Droplet Coalescence and Breakage Rates in a Packed Liquid Extraction Column: A Reassessment of the Data

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Introduction

Hamilton and Pratt (1984) described a novel method for the measurement of droplet coalescence and breakage rates involving the interaction of two streams of methyl isobutyl ketone (MIBK) droplets containing respectively dithizone (green) and nickel di(ethylxanthate) (yellow), which on coalescence formed red droplets, the proportions of which were determined photographically. Data was reported for a 76 mm dia. column packed with 13 mm Raschig rings, and the results were interpreted in terms of second-order coalescence and first-order breakage rate constants, which were then correlated with droplet diameter and holdup of dispersed phase. (See also Hamilton, 1981.)

The results showed considerable scatter which, apart from experimental error, was attributed largely to truncation of the range of droplet sizes considered in the analysis. It was therefore decided to reassess the data with the view of attempting to improve the fit to the model. In the course of this work an error was discovered in the predicted value of holdup used, and values of this were therefore determined experimentally and smoothed for use in this analysis.

Experimental

Measurements of dispersed phase holdup were made by the drainage method (Gayler and Pratt, 1951; Gayler et al., 1953) using a column of 76 mm dia. packed with 2 m of the same 13 mm Raschig rings as those used by Hamilton (1981). Runs were conducted with mutually saturated MIBK and deionized water at rates close to those used by Hamilton. As it appeared possible that the results had been affected by the reagents (Fitzpatrick et al., 1985), runs were also done with the reagents present in the same concentrations as those originally used. The results are summarized in Table 1, and are plotted in Figure 1 in terms of the usual slip velocity relation. The slope of the line through the origin representing the data, giving $\epsilon\bar{v}_o$, was 2.96 cm · s^{-1}. A measurement of voidage for the same column and packing gave $\epsilon = 0.715$, so that $\bar{v}_o = 4.14$ cm · s^{-1}. The amended holdup values for Hamilton's original data (1981) were therefore 3.11, 7.19, and 11.36%, respectively, for his three series of runs.

Analysis of Data

The original "fraction red" data were interpreted by Hamilton and Pratt (1984) in terms of nine drop sizes, d_j, ranging from 0.0712 to 0.452 cm dia., and were smoothed using the relation

$$1 - f_j = \frac{1}{(1 + Ah')^n} \tag{1}$$

where values of A and n were determined for each size range. It has now been found that A can conveniently be expressed as a quadratic function of d_j, as follows

$$A = a_1 + a_2 d_j + a_3 d_j^2 \tag{2}$$

The analysis was extended to include three additional size ranges above and three below those considered by Hamilton and Pratt; this obviated the need to truncate the size distribution and consequently to modify the droplet number balance equations to allow for the loss of droplets from the system. The values of a_1, a_2, a_3, and n in Eqs. 1 and 2 were obtained using the ℓ_1 norm regression analysis of Barradale and Roberts (1974). The resulting fit to the experimental data was appreciably better than that shown in Figure 2 of the Hamilton and Pratt paper, especially at the smaller packing heights.

Reanalysis of the data on this basis, using the method described by Hamilton and Pratt, resulted in values of the coalescence and breakage rate constants given in Table 2. (Appendices A and B of Hamilton and Pratt's original paper (1984)

Table 1. Experimental Values of Holdup

Flow Rates, cm · s^{-1}		Dispersed Phase Holdup, x_d				
V_c	V_d	S*	S + Dz*	S + NiX*	S + Dz + NiX	Mean
0.234	0.081	4.38	4.95	—	4.9	4.74
	0.178	6.45	7.26	7.20	7.41	7.08
	0.226	7.64	9.08	—	8.40	8.37

*S, solvent; Dz, dithizone; NiX, nickel di(ethylxanthate)

are available in microfilm form from the National Auxiliary Publications Service. For more information, see footnote at end of paper.) Plots of these rate constants against droplet diameter showed that the scatter, although significantly less than that reported by Hamilton (1981), was still appreciable; this is attributed, at least in part, to random variations in packing characteristics for each packing height used. To overcome this, further smoothing of the data was performed using a nonrecursive digital filter of the following type.

$$\bar{k}_j = 0.25(k_{j-1} + 2k_j + k_{j+1}) \qquad (3)$$

The smoothed values of the rate constants are given in Table 3, and are plotted against droplet size range, with holdup as parameter, in Figures 2 and 3. Also shown in the latter are the regression lines obtained by nonlinear least-square analysis, omitting the first and last size ranges in view of the small number of droplets present in them.

Applications of Rate Constants

Steady state size distribution

Application of the random selection procedure described by Hamilton and Pratt gave the values of the Sauter mean droplet diameter, d_{32}, listed in Table 4 together with the experimental values.

Effect on mass transfer

The theoretical study of Hamilton and Pratt of the effect of polydispersivity on mass transfer was repeated using the new values of the rate constants; this related to the extraction of 5% w/v aqueous acetic acid with MIBK to give a raffinate containing 0.1% acetic acid. Only the case of 10% holdup, with a flow ratio U_c/U_d, of 0.3815 and corresponding dispersed phase velocity, U_d, of 0.256 cm · s^{-1} was considered.

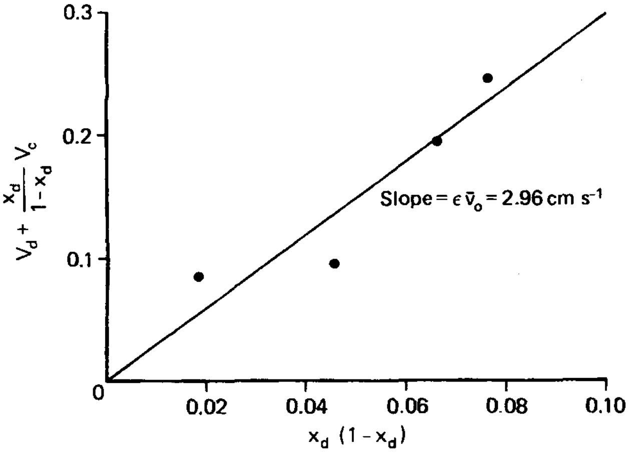

Figure 1. Determination of characteristic velocity of droplets from holdup data.

Table 2. Derived Coalescence and Breakage Constants

		Coalescence Rate Constants k_j, cm^3 · s^{-1}			Breakage Rate Constants K_j, s^{-1}		
j	d_j cm	x_d 0.0311	x_d 0.0719	x_d 0.01136	x_d 0.0311	x_d 0.0719	x_d 0.1136
1	0.0712	(6.1080)	(10.000)	(4.5861)	0.1236	0.2424	0.2108
2	0.0897	0.5853	0.3456	0.0534	0.3492	0.4926	0.5896
3	0.1130	0.6684	1.0838	0.7811	0.3096	0.3307	0.2662
4	0.1424	0.5511	(0.0000)	(0.0000)	0.3307	0.5973	0.7826
5	0.1794	0.7736	1.1042	0.6487	0.2872	0.2288	0.2583
6	0.2260	0.0721	0.2204	0.2615	0.4180	0.6489	0.6283
7	0.2847	0.9294	0.5734	0.3057	0.2214	0.3109	0.5957
8	0.3587	(0.0000)	0.4262	0.2823	0.6567	0.5075	0.5512
9	0.4520	1.9040	0.4842	0.3725	0.2637	0.8488	1.1935

As before, four cases were studied: three of a polydispersion with (i) no droplet breakage or coalescence, (ii) with measured k_j and K_j values, and (iii) with "infinite" k_j and K_j values, and (iv) one of a monodispersion with a droplet size of d_{32}. The results are summarized in Table 5.

Discussion

The present analysis has yielded rate constants with significantly less scatter than those presented by Hamilton and Pratt (1984), presumably because they were obtained without the constraint of a truncated size distribution and were based on experimentally determined holdup values. The major difference from the earlier results is that the coalescence rate constants are appreciably higher, leading to somewhat larger predicted values for the Sauter mean droplet diameters and broader size distributions. The d_{32} values in Table 4 are some 50% greater than those predicted by the method of Gayler and Pratt (1953), and the measured value of the characteristic velocity, i.e., 4.14 cm · s^{-1}, was 21% below the value of 5.25 cm · s^{-1} predicted by the colli-

Table 3. Smoothed Coalescence and Breakage Constants

		Coalescence Rate Constants k_j, cm^3 · s^{-1}			Breakage Rate Constants K_j, s^{-1}		
j	d_j cm	x_d 0.0311	x_d 0.0719	x_d 0.1136	x_d 0.0311	x_d 0.0719	x_d 0.1136
1	0.0712	(5.7000)	(7.5864)	(2.3064)	(0.1702)	(0.2444)	(0.2600)
2	0.0897	1.9867	2.943	1.3685	0.2829	0.3896	0.4141
3	0.1130	0.6182	0.6283	0.4039	0.3275	0.4378	0.4762
4	0.1424	0.6360	0.5470	0.3574	0.3145	0.4378	0.5724
5	0.1794	0.5425	0.6072	0.3897	0.3307	0.4260	0.4819
6	0.2260	0.4618	0.5296	0.3694	0.3361	0.4594	0.5277
7	0.2847	0.4827	0.4483	0.2880	0.3794	0.4446	0.5927
8	0.3587	0.7083	0.4775	0.3107	0.4496	0.5437	0.7229
9	0.4520	(1.1048)	(0.6153)	(0.4297)	(0.6995)	(0.9685)	(1.2235)

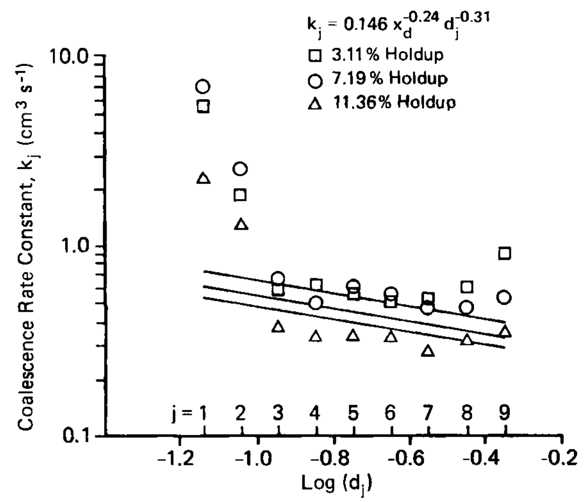

Figure 2. Correlation of derived droplet coalescence rate constants.

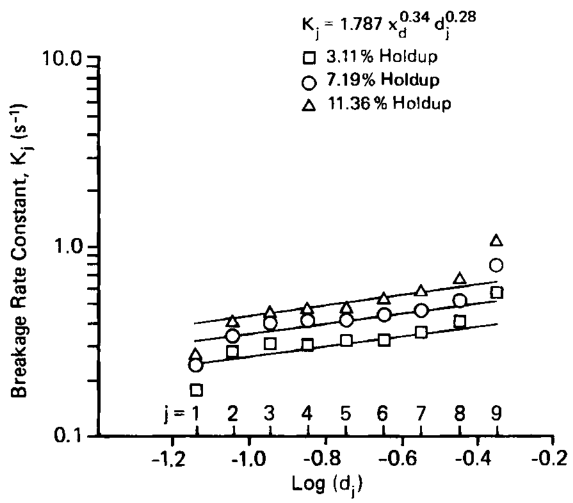

Figure 3. Correlation of derived droplet breakage rate constants.

sion theory of Gayler et al (1953). Both discrepancies are in a direction which suggests that the packing was close to the critical size for the MIBK-water system.

The effect on mass transfer of droplet coalescence and breakage is much the same as before, although the heights of packing required are some 20% greater; also, the differences in height between cases (i) and (iii), for no coalescence and for infinite coalescence, are about 40% higher. On the other hand, the differences between (i) and (ii), for no coalescence and for the measured coalescence/breakage rates, are smaller. The small difference was unexpected, but may be related to the fact that the droplets in cases (i) and (iii) retain their identity throughout, whereas in case (ii) the numbers in each size range vary continuously as a result of the random selection procedure. For practical design purposes the assumption of a monosized dispersion with the height increased by 20% to allow for polydispersivity would appear reasonable on the basis of the present results.

Table 4. Predicted and Experimental Values of d_{32}

Holdup %	Value of d_{32} (mm)	
	Exp. at Exit	Pred.
3.11	3.18	3.50
7.19	3.52	3.72
11.36	3.42	3.88

Finally, the results have been used to recalculate the mean droplet lifetime between interactions (coalescences and breakages). This led to a value of 0.405 s for Hamilton's (1983) results for a corrected holdup of 11.4%, i.e., one interaction for each 1.49 cm of rise in the packing.

Notation

a_i = constants in Eq. 2
d_j = mean diameter of jth droplet size range, cm
d_{32} = volume-surface (i.e., Sauter) mean diameter of droplets, cm
E_c = longitudinal dispersion coefficient, cm^2 · s^{-1}
f_j = number fraction of red droplets in size range j
H_{od} = height of a "true" overall transfer unit based on the dispersed phase, cm
h = height of packing, cm
h' = (h-2.5), cm
K_j = first-order breakage rate constant for droplets of size j, s^{-1}
$\bar{K}_j$ = smoothed breakage rate constant for droplets of size j, s^{-1}
k_j = second-order coalescence rate constant for droplets of size j, cm · s^{-1}
$\bar{k}_j$ = smoothed coalescence rate constant for droplets of size j, cm · s^{-1}
N_{od} = number of overall transfer units based on the dispersed phase
U_c, U_d = superficial velocities of continuous and dispersed phases in column, cm · s^{-1}

Table 5. Effect of Droplet Coalescence and Breakage on Column Height (10% Holdup Case)

Case No.	Simulation	Without Backmixing				With Backmixing†			
		N_{od}	H_{od} cm	h cm	Δh* %	N_{od}	H_{od} cm	H cm	Δh* %
(i)	No coalescence or breakage	6.42	47.8	307	18.0	10.09	48.2	487	14.0
(ii)	Measured coalescence and breakage rates	6.49	47.2	306	17.7	10.42	46.6	486	13.8
(iii)	Infinite coalescence	6.48	40.1	260	0	11.07	38.5	427	0
(iv)	Monosized dispersion	6.43	41.2	265	1.92	10.21	42.1	426	−0.23

*$\Delta h(\%) = 100\,(h - h_\infty)/h_\infty$ where h_∞ corresponds to case (iii).
†E_c = 1.955 cm^2 · s^{-1}.

$\overline{v}_o$ = characteristic velocity of droplets in column, i.e., mean velocity when $U_c = 0$ and $U_d \rightarrow 0$, cm · s^{-1}
x_d = fractional volumetric holdup of dispersed phase
ϵ = fractional voidage of packing

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