Coalescence Frequencies in Waldhof-Agitated Systems

INTRODUCTION

The existing methods for the measurement of coalescence frequency in agitated liquid-liquid dispersions can be broadly classified into two categories. The first of these involves direct observation of the rate of spread of a tracer due to mixing in the dispersed phase.\textsuperscript{1-3} For this purpose some drops having a continuous-phase-insoluble dye are introduced into an existing dispersion. Alternatively, the existing dispersion may have a chemical which on reacting with another chemical present in the freshly introduced drops may form a dye. The reaction must, however, be limited to the dispersed phase only. In both these cases, it is essential to add a dye or chemicals to the dispersed phase, and the contamination may result in substantial change in dispersion characteristics. In the second method, the speed of agitation is suddenly reduced to a lower value and the transient response of an optical probe measuring the Sauter-mean diameter is noted. From the initial slope of the curve, coalescence frequency is calculated.\textsuperscript{4,5} The underlying assumptions are that a step reduction in agitator speed results in a step change in the degree of turbulence and the new steady-state dropsize distribution is achieved by a coalescence-only process. In practice, however, it is very difficult to meet the first assumption since some time invariably lapses before turbulence decays to the new value, and the second assumption will be valid only for a very specific kind of dispersion.

In a previous paper, Bajpai et al.\textsuperscript{6} have proposed a coalescence-redispersion model for drop-size distribution in an agitated vessel. Based upon this model, a method for the measurement of interaction frequency can be proposed (see Appendix). This method is distinguished by the fact that it is derived from a model which satisfactorily predicts experimentally observed drop-size distributions (DSD) in diverse systems. Either a batch or a steady-state continuous system can be employed. In the case of a batch vessel, the method requires the measurement of unsteady-state drop-size distributions at various times from the start of agitation. According to the model predictions, a semilog plot of $(\mu_2 - 2\mu_1^2)$ versus time should yield a straight line. From the slope of this straight line, coalescence frequency can be calculated. The method does not require the addition of any chemical to the system and thus avoids deliberate contamination.

EXPERIMENTAL

Transient state DSD's in a $n$-alkane-water system in a vessel fitted with a Waldhof agitator were measured using a detergent stabilization method. This method has been described in detail elsewhere.\textsuperscript{7} Details of the vessel and the agitator are given by Prokop et al.\textsuperscript{8} Sampling was carried out from the region of intense mixing, i.e., near the tip of the turbines. Samples were drawn at different times from the start of the agitation. Care was taken to avoid changing the system volume appreciably due to repeated samplings. In case a large
TABLE I
Evolution of the First Moment with Time

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>15% n-paraffins (800 rpm)</th>
<th>15% n-paraffins (1200 rpm)</th>
<th>5% n-paraffins (1200 rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>13206</td>
<td>9102</td>
<td>8205</td>
</tr>
<tr>
<td>6</td>
<td>8458</td>
<td>6108</td>
<td>5312</td>
</tr>
<tr>
<td>9</td>
<td>5436</td>
<td>2791</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>4324</td>
<td>-</td>
<td>2469</td>
</tr>
<tr>
<td>15</td>
<td>2603</td>
<td>1150</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>1986</td>
<td>-</td>
<td>2627</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>1474</td>
<td>2069</td>
</tr>
<tr>
<td>24</td>
<td>1671</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>2253</td>
<td>2005</td>
<td>2080</td>
</tr>
<tr>
<td>30</td>
<td>2374</td>
<td>-</td>
<td>1354</td>
</tr>
<tr>
<td>33</td>
<td>1648</td>
<td>1670</td>
<td>-</td>
</tr>
</tbody>
</table>

number of samples were desired, the experiment was repeated under exactly similar conditions. Since it requires calculation of second moments of drop-size distributions, the experiments were conducted under carefully controlled conditions and high precision. Despite all the precautions, some samples still had to be discarded because coalescence took place before the dispersion could be adequately mixed with the detergent. Experiments were performed for various conditions of speeds of rotation and dispersed phase fractions.

RESULTS

In Table I the first moments of DSD's for some experimental conditions are listed. After an initial breakdown of drops for about 9 to 12 min, the first moment becomes almost steady (as predicted by eq. (4) with a fluctuation of ±30% from the mean. It is within the limits of reproducibility of our experiment and it is obvious if we recall that the Sauter mean diameter in our replicated experiments fluctuates within ±10%.7

Moments of the unsteady-state drop-size distributions were calculated and \((\mu_2 - 2\mu_1^2)\) were plotted versus time on semilog plots. Figure 1 shows the plots for a few experimental conditions. From the slopes of these straight lines, values of coalescence frequencies (defined as the number of dispersed phase volumes that undergo mixing in unit time) have been calculated using eq. (8). The results have been plotted in Figures 2 and 3. Figure 2 shows that a linear relation exists between \(\omega\) and the speed of rotation at constant \(\phi\). Similarly, Figure 3 indicates a linear dependence of \(\omega\) on \(\phi\).

DISCUSSION

In the present work, coalescence frequency has been measured in n-alkane-water systems agitated by a Waldhof agitator. However, most of the previous work in the measurement of coalescence frequencies in dispersed systems has
been done on those agitated by flat-blade turbines (FBT). It has been summarized in a review article by Shah et al.9 These two systems are widely different. The dispersions mixed by Waldhof agitators are characterized by marked zones of high turbulence and circulation and are referred to as circulation-stirring (CS) systems. The qualitative observation for FBT systems that \( \omega \) increases with mixing velocity and with dispersed phase ratio holds true in CS systems also. Based on the reported data, it can be concluded that for FBT systems, coalescence frequency is proportional to the powers of \( N \) ranging from 1.5 to 3.3 and proportional to the powers of \( \phi \) ranging from 0.5 to 1.1. However, as is clear from Figure 2, \( \omega \) in CS systems varies linearly with \( N \). This could be because in CS systems a significant fraction of energy supplied is utilized in creation of circulation currents. It has already been reported7 that in such systems the Sautermean diameter is inversely proportional to a 0.1 power of the Weber number in contrast to a 0.6 power for FBT systems. Thus, a rather weak dependence of coalescence frequency on speed of rotation is in accordance with other observations of CS systems.

Fig. 1. Plot of \((\mu_2 - 2\mu_1^2)\) vs. time in a batch stirred vessel.
Experiments have been undertaken with batch agitated vessels and, thus, only constant coalescence frequency could be calculated. But the assumption of constant coalescence frequency can be ignored if experiments are performed in continuous flow stirred tank vessels. In this case it is necessary to feed the CFSTR with finely dispersed suspension and expressions can be used to calculate the interaction frequency provided input and steady-state output DSD's are known.

APPENDIX

In the coalescence-redispersion model for DSD in a stirred vessel, Bajpai et al. have suggested that when two immiscible or partially miscible liquids are finely dispersed with an agitator, an almost instantaneous initial breakdown of the dispersed phase into a large number of droplets occurs. This process which is termed as the primary phase of breakdown, is followed by a secondary phase during which the droplet phenomenon occurs at a much slower rate. The breakage of the drops is confined to the coalesced drops only. Any two drops may coalesce and the coalesced drop breaks immediately into two drops of arbitrary sizes constrained by conservation of mass alone. During this process the number of drops remains essentially constant with time. The size distribution, however, continues to change as a result of drop-interaction until a dynamic balance is struck. Based upon this model expressions for coalescence frequency can be derived using the moment versions of the population balance equation in the following manner.
Fig. 3. Plot of coalescence frequency vs. dispersed phase fraction for various stirred speeds.

For unsteady-state case eq. (7)\textsuperscript{9} may be written as

\[
\begin{align*}
\frac{\partial}{\partial t} n(v,t) &= \omega_0 \int_0^\infty \int_{v'+v'' > v} \frac{v'' n(v',t) n(v'',t)}{(v' + v'')} dv' dv'' \\
&\quad - \omega_0 \omega_n n(v,t) \int_0^\infty v'' n(v,t) \int_0^\infty v'' n(v',t) dv'
\end{align*}
\] (1)

Since the total number of drops in the vessel is assumed to be constant during the secondary phase,

\[
\begin{align*}
\frac{\partial}{\partial t} f(v,t) &= \omega_0 N \int_0^\infty \int_{v'+v'' > v} \frac{v'' f(v',t) v'' f(v'',t)}{(v' + v'')} dv' dv'' \\
&\quad - \omega_0 N v'' f(v',t) \int_0^\infty v'' f(v'',t) dv'
\end{align*}
\] (2)

where

\[ n(v,t) = N f(v,t) \]
The moment equations may be generated to obtain

\[ \frac{d}{dt} \mu_0 = 0 \]  
\[ \frac{d}{dt} \mu_1 = 0 \]  
\[ \frac{d}{dt} \mu_2 = \omega_0 N \left[ \frac{3}{2} \mu_m \mu + 1 - \frac{1}{2} \mu_m \mu_m + z \right] \]  

Equation (3) is a reflection of the assumption of a constant number of droplets in the secondary phase while eq. (4) is a statement of mass conservation. Equation (5) and those of higher moments are unclosed set when \( m \) is not zero.

However, for \( m = 0 \) (i.e., constant coalescence frequency), one obtains

\[ \frac{d \mu_2}{dt} = - \frac{\omega_0 N}{3} \left[ \mu_2 - 2 \mu_1^2 \right] \]  

which is easily solved to obtain

\[ \mu_2 = 2 \mu_1^2 + (\text{constant}) \exp \left( - \frac{\omega_0 N}{3} t \right) \]  

so that a semilog plot of \((\mu_2 - 2 \mu_1^2)\) versus time should yield a straight line of slope \((- \omega_0 N/3\)). It would of course be necessary to test the constancy of \( \mu_0 \) and \( \mu_1 \).

Defining coalescence frequency, \( \omega = \omega_0 \cdot N \), eq. (7) may be written as

\[ \mu_2 = 2 \mu_1^2 + (\text{constant}) \exp \left( - \frac{\omega}{3} t \right) \]  

Alternatively, the steady-state solution of the continuous flow equation may be shown to be

\[ \omega = \frac{3\bar{\mu}_1}{\phi_0} \frac{(\mu_{2f} - \bar{\mu}_2)}{(2\bar{\mu}_m \bar{\mu} + 1 - \bar{\mu}_m \bar{\mu} + 2)} \]  

where \( \mu_{2f} \) is the second moment of the feed droplet size distribution which may be obtained by feeding identically sized droplets such as those produced by a hypodermic needle.

\textbf{Nomenclature}

- \( f \): drop-size distributions in volume
- \( m \): exponent of \( v \) in the expression for coalescence frequency
- \( n \): number density of droplets of volume \( v \)
- \( N \): total number of drops per unit volume of the dispersion, also, the speed of rotation
- \( t \): time
- \( v \): droplets
Greek Letters
\( \phi \) dispersed phase volume fraction
\( \omega_0 \) constant in interaction frequency
\( \omega \) coalescence frequency
\( \mu_i \) \( i \)th moment of drop-size distribution
\( \theta \) residence time in the vessel

Superscripts
\( \sim \) steady state

Subscripts
0,1,2 signify orders of moments
\( f \) property pertaining to feed stream

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