

UNIT OPERATIONS LAB

Mass Transfer and Axial Dispersion in a Reciprocating-Plate Liquid Extraction Column

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The BSChE program at the University of Washington (UW) includes a required 2-quarter lab sequence. The first course emphasizes measurement fundamentals, transport phenomena, statistical analysis of data, and technical communication skills. Experiments are relatively simple.

The second course involves open-ended assignments and the equipment is more complex. Educational goals are to

- Reinforce and integrate the material covered in lecture courses
- Develop students' abilities to plan an experiment, carry it out with good technique, and analyze results in a professional manner
- Refine oral and written communication skills

Students work in teams of three and have three 4-hour lab periods to collect data. A team performs three experiments during the quarter. For each experiment, a designated leader submits a written plan (including a safety analysis) and defends it in a conference with the instructor prior to the first day of data collection. At the end of three weeks, the leader submits a detailed written report, and another team member gives an oral report. The leadership role and other responsibilities rotate from one experiment to the next.

We have recently developed a multifaceted experiment on an important unit operation (liquid-liquid extraction). A typical assignment asks a team to characterize one or more of the following:

- Equilibrium solute distribution between two liquid phases as a function of solute concentration
- Mass transfer coefficients (or HTUs) for steady-state extraction in a reciprocating-plate column as a function of operating conditions
- Residence-time distribution and the influence of axial dispersion on column efficiency

In this paper we will describe the experiments briefly, explaining how they fit in with the educational mission of the course.

EXPERIMENTAL EQUIPMENT

Our liquid-liquid contactor is a standard Karr^[1] reciprocating-plate column (see Figure 1). The mass transfer zone is a glass tube, 2.5 cm ID, 2 m long. It contains 36 perforated stainless steel plates (approximately 60% open area) spaced at 5-cm intervals on a central stainless shaft. An electric motor makes the shaft oscillate vertically at frequencies of 0-180 cycles/minute (displayed on a meter and easily varied during operation). The vertical stroke length is 0-5 cm (variable, but constant for the duration of a run). We bought the column, drive system, and internals as a package from the Chem-Pro Equipment Company.

Kerosene is the dispersed phase (a 40-liter stainless steel reservoir allows runs of several hours). It passes through a rotameter and enters as large droplets at the bottom of the column. Smaller droplets form as the kerosene flows upward through the reciprocating plates in the contacting zone. Droplets coalesce above the aqueous inlet location, and the kerosene flows by gravity to a collection vessel.

A feed of tap water passes through a rotameter, enters the column about a foot below the top, and flows downward by gravity, eventually leaving at the bottom. With the drain



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valve of Figure 1 closed, the exiting water flows upward through flexible tubing to a tee, then back down to a collection vessel. The location of the tee (adjusted by a sliding clamp) controls the water/kerosene interface location inside the column. The section above the tee provides an emergency overflow line and a vent

A 6-mm sampling port with a rubber septum allows either tracer injection or removal of an internal sample at the water feed entry point. A conductivity meter (Omega CDTX-81, 0-200 $\mu\text{S}/\text{cm}$) monitors the conductivity of the exiting water phase. We added a zone of 5-mm glass beads between the kerosene inlet and conductivity meter to promote plug flow in that region. Otherwise, flow is laminar and Taylor dispersion biases the measurement of the residence-time distribution. The conductivity meter provides an analog output to a microcomputer.

PHASE EQUILIBRIA

The system n-butylric acid/kerosene/water offers the following advantages:

- ▶ Butylric acid concentrations can be measured accurately by titration, even at high dilution. Use of a dilute solute simplifies analysis of mass transfer experiments and minimizes chemical consumption and waste-disposal problems. Dilute aqueous solutions of butylric acid and its salts may be sewered. Other acids could be used, but butylric is one of the few having a distribution coefficient of order unity in a nonpolar organic. This makes it easy to avoid a pinch of operating and equilibrium lines in mass transfer experiments.
- ▶ Butylric acid's strong, unpleasant odor is a disadvantage; good ventilation is essential.
- ▶ Kerosene is inexpensive, insoluble in water, and reasonably safe and odorless. Nearly all of it can be recovered and recycled. The lack of a known molecular weight forces students to think about the choice of

... the challenge is to work within the constraints of the lab, obtain consistent, credible results, understand their limitations, and communicate it all effectively. Some students appreciate this and rise to the challenge immediately.

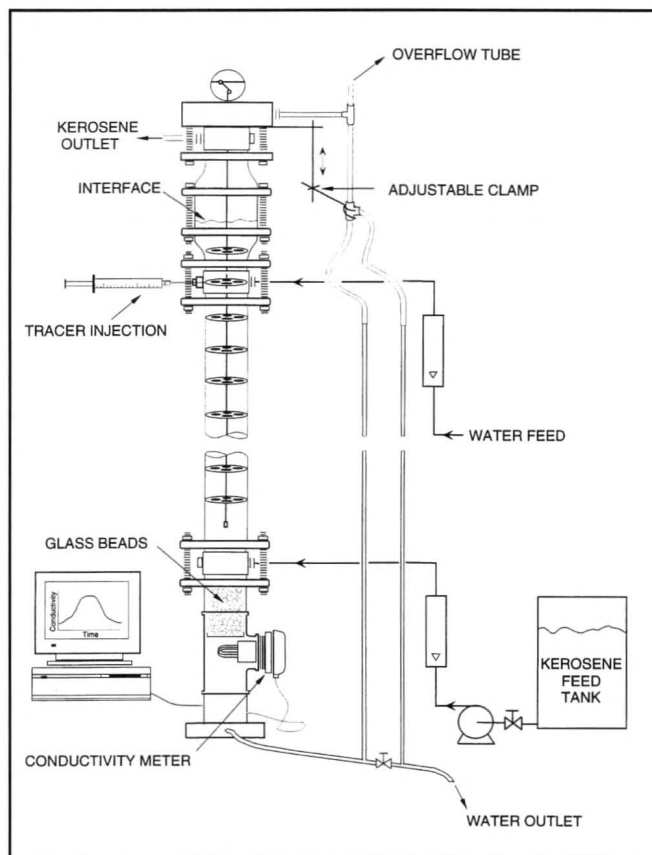


Figure 1. Standard Karr Reciprocating-Plate Column.

the basis for equilibrium and mass-transfer calculations. One could easily substitute a pure hydrocarbon, however.

- ▶ Distribution coefficient data are unavailable in the literature; they must be measured to determine mass transfer driving forces. We provide the students with published data for the analog system butylric acid/hexane/water, however. This gives them a basis for comparison and allows them to estimate appropriate solvent/feed ratios for extraction runs.
- ▶ Results are insensitive to variations in ambient temperature in the lab, avoiding the need for temperature control.

Measurement of Solute Distribution • This bench-top experiment seems simple, but it requires careful planning and execution. Mixtures of the three chemicals equilibrate in a suitable container at room temperature. Analysis of samples from one or both phases follows. Students must choose overall mixture compositions such that equilibrated phases have solute concentrations

in the correct range (*i.e.*, as expected in mass transfer experiments). Other considerations include the agitation protocol, time needed to reach equilibrium (we suggest at least one-half hour), and whether it is necessary to measure the solute concentration in both phases. An alternative is to measure one and estimate the other by mass balance. We ask the students to perform an error analysis that compares these alternatives.

Example data appear in Figure 2. The empirical relationship $y=0.20x^{1.82}$ fits well over the range $x=0$ to 2 wt. % butylric acid in the aqueous phase, $y=0$ to 0.8 wt. % butylric acid in the kerosene phase. Heinonen and Tommila^[2] observed similar nonlinear behavior for n-butylric acid/hexane/water, attributing it to the dimerization of butylric acid in the nonpolar organic phase.

Team leaders usually assign one member to this task,

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which can run in parallel with mass transfer experiments. Study of the full composition range is a significant effort, however. The instructor might instead provide data from a previous group's report, asking the current team to verify some aspect of it. A variant is to provide two or more old reports (good and bad), forcing the team to separate the wheat from the chaff.

Titration • Analysis of aqueous samples for butyric acid content is straightforward. We titrate with aqueous NaOH (usually 0.5 N). A phenolphthalein indicator gives a sharp endpoint. For organic samples, one approach is to add the sample to a beaker containing water and phenolphthalein, then slowly titrate with NaOH while stirring vigorously (using a magnetic stir bar). The butyric acid transfers to the aqueous phase where it reacts to form sodium butyrate, which is insoluble in kerosene. Mass transfer is slow, however, so the endpoint is less obvious. An alternative is to equilibrate the sample with an excess of aqueous NaOH, then titrate the unreacted NaOH with aqueous HCl. Another is titration with NaOH in a suitable organic solvent, such as methanol. This requires a pH meter to detect the endpoint.

MASS TRANSFER EXPERIMENTS

A typical assignment asks the team to measure the overall height of a transfer unit (HTU) as a function of shaft oscillation frequency. The feed is kerosene with a specified concentration of butyric acid (usually less than 1 wt. %), and the solvent is tap water. We also specify the shaft stroke length and the kerosene feed rate. The team must select the water rate(s) and determine the region of operability. The main constraint is flooding, which occurs at high feed rates or high oscillation frequency. Another is phase inversion, *i.e.*, a transition from water-continuous to kerosene-continuous operation. It is also important to avoid a pinch of the operating and equilibrium lines. Otherwise the calculated HTU value is very uncertain.

Students find that running the equipment is non-trivial. The minimum HTU is usually close to the flooding point, where small changes in operating conditions (especially insufficient attention to flow control) can have dramatic effects, easily seen within the glass column. It usually takes a team one full lab period to develop the skill needed to collect useful data in this region. To reduce frustration, we instruct them to avoid flooding conditions in early experiments.

We emphasize the importance of steady-state operation, suggesting that they measure the outlet aqueous butyric acid concentration—the easiest to titrate—periodically until the value is essentially constant, then analyze a sample from the kerosene raffinate to check mass-balance closure. It takes about one-half hour (or turnover of four column volumes) to reach steady state after a change in operating conditions.

Figure 2 shows a typical operating line for the measured

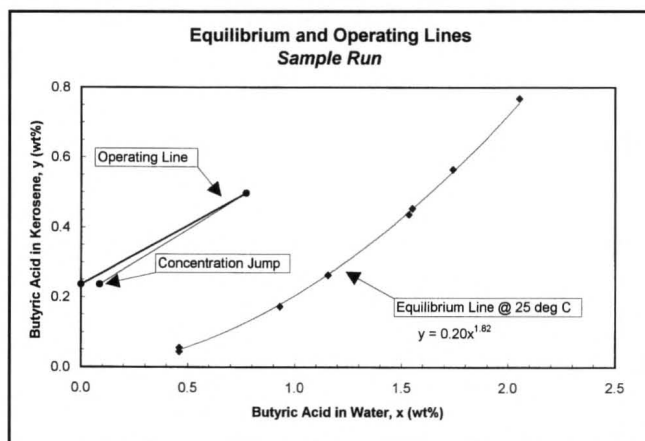


Figure 2.

concentrations of inlet and outlet streams under the assumption of plug flow in two immiscible phases, and dilute operation. Other operating conditions were oscillation frequency = 110 cycles/minute, kerosene feed = 3.0 g/s, and water feed = 1.1 g/s. Calculation of the overall number of transfer units (NTU) would be trivial if the equilibrium line were straight.^[3] With a curved equilibrium line, however, students must review the theory carefully, which enhances their understanding.

For the case shown in Figure 2, the NTU is 0.83, giving an HTU of 225 cm. Although the HTU decreases with increasing frequency as expected, the values remain well above the 5-25 cm reported in the literature.^[1] This motivates the assignments for the follow-on teams, who are asked to determine the reason for the large HTUs. Possible variations (other than changes in the chemical system) are the stroke length, tray spacing and design, and choice of the dispersed phase (water-dispersed operation is poor with stainless trays, however). Axial dispersion can also affect liquid extraction performance,^[4,5] suggesting a study of this possibility.

AXIAL DISPERSION EXPERIMENTS

There are two ways to check the extent of axial dispersion. The more direct way is to analyze samples from within the column. For example, if one expects strong axial dispersion in the continuous phase, there should be a discontinuity in the continuous-phase concentration at the feed location (a "concentration jump," as shown in Figure 2).

Good technique is needed to remove a representative internal sample. Significant amounts of the dispersed phase may be entrained, and the students must decide how to deal with this. Figure 2 shows that the jump was rather small in the sample run; the corresponding HTU is 220 cm, a decrease of only 2% from the plug-flow value.

The alternative is to measure the residence-time distribution (RTD). This has been advocated in *CEE* previously for gas-liquid contactors.^[6] Several texts provide good back-

ground on calculational methods and interpretation.^[7,8]

The continuous phase is most prone to axial dispersion. To measure the RTD, a student injects about 1 ml of KMnO_4 dye tracer into the aqueous (continuous) phase at the feed point (Figure 1). The pulse is easy to follow visually, and the concentration transient at the outlet can be analyzed quantitatively using the conductivity meter.

The KMnO_4 is insoluble in kerosene, so it is possible to measure the continuous-phase RTD during normal counter-current operation. We have found, however, that entrained kerosene droplets can interfere with conductivity measurements. The main problem is development of an insulating coating on the probe surface. Students can mitigate this by operating far from the flood point (to minimize entrainment), making baseline corrections on conductivity measurements and cleaning the probe periodically—but this is inconvenient. Thus, we usually assign a study of RTD in the absence of kerosene. Variables are then the water feed rate and the degree of agitation.

An alternative would be to measure dye concentration via UV-vis spectroscopy, which should be less sensitive to the presence of kerosene. We have not tried this yet because our measurements show that the presence of the dispersed phase has little impact on the RTD in our 2.5-cm column. This would not be the case in general.

The students use the measured RTD to calculate a Peclet number at each condition. Peclet numbers can be related to the mass transfer results using the equations developed by Sleicher,^[5] which provide a correction to the assumption of plug flow. Laddha and Degaleesan^[4] (pp. 125-127) illustrate the calculations in detail. For the conditions of the sample run, assuming plug flow in the dispersed phase, the observed continuous-phase Peclet number leads to a correction of only 2%, *i.e.*, essentially the same as the correction based on the measured concentration jump.

DISCUSSION

For our 2.5-cm reciprocating-plate column, axial dispersion increases with increasing plate oscillation frequency and decreasing feed rate, but is never a dominant factor. Continuous-phase Peclet numbers are of order 30 or greater under most conditions. The presence or absence of the dispersed phase has only a small effect. These observations are in agreement with those described in the literature.^[9]

This forces students to look elsewhere to explain the large HTU values found in mass-transfer runs. It is instructive to follow up with a more polar-dispersed phase having a density closer to water and a lower interfacial tension (*e.g.*, MIBK), which exhibits much lower HTUs. It would also be interesting to run RTD experiments in a column with a much lower length-to-diameter ratio where axial dispersion would

be more significant.

We occasionally ask a team to quantify flooding behavior. It would be logical to do this prior to mass-transfer experiments. Useful information on expected behavior is available in the literature.^[10]

Student reaction to the RTD experiments has been very positive. They appreciate the visualization of axial dispersion and the automated collection of conductivity data, which makes calculation of the RTD easy. They enthusiastically vary operating conditions over a wide range, check repeatability, etc.

They are less pleased with the phase-equilibrium and mass-transfer experiments. Most complaints concern the odor of butyric acid and the tedium of multiple titrations. We could change the solute, but butyric acid has important advantages, as noted previously. Odor can be reduced, but is difficult to eliminate. Automated titration would increase student productivity and morale.

In general, we want the students to have some hands-on responsibilities in each experiment. In contrast to their *a priori* expectations, the point is not to demonstrate perfect (or even good) agreement between the textbook and reality, nor is it to see modern industrial equipment and instrumentation in action (although such exposure is certainly worthwhile). Rather, the challenge is to work within the constraints of the lab, obtain consistent, credible results, understand their limitations, and communicate it all effectively. Some students appreciate this and rise to the challenge immediately. Others grumble throughout the quarter, but judging by alumni surveys, their frustration with the course often turns to praise once they have graduated.

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