frequencies, they were integrated numerically. Here a Simpson's formula based method was utilized–*quad* in MATLAB 2015a.

3. Results and discussion

Each of the three abovementioned non-idealities are investigated separately by deriving an expression for the error as a function of experimental setting and properties of the emulsification system. The error resulting from using a finite drop-size sampling rate is discussed in Section 3.1, the error due to having a non-instantaneous step-down in Section 3.2 and the error due to non-negligible fragmentation after the step-down in Section 3.3. The estimated errors are summarized in Section 3.4 and translated into explicit conditions and best practice guidelines on the setting of a step-down experiments using the model system described in Section 2.1. The influence of additional sources of errors is discussed in Section 3.5.

3.1. Error due to finite drop-size sampling rate

Theoretically, the coalescence frequency is derived from the time derivative of drop size at the time of the instant intensity step-down (Eq. (3)).

$$\hat{\omega}_N^{(1)} = \frac{3}{D_{t=0}} \frac{\Delta D}{\Delta t}\bigg|_{t=0} \tag{11}$$

However, experimentally, the drop size is sampled with a finite measurement resolution (see Eq. (4)). The first sample is collected just before the step-down (at $t = 0$). The time-point where the first measurement point after the step is obtained depends on the sampling resolution, ΔT (see Fig. 1). The finite difference in Eq. (11) must, therefore, be estimated using a differentiation scheme. If the drop size is accurately determined, the slope can be estimated from the first two measurement points ($t = 0$ and $t = \Delta T$) using a finite difference method. The central difference method is the generally recommended discretization scheme here due to its second order accuracy. However, when using the two first points, it will accurately estimate the derivate in $t = \Delta T/2$ and not at the desirable $t = 0$, i.e. it corresponds to the assumption,

$$\frac{\Delta D}{\Delta t}(t=0) \approx \frac{dD}{dt}\left(t = \frac{\Delta T}{2}\right) = \frac{D(\Delta T) - D(0)}{\Delta T} + O(\Delta T^2) \tag{12}$$

(where the last term in Eq. (12) denotes the second order accuracy of the central difference scheme.) Using Eq. (12) to estimate the initial derivate (at $t = 0$) introduces an error that increases with ΔT. If ΔT is short, the coalescence frequency is approximately constant in $0 < t < \Delta T$ and (see Eq. (7))

$$D(t) = D_0 \left(1 + \omega_N^{(1)} t\right)^{1/3} \tag{13}$$

with a constant $\omega_N^{(1)}$. Thus the actual derivate at $t = \Delta T/2$ is

$$\frac{dD}{dt}\left(t = \frac{\Delta T}{2}\right) = \frac{\omega_N^{(1)} D_0}{3}\left(1 + \omega_N^{(1)}\frac{\Delta T}{2}\right)^{-2/3} \tag{14}$$

By equating the analytic derivate (Eq. (14)) with the standard step-down technique equation for estimating coalescence frequency (Eq. (11)), we arrive at the following estimation,

$$\hat{\omega}_N^{(1)} = \frac{3}{D}\frac{\Delta D}{\Delta t} = \frac{3\left[\left(1 + \omega_N^{(1)}\Delta T\right)^{1/3} - 1\right]}{\Delta T} \tag{15}$$

which deviates systematically from the true frequency $\omega_N^{(1)}$. This is the coalescence frequency estimate that will be obtained experimentally when applying the step-down technique with a limited sampling rate. The relative sampling-rate error when compared to the true frequency is

$$\%E_{SR} = \frac{\hat{\omega}_N^{(1)} - \omega_N^{(1)}}{\omega_N^{(1)}} = 1 - \frac{3\left[\left(1 + \omega_N^{(1)}\varDelta T\right)^{1/3} - 1\right]}{\varDelta T \omega_N^{(1)}} \tag{16}$$

Since $\omega_N^{(D)}T_D$ is generally small, the expression can be simplified by applying Taylor expansions,

$$(1 + x)^{1/p} = 1 + \frac{x}{p} + O(x^2) \approx 1 + \frac{x}{p} \tag{17}$$

resulting in

$$\%E_{SR} = \frac{\hat{\omega}_N^{(1)} - \omega_N^{(1)}}{\omega_N^{(1)}} = -\frac{\omega_N^{(1)}\varDelta T}{3} + O((\omega_N^{(1)}\varDelta T)^2) \tag{18}$$

In summary, the conclusion from the derivations above, is that when using a central difference scheme for the differentiation, the step-down technique results in an estimated coalescence frequency of

$$\hat{\omega}_N^{(1)} = \frac{3}{D}\frac{\varDelta D}{\varDelta t} = \frac{3\left[\left(1 + \omega_N^{(1)}\varDelta T\right)^{1/3} - 1\right]}{\varDelta T} \tag{19}$$

which corresponds to a relative error in the coalescence rate determination equal to

$$\%E_{SR} = \frac{\hat{\omega}_N^{(1)} - \omega_N^{(1)}}{\omega_N^{(1)}} \approx -\frac{\omega_N^{(1)}\varDelta T}{3} \tag{20}$$

Fig. 2 displays the expected relative error as a function of coalescence frequency at three experimentally relevant sampling rates ($\varDelta T = 1$ s, 10 s and 60 s). As
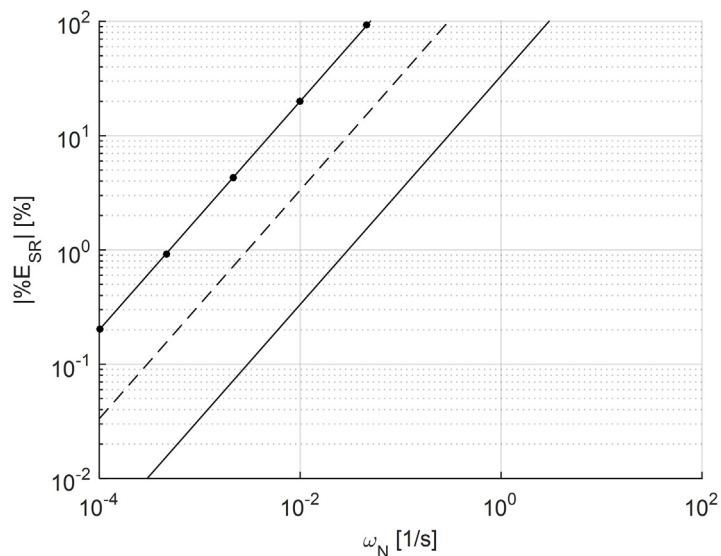

Fig. 2. Sampling rate error ($\%E_{SR}$), Eq. (20), as a function of coalescence frequency at three different sampling rates $\varDelta T = 1$ s (solid line), $\varDelta T = 10$ s (dashed line) and $\varDelta T = 60$ s (line with markers).

previously noted and seen in the figure (and Eq. (20)), the finite sampling rate leads to a systematic underestimation of the coalescence frequency, unless corrected for. Moreover, when conducting experiments over a range of different coalescence frequencies (e.g. at different turbulence intensities or emulsifier concentrations), the method will give rise to a systematic distortion of the effect on coalescence frequency unless making sure that the product between sampling time and coalescence frequency is kept constant.

Further insight in the meaning of the error estimate of Eq. (20) can be obtained by comparing it to previously reported experiments. The stirred tank example from Coulaloglou and Tavlarides [17] run with a disperse phase volume fraction of 10% would result in coalescence frequencies between 10^{-2} and 10^{-4} s^{-1} for rotor speeds between 200 and 2000 rpm when the drop diameter has reached its steady-state vale (calculate using Eqs. (6)–(10)). If analyzing the coalescence rate in this system using a step-down experiment, the systematic error due to finite sampling time would be up to 20% if using a sampling time of one minute. The largest systematic error would be obtained for the highest speeds, for the lowest speed the error would decrease down to 0.2%.

As a second example of the size of this effect, Niknafs et al. [8] applied the step-down technique to a stirred tank system and reports coalescence rates of approximately 0.05 s^{-1} using a sampling time of 30 s. This results in an error equal to 5% due to non-instantaneous sampling according to Eq. (20).

3.2. Error due to not-instantaneous step-down

Ideally, the intensity step-down is instantaneous from N_0^* to N_1^* (as it is illustrated in Fig. 1). However, in practice the intensity is often adjusted manually. Furthermore, even under automatic control, time is needed for the motor speed to change and for the hydrodynamics close to the drops to adjust to the new impeller behavior. Thus, there will always be a dynamic time period, T_D, under which the intensity, as experienced by the emulsion drops, decreases from N_0^* to N_1^*, see Fig. 3. During this period, the turbulence intensity is higher than at the final level and, consequently, the coalescence frequency is higher. Therefore, there is a risk of overestimating the coalescence frequency at N_1^* when using the step-down technique with a non-instantaneous step-down.

In order to estimate the size of the error introduced due to this dynamic effect, first assume that the coalescence frequency during the short time required to perform the intensity step-down can be described by the constant, $\omega_N^{(D)}$. Then the time evolution of drop diameter before the hydrodynamic conditions is
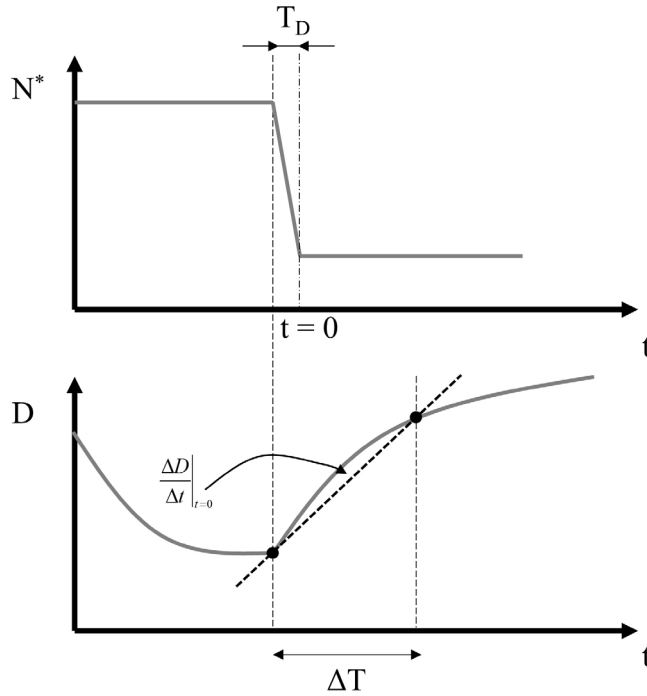
Fig. 3. Illustration of the dynamic time period, T_D, required to change the hydrodynamic conditions as experienced by the emulsion drops from ones corresponding to $N_0{}^*$ to $N_1{}^*$.

$$D(t) = D_0(1 + \omega_N^{(D)}t)^{1/3} \quad 0 < t < T_D \tag{21}$$

where D_0 is the drop diameter prior to the step-down. Moreover, if the sampling-time, ΔT, is sufficiently small to allow accurate estimation of the initial rate of drop diameter increase (i.e. a ΔT with a small error as given by Eq. (4)), then the coalescence frequency is nearly constant during the short period after the new conditions have developed and before the first sampling point, ΔT, and we have:

$$\begin{aligned}D(t) &= D(T_D)(1 + \omega_N^{(1)}[t - T_D])^{1/3} \\ &= D_0(1 + \omega_N^{(D)}T_D)^{1/3}(1 + \omega_N^{(1)}[t - T_D])^{1/3} \quad T_D < t < \Delta T\end{aligned} \tag{22}$$

Provided that T_D is shorter than half the drop diameter sampling time (which is a reasonable assumption when comparing the conditions of reported experimental studies using the technique), the derivative at the point $t = \Delta T/2$ is:

$$\frac{dD}{dt}\left(t = \frac{\Delta T}{2}\right) = \frac{D_0\omega_N^{(1)}}{3}\left(1 + \omega_N^{(D)}T_D\right)^{1/3}\left(1 + \omega_N^{(1)}\left[\frac{\Delta T}{2} - T_D\right]\right)^{-2/3} \tag{23}$$

Thus the relationship between the estimated coalescence frequency, $\hat{\omega}_N^{(1)}$ and actual coalescence frequency, $\omega_N^{(1)}$, can be estimated by using Eq. (23) as the finite difference in the step-down technique equation, Eq. (4). This results in

$$\hat{\omega}_N^{(1)} = \frac{3}{D_0}\frac{\Delta D}{\Delta t} = \omega_N^{(1)}\left(1 + \omega_N^{(D)}T_D\right)^{1/3}\left(1 + \omega_N^{(1)}\left[\frac{\Delta T}{2} - T_D\right]\right)^{-2/3} \tag{24}$$

Hence, this is the coalescence frequency estimate obtained from a step-down experiment if the step-down is not instantaneous. Since both $\omega_N^{(D)}T_D$ and $\omega_N^{(1)}$ ($\Delta T/2 - T_D$) are generally small, the expression can be estimated by applying Taylor expansions (Eq. (17)). Eq. (24), thus, simplifies to

$$\hat{\omega}_N^{(1)} = \frac{3}{D_0}\frac{\Delta D}{\Delta t} = \omega_N^{(1)}\left(1 + \frac{\omega_N^{(D)}T_D}{3}\right)\cdot\left(1 - \frac{2\omega_N^{(1)}}{3}\left[\frac{\Delta T}{2} - T_D\right]\right) + R \tag{25}$$

Under the assumptions of small ΔT and T_D, the remainder term R is small (numerical investigations reveal $R < 1\%$ of $\hat{\omega}_N^{(1)}$ if ΔT is chosen according to Eq. (32)). Thus, by assuming $R \approx 0$, the relative error in the coalescence frequency due to a non-instantaneous step-change is approximately:

$$\%E_D = \frac{\hat{\omega}_N^{(1)} - \omega_N^{(1)}}{\omega_N^{(1)}} \approx \frac{-\omega_N^{(1)}\Delta T}{3}\left[1 - \frac{T_D}{\Delta T}\left(2 + \frac{\omega_N^{(D)}}{\omega_N^{(1)}}\right)\right] \tag{26}$$

Since the turbulence intensity during T_D varies from N_0^* to N_1^* we have $\omega_N^{(0)} < \omega_N^{(D)} < \omega_N^{(1)}$. Assuming that the coalescence frequency is equal to the average of the two end-points, $\omega_N^{(D)} = (\omega_N^{(0)} + \omega_N^{(1)})/2$, results in a relative error of

$$\%E_D \approx \frac{-\omega_N^{(1)}\Delta T}{3}\left[1 - \frac{T_D}{2\Delta T}\left(5 + \frac{\omega_N^{(0)}}{\omega_N^{(1)}}\right)\right] \tag{27}$$

which can be calculated given experimental settings (T_D, ΔT, N_0^*, N_1^*) and the coalescence frequency before and after the step. The error increases with the time required to carry out the step-down, T_D. Also, note that the error increases with the size of the intensity step-down. This illustrates that the lower limit of permissible intensity step-downs proposed in previous studies [9, 10] must be supplemented with an upper limit for step-down technique experiments.

In order to illustrate the magnitude of this term, we need to apply a specific experimental condition, e.g. the experiment reported by Niknafs et al. [8]. Assuming that the adjustment time is approximately one second, and that coalescence rate scales lineally with rotor speed (cf. Eq. (10)) the error according to Eq. (27) would then become approximately 4%. A more detailed discussion on the implications of Eq. (27) will follow in Section 3.4.

3.3. Error due to fragmentation after the step-down

The step-down technique is based on the assumption that fragmentation-free conditions are obtained for a short time-period following an intensity step-down. However, if the intensity step-down is small, the largest drops will have a non-negligible probability of breaking even after the step, which will distort the

coalescence frequency estimation. If a non-zero fragmentation frequency, $\Omega_N^{(1)}$, is present after the step, the average drop diameter evolves according to Eq. (7). Thus, in the presence of fragmentation the step-down technique estimation (Eq. (4)) will result in

$$\hat{\omega}_N^{(1)} = \frac{3}{D}\frac{\Delta D}{\Delta T} = \omega_N^{(1)} - (m-1)\cdot\Omega_N^{(1)} \tag{28}$$

which is a systematic underprediction of the coalescence frequency with a relative error equal to

$$\%E_F = \frac{\hat{\omega}_N^{(1)} - \omega_N^{(1)}}{\omega_N^{(1)}} = \frac{-(m-1)\Omega_N^{(1)}}{\omega_N^{(1)}} \tag{29}$$

In order to compare the error estimation from Eq. (29) to the previously used rule-of-thumb [12, 13], it first must be combined with suitable expressions for fragmentation and coalescence rates, see Section 2.1. Secondly, in order to evaluate Eq. (29) it should be noted that both $\Omega_N^{(1)}$ and $\omega_N^{(1)}$ depend on drop-size (see Eqs. (8), (9)). Just after the step-down, the drop size distribution is still approximately equal to the steady-state DSD at the intensity before the step. The steady-state drop-size as a function of this initial stirrer speed can be calculated by solving Eq. (6) with the kernels in Eq. (10). The result for a system with a volume fraction of disperse phase at 10% (v/v) can be seen in Fig. 4. (The steady-state drop size is here defined as the area weighted mean diameter, D_{32}, that does not decrease more than 1% by stirring for an additional 10 min).
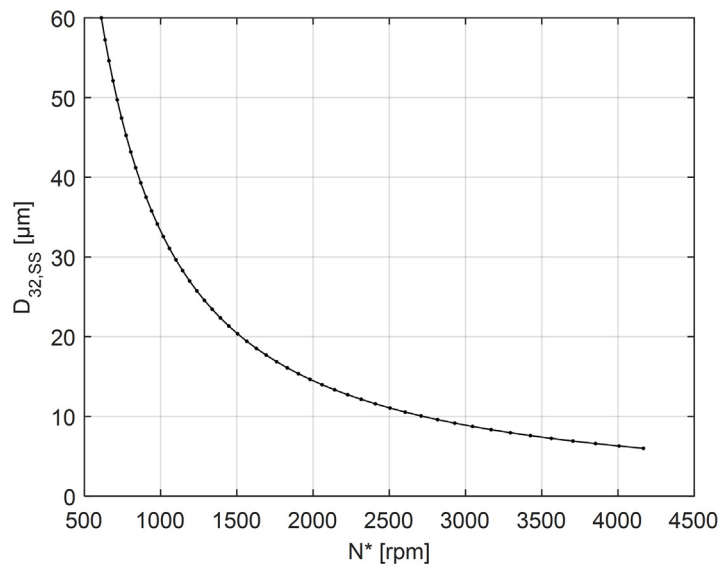

Fig. 4. Steady-state drop diameter, D_{32}, (calculated by solving Eqs. (6) and (10)) as a function of impeller speed (N^*) for the system described in Section 2.1.

Fig. 5 displays the error due to fragmentation being present after the step-down as a function of intensity step-down size for the example case, assuming that the DSD before the step-down is monodisperse, $n(D,t) = \delta(D-D_{32})$. Results are shown for five different initial impeller speeds between 1 300 and 7 400 rpm (markers). As seen in Fig. 5 the markers almost overlap (far left of Fig. 5), showing that the error is independent of the initial impeller speed when keeping the ratio between initial and final impeller speed constant. Moreover, if the step-down is made sufficiently large, it is possible to ensure that the error is small; keeping the step-ratio (N_0^*/N_1^*) above 1.2 ensures that the error is below 1%.

If the drop-size distribution is broad, the risk of residual fragmentation after the step is higher and a steeper step-down is needed to ensure that the largest drops present prior to the step do not fragment after the step. In order to quantify the effect, the calculation were repeated assuming that the size distribution before the step is a lognormal distribution with D_{32} as given by Fig. 4 but with different distribution widths. Tobin et al. [12] and Wright et al. [13] discuss distribution widths in terms of maximum to minimum drop diameter (D_{max}/D_{min}). Here the experimental equivalent, the ratio between the limiting diameter of the largest and smallest 5% of the drops, $D_{v,95}/D_{v,05}$, is used instead in order to comply with experimental standards. The estimated error at different distribution widths can be seen in Fig. 5. For narrow size distributions ($D_{v,95}/D_{v,05} \leq 1.1$), the error is indistinguishable from the monodisperse case. For wider distributions the error is
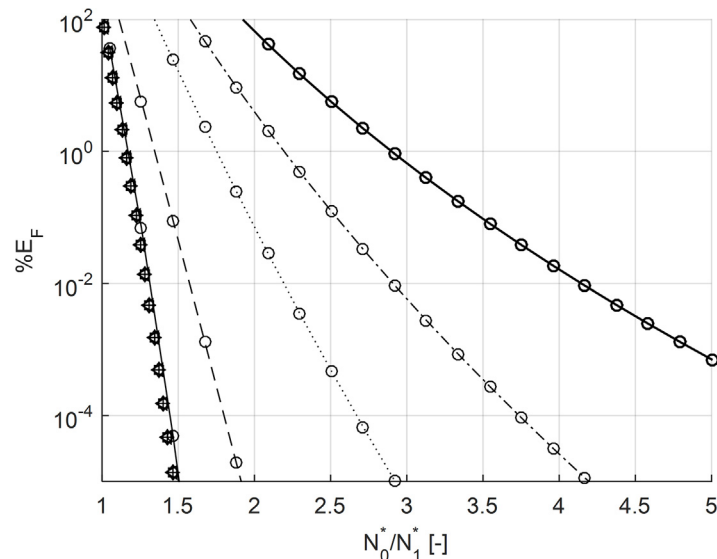

Fig. 5. Error due to fragmentation present after the step-down, $\%E_F$, as a function of step-ratio (N_0^*/N_1^*). Assuming a monodisperse DSD before the step with $N_0^* = 1\ 300$ rpm (+), $N_0^* = 2\ 200$ rpm ($\square$), $N_0^* = 4\ 100$ rpm ($\lozenge$), $N_0^* = 7\ 400$ rpm (o); and with a before-step DSD with $D_{v,95}/D_{v,05} = 1.1$ (−), $D_{v,95}/D_{v,05} = 1.6$ (–), $D_{v,95}/D_{v,05} = 2.4$ (:), $D_{v,95}/D_{v,05} = 3.5$ (-.) and $D_{v,95}/D_{v,05} = 5.5$ (bold line).

substantially larger. This illustrates that a steeper step-down is needed under conditions that produce broader DSDs.

In order to compare the error estimates in Fig. 5 to the rule-of-thumb used in previous studies it is of special interest to know how large the step must be in order to ensure that the error is sufficiently small. Fig. 6 displays this limiting step required to have an error below 0.1% (o), 1% (◇) and 10% (□) as a function of distribution width. The previously suggested rule-of-thumb [12, 13],

$$\frac{N_0^*}{N_1^*} > \left(\frac{D_{v,95}}{D_{v,05}}\right)^{5/6} \tag{30}$$

has been included as a comparison in Fig. 6 (dashed line). The comparison shows that an intensity step-down in accordance with Eq. (30) will ensure that the fragmentation-error is less than 0.1% for distribution width larger than 1.4. However, in the case of a very narrow DSD ($D_{v,95}/D_{v,05} < 1.4$) the rule-of-thumb is insufficient. As seen in Fig. 5, even a monodisperse initial DSD will give rise to an error at small intensity step-downs. This is expected since the breakup probability of the before-step drop size becomes non-negligible at the after-step conditions even for monodisperse distributions. The rule of thumb should therefore be supplemented to ensure that the step-ratio is always above 1.5, regardless of distribution width. The resulting recommendations for ensuring a negligible error due to fragmentation after the step then becomes
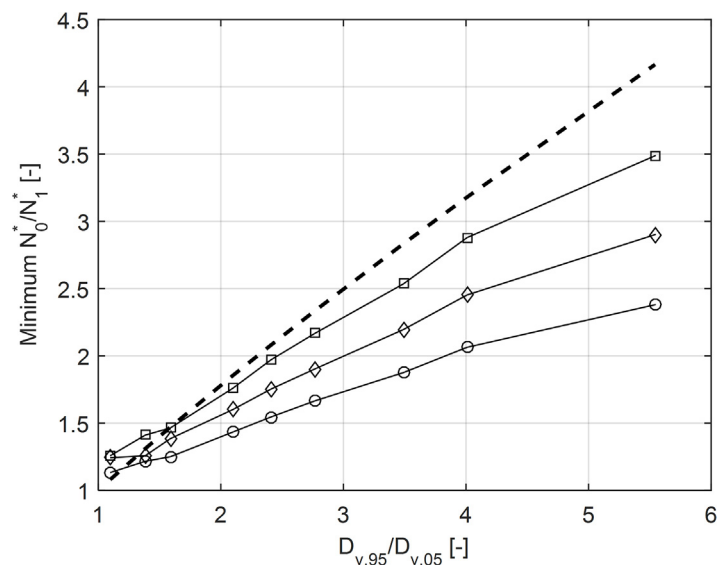

Fig. 6. Minimum step-ratios (N_0^*/N_1^*) as a function of distribution width for ensuring that $\%E_F$ is below 10%, 1% and 0.1%. The previously suggested rule-of-thumb, Eq. (30), is illustrated by the dashed line.

$$\frac{N_0^*}{N_1^*} > \max\left[\left(\frac{D_{\max,0}}{D_{\min,0}}\right)^{5/6}, 1.5\right] \qquad (31)$$

3.4. Best practice experimental settings

In summary, step-down technique experiments for measuring coalescence frequency should meet three conditions to give valid estimations:

i. The evolving drop-size must be sampled with a temporal resolution, ΔT, that is sufficiently high:

$$\Delta T < 3 \cdot \frac{\%E_{SR}}{\omega_N^{(1)}} \qquad (32)$$

Where $\%E_{SR}$ is some small allowable error.

ii. The intensity step must be realized sufficiently fast. New conditions must have been established in a time, T_D,

$$T_D < \frac{3\%E_D + \%E_{SR}}{2\omega_N^{(1)}}\left(5 + \frac{\omega_N^{(0)}}{\omega_N^{(1)}}\right)^{-1} \qquad (33)$$

where $\%E_{SR}$ and $\%E_D$ are small allowable errors.

iii. In order to ensure that the fragmentation at the conditions after the step does not significantly influence the results, the intensity step-down size must fulfill

$$\frac{N_0^*}{N_1^*} > \max\left[\left(\frac{D_{\max,0}}{D_{\min,0}}\right)^{5/6}, 1.5\right] \qquad (34)$$

Both Eqs. (32) and (33) are formulated in terms of the true coalescence frequency. This makes them difficult to use in designing experiments when the coalescence frequency is unknown. In some cases the coalescence frequency can be estimated based on previous experiments or models. However, in order to provide more easily interpreted best practice guidelines, we will investigate an example with settings and kernels as described in Section 2.1. We will then continue to investigate how changing the experimental conditions would influence the validity of the coalescence rate determination.

Fig. 7 displays the permissible combinations of initial speeds (N_0^*) and step-sizes (N_0^*/N_1^*) in order to ensure that all three conditions (Eqs. (32)–(34)) are met with errors smaller than 1% ($\%E_{SR} < 1\%$ and $\%E_D < 1\%$) for the example setup with a disperse phase volume fraction of 40% (dark grey area in Fig. 7). The sampling time (ΔT) is assumed to be 10 s and the time needed to adjust the hydrodynamic conditions, T_D, is assumed to be 0.5 s. The DSD width in terms of $D_{v,50}/D_{v,05}$ is 4 (see discussion in ref. [4], p. 54).
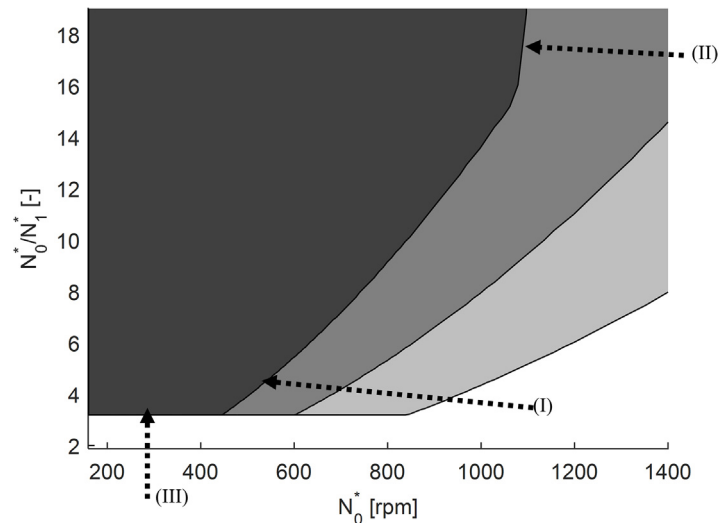
Fig. 7. Range of admissible parameters (N_0^* and N_0^*/N_1^*) in order to ensure small systematic errors. Based on the example settings in Section 2.2, with $\phi_D = 40\%$ (dark grey), 20% (grey) and 10% (light grey). $\%E_{SR} = \%E_D = 1\%$. $D_i = 10$ cm. $\Delta T = 10$ s. $T_D = 0.5$ s.

The space of permissible experimental setting has three boundaries (I, II and III), each representing one of the abovementioned conditions. The limited sampling-time (Eq. (32)) results in an upper boundary on the impeller speed after the step, boundary (I). The time required to adjust the impeller speed (Eq. (33)) results in an upper boundary on the intensity step-down, boundary (II), whereas the requirement on obtaining fragmentation free conditions after the step (Eq. (34)) results in a lower limit on the step, boundary (III). When disregarding the details in Fig. 7, the main limitations are in terms of a maximum allowable before-step impeller speed determined by (I), and a minimum step-size determined by (III). The adjustment time, T_D, does not significantly limit the space of permissible operating parameters at these settings.

In planning a step-down technique experiment for measuring coalescence rate during emulsification, an interesting question is how the setup should be chosen so as to maximize the validity of the method. This question can be answered by studying how the permissible range of operating parameters are influenced by the experimental settings. For example, increasing the sampling rate of the drop size-distribution, e.g. by switching to an inline method for measuring drop-size, will shift boundary (I) to the right. Increasing the adjustment speed from N_0^* to N_1^*, e.g. by using a motor with fast and automatic control, will shift (II) further to the right, and working with a narrower DSD will shift (III) downwards in Fig. 7.

Fig. 7 also displays the permissible parameter range for a disperse phase volume fraction of 20% (grey) and 10% (light grey). Decreasing the volume fraction of disperse phase decreases the coalescence frequency and thus extends the

permissible range, this would be one possibility for an experiments aiming at investigating the effect of higher stirrer speeds, $N_0{}^*$. However, it should be noted that decreasing the volume fraction of disperse phase also decreases the coalescence frequency which might have an adverse effect on reliability by reducing the signal-to-noise ratio.

Fig. 7 is based on the particular setup in Coulaloglou and Tavlarides' experiments. Most studies using the step-down technique have been based on similar, but not identical, stirred-tank systems [5, 6, 7, 8, 9]; they differ in type and size of tank and impeller, in liquid phases and studied emulsifier systems. By varying the different parameters, more insight into an optimal choice of experimental setup can be obtained. The parameter space is relatively insensitive to interfacial tension, density and viscosity − varying the interfacial tension between 20 and 50 mN/m, the densities between 700 and 1000 kg/m^3 and the disperse phase viscosity between 1 and 60 mPa s, influence the limiting parameters by less than 5%. The impeller diameter, on the other hand, has a large influence since the dissipation rate of turbulent kinetic energy increases fast with impeller diameter resulting in substantially higher coalescence rates. Parameter space-figures for impeller diameters equal to 20 cm and 5 cm are provided in Fig. 8 (A and B respectively). As expected, the permissible impeller speed increases with decreasing rotor diameters.

In summary, the investigations in Figs. 7 and 8 show that although the step-down technique can potentially give rise to systematic errors in estimating coalescence frequencies, these problems can be avoided by carefully choosing suitable experimental parameters. For stirred tank oil-in-water emulsification systems, Figs. 7 and 8 give guidelines showing which impeller speeds and step-sizes that are permissible for a relevant range of impeller diameters and disperse phase volume fractions. When applied to other emulsification processes, e.g. high-pressure homogenization [10, 11], the corresponding analysis can be carried out using a
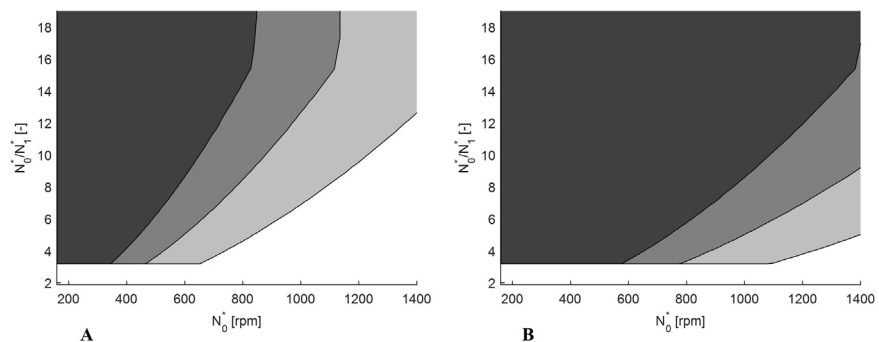

Fig. 8. Range of permissible parameters for two impeller diameters (A) $D_i = 0.20$ m and (B) $D_i = 0.05$ m. Volume fraction of oil equal to 40% (dark grey), 20% (grey) and 10% (light grey). $\%E_{SR} = \%E_D = 1\%$. $\Delta T = 10$ s. $T_D = 0.5$ s.

relevant set of kernels and the more general expressions in Eqs. (32)–(34). (In order to aid in applying the abovementioned guidelines, and for investigating their effect during the design and setup of a step-down technique experiment, the commented source code for the function creating parameter plots such as Figs. 7 and 8 has been provided in the supplementary material as a MATLAB function.)

3.5. Remaining sources of error

As seen in Figs. 7 and 8, the three non-idealities in Section 3.1–3 impose relevant limitations on the available range of parameters where the step-down technique results in valid estimations of coalescence frequency. Furthermore, the technique relies on using an accurate method for determination of drop diameter. In particular the reliability of the method must be sufficiently high.

This study offers only a first step towards a best-practice procedures for measuring coalescence during emulsification. In addition to these theoretical investigations, experimental validation and between-method comparison is of great relevance for continued studies.

Two general disadvantage with methods for quantifying the extent of coalescence during emulsification should also be noted [4]. First, the turbulence intensity varies over the tank volume; the coalescence rate obtained by the techniques will therefore always be a volume average. Without knowing how the coalescence frequency depends on turbulence intensity, and without knowing the distribution of turbulence intensity across the volume, the method does not provide local estimation of coalescence frequencies. Secondly, the obtained coalescence frequency, $\omega_N^{(1)}$, describes the frequency of coalescence when subjecting small drops to a rather mild turbulence − the drop-sizes under investigations have been created at N_0^* and their coalescence frequency is measured at the higher speed N_1^*. In describing coalescence taking place during emulsification, we are mainly interested in the opposite situation– the coalescence of drops larger than the steady-state drop-size. As previously noted [4], coalescence frequency cannot be translated to the general drop-size independent coalescence rate without imposing severe restrictions. Although a general drawback of the entire class of coalescence frequency-based methodologies, and not specific for this particular technique, it should be kept in mind when planning and evaluating results from step-down technique experiments.

4. Conclusions

The investigations show that systematic errors will arise when using the step-down technique to estimate coalescence frequency during emulsification when a limited drop diameter sampling frequency is used, when the emulsification intensity step-down is not instantaneous and when the step-down size is insufficiently large to

suppress all fragmentation after the step. Quantitative estimations of the size of each of these three error have been presented. Moreover, these errors can be kept small by carefully designing the experimental conditions of the experiment. And, consequently, the step-down technique remains a relevant method for estimating coalescence frequency during emulsification.

General best-practice recommendations to ensure that these errors are small are presented (Eqs. (32)–(34)). For the most commonly used case, when the step-down technique is used to estimate coalescence frequency for oil-in-water emulsions in stirred tank, best practice recommendations have been formulated in terms of explicit limitations on the impeller speed before the step and on the ratio between before-step and after-step impeller speed, for a range of commonly used volume fractions of dispersed phase and impeller diameters, as seen in Figs. 7 and 8 .

Declarations

Author contribution statement

Andreas Håkansson: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Additional information

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