Single Droplet Mass Transfer Measurements Using an ESCR-Scintillation Method

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Mass and heat transfer have been treated analogously in a wide variety of transport problems. Implicit to this treatment in the case of liquid/liquid systems is the assertion that the hydrodynamics of the bulk phases can be used via correlation to predict conditions at the interface. Sawistowski (1971) disputes this assertion, citing experimentally-observed interfacial convection; more recent experimental evidence is given by Thornton et al. (1985). Such convection appears to be influenced by both mass transfer direction (MTD) and system cleanliness, and has a pronounced influence on mass transfer rate (MTR).

The purpose of the present work is to determine the extent of these influences in the systems toluol(dispersed)-acetone-water and toluol(d)-butanone-water. The validity of the classical mass transfer treatment as an engineering approximation is of primary importance, and not the causes or explanation of the interfacial effects themselves, as the dependency of MTD on either MTR or system cleanliness yields at best only indirect indication of the mechanism responsible for mass transfer in and near the interface.

Theoretical Basis

The Lewis-Whitman two-film theory, as modified by Gordon and Sherwood (1954) is used. A change in the continuous-phase bulk concentration $C_{cb}(t)$ given by a time lag TZ and a time constant τ_s is:

$$\frac{C_{cb}(t') - C_{cb}(t' = 0)}{C_{cb}(t' = \infty) - C_{cb}(t' = 0)} = 1 - e^{-t'/\tau_s}, \quad t' > 0 \qquad (1)$$

then, it yields for the droplet ($\tau_d \neq \tau_s$):

$$\frac{C_{db}(t') - C_{db}(t' = 0)}{mC_{cb}(t' = \infty) - C_{db}(t' = 0)} = 1 - \frac{e^{-[(\tau_d/\tau_s)(t'/\tau_d)]}}{1 - \left(\dfrac{\tau_d}{\tau_s}\right)} - \frac{e^{-(t'/\tau_d)}}{1 - \left(\dfrac{\tau_s}{\tau_d}\right)} \qquad (3)$$

The determination of τ_d from an experimental $C_{db}(t)$ curve is based on the trial and error and requires in practice that $\tau_d > \tau_s$. If the difference $C(t = 0) - C(t = \infty) = C_i - C_f$ in either phase is small, then all physical properties remain approximately constant. Reversal of the MTD between indentical final/initial concentrations has negligible effect on the mean physical properties. K_o in engineering practice is a function of the physical properties of both phases and the droplet diameter; therefore, both K_o and τ_d should be independent of MTD.

Experiment

Apparatus

The measurement section consists of a quartz nozzle, in which an immiscible, free-swimming toluol droplet can be held stationary in downward flowing water, (Figure 1). A venturi nozzle and mixer packing are located immediately upstream of the nozzle. Injection of an aqueous acetone (or butanone) solution into the throat of the venturi yields a rise in the continuous-phase concentration that is closely approximated by Eq. 1, the parameters τ_s and TZ being identified in a separate tracer experiment. The entire flow system is constructed of glass, teflon, and stainless steel. For data acquisition, an essentially unmodified scintillation spectrometer (Packard 3320) was connected to a multichannel scalar/analyzer (Silena 7924/7934), and in turn to a live display and computer/plotter (Hewlett Packard 9825). The

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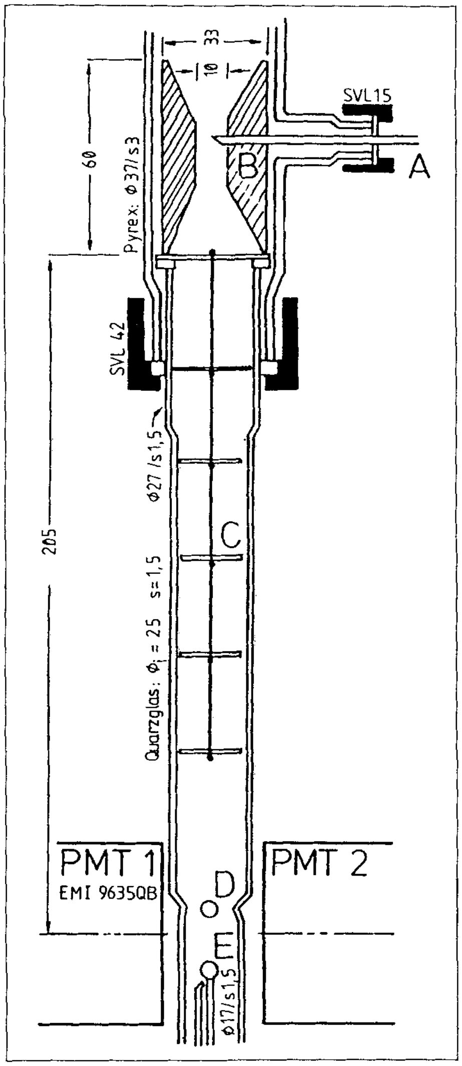


Figure 1. Measurement section.

A = injection needle
B = venturi nozzle
C = wire mesh screens and stainless steel wool packing
D = free-swimming drop
E = droplet on the formation needle
SVL = sovirel fitting
All dimensions in mm.

stepping time varied between 1 and 3 s. Full details are given in Hubis (1987).

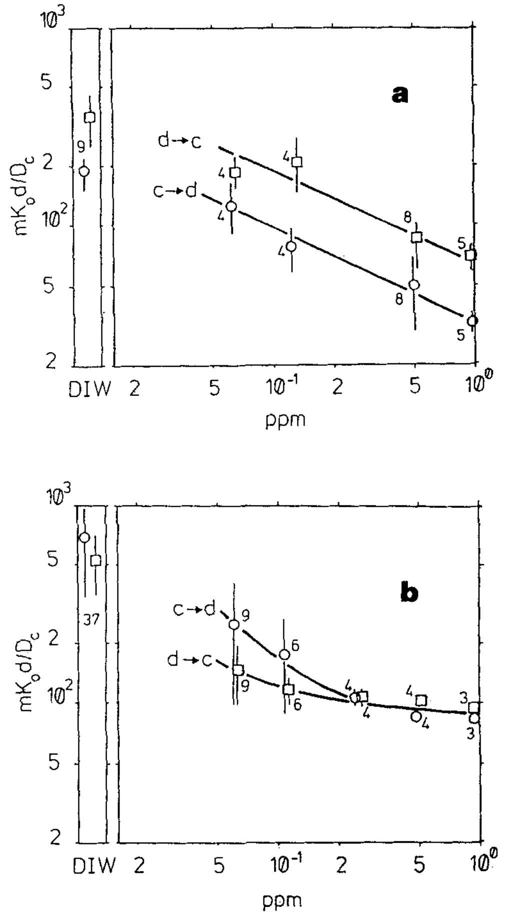
Scintillation method

The toluene droplet contains 8 g/L of the scintillator Butyl-PBD (Ciba-Geigy) and is irradiated by two symmetrically mounted 133-Ba sources (or "external standards"), each 1 mCi, leading to photons in the UV and near-visible ranges, which are then detected by two photomultiplier tubes. Introduction of a chemical quencher (acetone or butanone) decreases the energy transfer efficiency and shifts the scintillation spectrum. (See, for example Gibson and Gale, 1967.)

Previous mass transfer applications of the external-standard method (Halwachs and Schügerl, 1983) used calibrations of the type quencher concentration $[Q]$ vs. count rate. This was not possible in the present study, as even minute motions of free-swimming drops led to appreciable fluctuations in count rate. Sufficiently stable count rates were achieved only if the drop remained on the formation needle or adhered to the quartz nozzle wall. The calibration was, instead, based on the "external standard channels ratio" (ESCR) method (Jordan and Köberle, 1970). Spatial quencher distributions during mass transfer were found in a related study to have negligible influence on the measurement (Hubis et al., 1987).

Measurement procedure

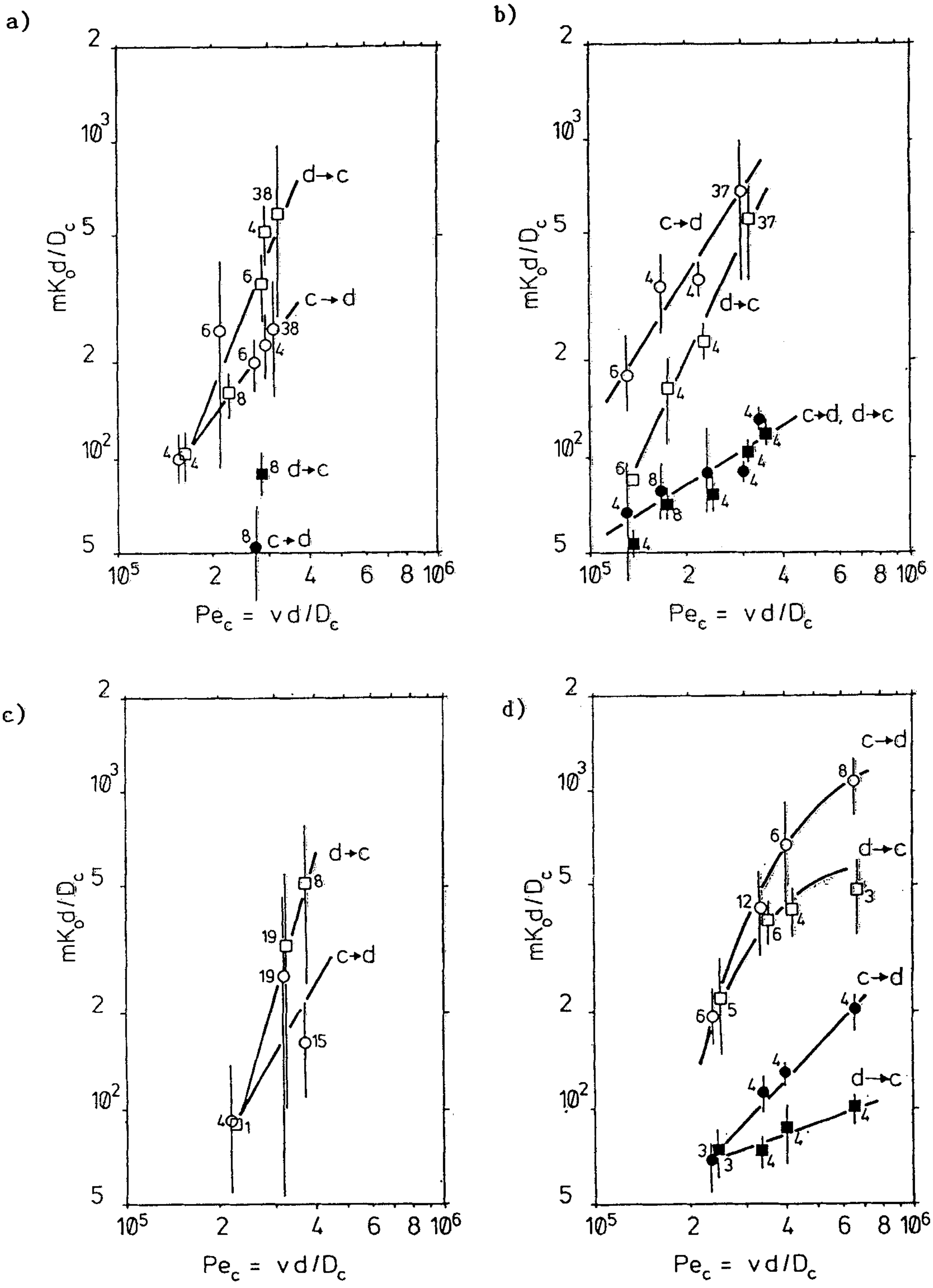
A drop of known volume was formed and, for measurements on free-swimming droplets, dislodged. The data acquisition system was started, and the drop allowed to swim freely for approximately 60 s. Acetone (or butanone) was then injected into the venturi throat. Transfer $c \rightarrow d$ was observed for approximately 4–5 τ_d (known from trial experiments), at which time the acetone injection was stopped, allowing measurement of transfer $d \rightarrow c$ on the same drop. Confirmation that the drop had remained free-swimming (no visual proof is available) was provided by decreasing the aqueous flow rate by approximately 5% and allowing the drop to rise from the nozzle throat. The mea-



a) transferring component acetone ($m = 0.95$)
b) transferring component butanone ($m = 3.85$)

Figure 2. K_o vs. aqueous surfactant concentration (Emulgator 913) for a 20-μL droplet held on the formation needle at $Re_c = 277$.

The data in the DIW-box are from measurements with deionized water in the freshly cleaned apparatus. Average, standard deviation, and number of repeated trials are given for each point. $T = 20°C$.



a) droplets on the formation needle, acetone
b) droplets on the formation needle, butanone
c) free-swimming droplets, acetone
d) free-swimming droplets, butanone

Figure 3. Measured variation of K_o vs. Pe_c.

Open points are for deionized water without added surfactant (the residual surfactant content is, strictly speaking, unknown), shaded points are for an aqueous surfactant concentration of 0.5 ppm Emulgator 913. $T = 20°C$.

sured count rate would immediately decrease in the case of a free-swimming drop and remain constant if the drop had adhered to the nozzle wall. Downward flushing removed both free-swimming and adhered drops and could not be used as a criterion.

Results and Discussion

MTR to and from a 20 μL droplet held on the formation needle at $Re_c = 277$ was first studied as a function of MTD and system cleanliness. Results are given in Figure 2 for the nonionic surfactant Emulgator 913 (alkylphnol-polyglycolether, Supplier: G. Zimmerli AG, Switzerland) and are similar to those for anionic (Gezavon LL20Na, a sodium salt of a laurylalcoholether) and cationic (cetyltrimethylammoniumbromide) surfactants. The convergence of both trend lines at 0.2–1.0 ppm surfactant with butanone as transferring component suggests the absence of surface hydrodynamic and barrier resistances, a trend not seen with acetone.

K_o was studied as a function of Pe_c with 10–30 μL droplets on the formation needle in a second series of experiments, Figure 3. K_o is influenced by the MTD in clean systems, whereas this trend is not observed in the contaminated butanone system. No further experiments were attempted with the contaminated acetone system. The results from free-swimming droplets in clean systems show similar trends with more scatter. Contamination in the butanone system leads to a reduction of MTR but does not eliminate the influence of MTD. A possible—but admittedly speculative—interpretation of this observation is that fresh surface elements are formed in even contaminated free-swimming droplets, which are then susceptible to the same surface instabilities seen in the clean systems. Surface hydrodynamic effects may thus be present even in relatively contaminated extraction equipment, especially if the phases are continually redispersed and coalesced.

The results suggest that the correlation of mass transfer coefficients for these systems may ultimately prove to be of limited engineering utility. The same surfactant concentrations which led to a fivefold reduction in K_o were too small to be detected reliably with interfacial tension measurements (Hubis, 1987). In the absence of a measurement technique that adequately characterizes the contamination level of the system, a limiting case approach (corresponding roughly to the contaminated and clean trends in the present study) appears to be the limit of prediction accuracy.

Acknowledgment

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Notation

A = area, l^2
C = volume-average concentration, mol $\cdot\ l^{-3}$
D = diffusion coefficient, $l^2 \cdot t^{-1}$
d = droplet diameter, l
k = individual mass transfer coefficient, $l \cdot t^{-1}$
$K_o = 1/[(1/k_d) + (m/k_c)], l \cdot t^{-1}$
$m = (C_d/C_c)$ at equilibrium
Pe_c = Peclet Number, vd/D_c
Re_c = Reynolds Number, $\rho_c dv/\mu_c$
s = wall thickness
t = time
$t' = t - TZ, t$
TZ = system dead time, t
v = droplet rise velocity, $l \cdot t^{-1}$
V = droplet volume, l^3

Greek letters

ρ = density, ml^{-3}
Φ = interior diameter, l
μ = viscosity, $ml^{-1} \cdot t^{-1}$
τ_d = droplet time constant, $V/AK_o, t$
τ_s = system time constant, t

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