RESEARCH NOTES

Terminal Effect of Drop Coalescence on Single Drop Mass Transfer Measurements and Its Minimization*

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Abstract   For the mass transfer to single drops during the stage of steady buoyancy-driven motion, experimental measurement is complicated with the terminal effect of additional mass transfer during drop formation and coalescence at the drop collector. Analysis reveals that consistent operating conditions and experimental procedure are of critical significance for minimizing the terminal effect of drop coalescence on the accuracy of mass transfer measurements. The novel design of a totally-closed extraction column is proposed for this purpose, which guarantees that the volumetric rate of drop phase injection is exactly equal to that of withdrawal of drops. Tests in two extraction systems demonstrate that the experimental repeatability is improved greatly and the terminal effect of mass transfer during drop coalescence is brought well under control.
Keywords   solvent extraction, mass transfer, single drop, terminal effect, drop coalescence

1 INTRODUCTION

Single drop extraction experiment provides basic data useful for the process research and development. The overall process of mass transfer may be divided into three stages, namely (a) drop formation and subsequent accelerating motion after released from the nozzle; (b) steady buoyancy-driven motion of drops at a constant terminal velocity, and (3) coalescence of drops at the drop collector. Since the corresponding theory on steadily-moving drops is more developed, many experiments were devoted to verify the mathematical models for mass transfer in the stage of steady motion. Many methods are proposed to separate the combined terminal effect of drop formation and coalescence from that during steady motion. In an early paper, Wu *et al.* reviewed the various ways of such correction, and the common point among them was to duplicate the extraction experiments at different drop rising (or falling) distance and obtain the mass transfer during steady motion by the difference of corresponding measurements of extracted fraction[1]. In fact, the difference is not solely due to the contribution of mass transfer during the steady motion, and the error due to the terminal drop coalescence is included.

In a conventional "droplet file" column for settling drop experiments (Fig. 1) the conical-shaped bottom or a funnel is used to sample the dispersed drop phase[2−4]. In experiments on single rising drops, siphon is generally used to remove the coalesced disperse phase from the drop collector at the column top[5−9]. In all cases, manual operation of valves is relied to remove the drop phase at a proper rate so as to minimize the additional mass transfer at the coalescence interface. That is a difficult task for intermittent human interference. Sometime the coalescence-promoting materials are stuffed in the drop collector to minimize the residence time of arrived drops[7]. Vacuum suction method was also used in the Institute of Chemical Metallurgy to remove the coalesced drops by a fine capillary inserted into the neck of the drop collecting funnel, and for avoiding suction of continuous phase the capillary was made of the material showing strong affinity to dispersed phase[10]. Therefore, minimizing the error due to terminal effect remains a consideration in designing and conducting the extraction experiments nowadays.

In this note, the terminal effect due to drop coalescence at the drop collector is analyzed and quantified, which suggests the necessity of better control of the area and rate of mass transfer at the terminal interface. For this purpose, an air-tight experimental column for single drop extraction experiments is introduced. The volumetric rate of drop phase injection and coalesced drop removal is made exactly equal so as to easily minimize mass transfer at the

drop coalescence interface. Single drop mass transfer experiments in the n-butanol[drop(d)]-succinic acid [solute(s)]-water[continuous phase(c)] and the carbon tetrachloride(d)-acetic acid(s)-water(c) systems demonstrate the effectiveness and suitability of the above-mentioned improvement on coalesced drop phase removal and show that the terminal effect of mass transfer at the drop phase collector is brought under better control.
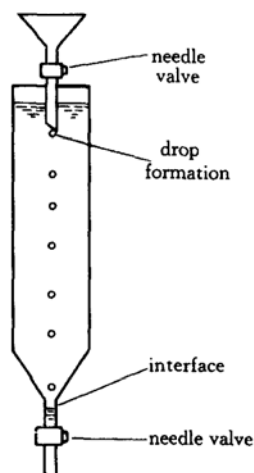

Figure 1   Conventional design of experimental column for single settling drop mass transfer

2 ANALYSIS OF TERMINAL EFFECT

It is generally believed that the interference of terminal coalescence and drop formation may be eliminated by repeating mass transfer experiments with drops freely rising (or falling) for different distances as depicted in Fig. 2. In Fig. 2(a), the collector is located at the position where a drop has reached its terminal velocity, and in Fig. 2(b) the collector is raised up further by h. The effect of drop formation and subsequent accelerating motion is thus eliminated by accounting only for the mass transfer to the drop from c_1 to c_2 at two locations of the collector. The rate of mass transfer between the disperse and continuous phases is usually expressed by the overall drop mass transfer coefficient k_{od} across the height of h calculated by

$$k_{od} = -\frac{d}{6\Delta t} \ln \frac{c^* - c_2}{c^* - c_1} \qquad (1)$$

where $c^* = mc_c$, c^* is the solute concentration in equilibrium with c_c (the concentration of the continuous phase), c_1 and c_2 the drop phase concentration immediately before captured at the respective drop collectors (Fig. 2).
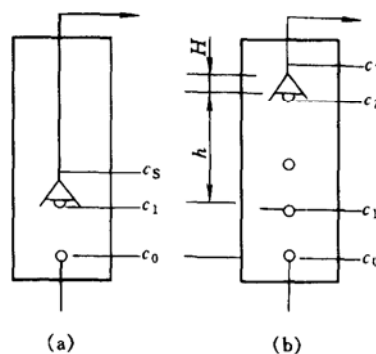

Figure 2   Schematic for analysis of terminal effect of drop coalescence

Nevertheless, the concentration of samples of collected dispersed phase are c_S and c_T, which are altered due to the terminal effect of mass transfer. The difference in concentration is approximately

$$c_S - c_1 = \frac{6k_1 a_1}{\pi n d^3}(c^* - c_S),$$
$$c_T - c_2 = \frac{6k_2 a_2}{\pi n d^3}(c^* - c_T)$$

where k_i is the mass transfer coefficient between the continuous and coalesced drop phases at the collector and a_i their contacting area of the coalescence interface in the funnel. If denoting $\alpha_i = 6k_i a_i / \pi n d^3$ ($i = 1, 2$), then we have

$$c_1 = c_S(1 + \alpha_1) - \alpha_1 c^*$$
$$c_2 = c_T(1 + \alpha_2) - \alpha_2 c^*$$

Thus, the error of measurement due to the terminal effect is

$$\Delta k_{od} = k_{od}^{Exp} - k_{od}^{True} = \frac{d}{6\Delta t}\left[\ln \frac{c^* - c_T}{c^* - c_S} - \ln \frac{c^* - c_2}{c^* - c_1}\right] \qquad (2)$$

or

$$\Delta k_{od} = -\frac{d}{6\Delta t} \ln \frac{1 + \alpha_1}{1 + \alpha_2} \qquad (3)$$

Therefore, the error is directly relied on the consistence of the experimental condition on dispersed phase coalescence at the collecting interface and the technique of withdrawal. Unfortunately, it is usually difficult to manage to make sure of $\alpha_1 = \alpha_2$ exactly so that the terminal effect cancels out completely. It is easy to show that under the typical conditions of "droplet file" column experiments, the value of α may be quite large. For example, when experiments as described in the next section were carried out, the following numerical values may be considered reasonable: $k = 3 \times 10^{-6}$ m·s^{-1}, $a = 0.2$ cm^2, $n = 0.25$ s^{-1}, $\Delta t = 13.5$ s and $d = 1.5$ mm. This makes $\alpha_2 = 0.136$ and an error of $\Delta k_{od} = 6.9 \times 10^{-6}$ m·s^{-1} occurs if $\alpha_1 = 0.5\alpha_2$, which is of the same order of magnitude of k_{od} reported in Table 1. The ratio of α_2/α_1 can vary

widely if lack of accurate control of the area of terminal coalescence interface. However, as a is reduced to $0.008\,cm^2$, $\alpha = 0.0054$, which generates much smaller error of at most $0.6 \times 10^{-6}\,m \cdot s^{-1}$ to k_{od}.

3 EXPERIMENTAL

To minimize the up-and-down fluctuation of terminal coalescing interface in the drop collector and the consequent variation of interfacial area, the experimental column was designed to be totally closed from the atmosphere, in contrast to the conventional extraction being open to the ambient environment. The key point is that the newly designed closed extraction column vents to the atmosphere only through the drop phase collecting tubing. Thus, when a drop is forced into the column by a precision injection pump, equal amount of dispersed phase must be displaced out of the column. This guarantees the area of coalescing interface being constant with the least fluctuation, so that the contribution of mass transfer during drop coalescence becomes a consistent amount. Moreover, effort is made to maintain the interface at the conic base of the collecting funnel, resulting in minimized a and error to measurements of k_{od}.

The experimental setup for rising drops is sketched in Fig. 3. The glass column was 50 mm ID and 1500 mm high, having several side taps for fitting the injection nozzles at different heights below the top drop-collecting funnel. All parts in the experimental setup are either glass, stainless steel, PTFE tubing or tapes. Other precautions were also taken to avoid possible contamination to the extraction systems.
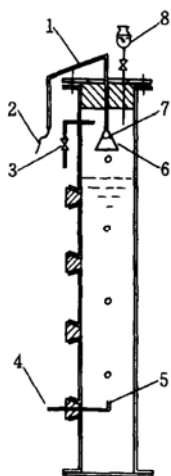

Figure 3   Totally closed experimental column for single drop extraction

1—oleophilic fibre; 2—PTEE capillary; 3—adjusting valve;
4—PTEE capillary to injection jump; 5—injection nozzle;
6—collecting funnel; 7—coalescence interface;
8—separatory funnel

A separatory funnel atop the column and a micro-draining valve work jointly for adjusting the coalescing interface at the base of the conic collecting funnel. The column is first loaded by continuous phase without air bubbles, and then drops are injected. If the coalescence interface is stabilized below the conic base, some continuous phase is added in through the separatory funnel. Otherwise, a little liquid is drain from the adjusting valve at the side to lower the interface down to the base. The first part of the tubing for drop phase removal is stuffed with fibers of high affinity to the dispersed phase to promote the drop phase removal.

To demonstrate the suitability of intended improvement for eliminating the terminal effect of drop coalescence, the new column was tested by single drop extraction experiments in the n-butanol(d)-succinic acid(s)-water(c) system (distribution coefficient $m=1.17$) and the carbon tetrachloride(d)-acetic acid(s)-water(c) system with the distribution coefficient far greater than unity ($m=3.94$). The concentration of solute (succinic and acetic acid) in the sampled drop phase is analyzed by chemical titration.

4 RESULTS AND DISCUSSION

Tests are focused on the effect of the area of coalescing interface on the mass transfer measurements and the results are listed in Tables 1 and 2. It is indicated that the influence of the interfacial area at the collecting funnel is very significant to the terminal effect of mass transfer. If the interfacial area is not well controlled at the minimum, the variation of coalescing interface produces large fluctuation in the terminal effect, thus leading to poor repeatability of experimental data. If H is large, the terminal mass transfer becomes difficult to be kept at the same extent, thus resulting in poor repeatability. The terminal effect seems likely to overestimate the true mass transfer coefficient when the direction of mass transfer is toward drops as is revealed in Table 1. On the other hand, the terminal effect seems to underestimate mass transfer coefficient in the carbon tetrachloride(d)-acetic acid(s)-water(c) system (Table 2). These suggest that other factors, such as the flow detail in the drop collector and possible Marangoni effect, affect the terminal effect and require quantitative analysis. Therefore, to assure accuracy of measurements on single drop mass transfer, it is important to follow the same experimental procedure in every detail and under the condition of minimized coalescence interface. Using the new designed column, the experimental repeatability of k_{od} was reduced from around 20% with the conventional extraction experiments down below 5%.

Table 1 Results of testing the effect of terminal coalescence on mass transfer of single drops in butanol(d)-succinic acid(s)-water(c) system

$(d=1.51\ \text{mm},\ U=4.42\ \text{cm·s}^{-1},\ \Delta t=13.5\ \text{s},\ h=60\ \text{cm},\ \text{transfer direction: c}\rightarrow\text{d})$

H cm	a cm²	Distance from nozzle, cm	c_d, % I	c_d, % II	c_c %	$k_{od} \times 10^6$, m·s^{-1} I	$k_{od} \times 10^6$, m·s^{-1} II	Relative error, %
0.1	0.008	10	0.760	0.761	2.94			
0.1	0.008	70	1.211	1.212	2.94	3.446	3.454	2.7
0.5	0.196	10	1.069	1.029	2.94			
0.5	0.196	70	1.663	1.742	2.94	5.393	6.556	19.5
1.0	0.785	10	0.950	1.148	2.94			
1.0	0.785	70	1.980	1.916	2.94	9.983	7.630	27.0

Note: I, II—Duplicate experimental runs

Table 2 Results of testing the effect of terminal coalescence on mass transfer of single drops in carbon tetrachloride(d)-acetic acid(s)-water(c) system

$(d=1.42\ \text{mm},\ U=16.52\ \text{cm·s}^{-1},\ \Delta t=4.7\ \text{s},\ h=80\ \text{cm},\ \text{transfer direction: d}\rightarrow\text{c})$

H cm	a cm²	Distance from nozzle, cm	c_d, % I	c_d, % II	$c_{d,0}$ %	$k_{od} \times 10^6$, m·s^{-1} I	$k_{od} \times 10^6$, m·s^{-1} II	Relative error, %
0.1	0.008	10	2.938	2.939	4.748			
0.1	0.008	90	1.663	1.675	4.748	2.85	2.81	1.4
0.5	0.196	10	3.125	2.982	4.748			
0.5	0.196	90	1.750	1.783	4.748	2.90	2.57	12.0
1.0	0.785	10	3.146	3.184	4.748			
1.0	0.785	90	2.167	2.152	4.748	1.86	2.33	22.4

It is also noticed that this new design is successfully applied for solvent extraction experiments on the interaction of packing with drop swarms under high rates of drop phase injection and withdrawal[11].

NOMENCLATURE

a	area of coalescence interface at the collector, m²
c	concentration (by mass), %
c^*	concentration equilibrated with c_c (by mass), %
d	drop diameter, m
H	distance from coalescence interface to conical funnel base, m
h	distance of steady motion of drop, m
k_{od}	overall mass transfer coefficient, m·s^{-1}
m	distribution coefficient
n	single drop frequency, s^{-1}
Δt	transit time for a drop to travel the distance of h, s
U	terminal velocity of drop, m·s^{-1}
α	parameter $6ka/\pi n d^3$

Subscripts

c	continuous phase
d	drop
S	lower drop collector
T	upper drop collector

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