ChE *laboratory*

LOW-COST EXPERIMENTS IN MASS TRANSFER

Part 2[1]

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Liquid-liquid (or solvent) extraction is an important unit operation in mineral processing, in nuclear and non-nuclear waste treatment, and in the chemical and pharmaceutical industries. It usually involves the transfer of a solute from an aqueous to an organic phase, or vice versa. The two phases are generally immiscible with each other, and one phase is *dispersed* in the other, which is known as the *continuous* phase. This provides a large interfacial area for mass transfer and improves the process kinetics.

Prediction of mass transfer coefficients for a solvent extraction process becomes difficult because of the absence of any accurate knowledge of the interfacial area and is complicated further by the influence of ionic strength and surface contaminants on the area.

The study of extraction rates at the bench scale, with a known interfacial area, has been carried out using batch cells with rotary agitation. Special baffles are provided to ensure that the liquid-liquid interface remains flat. The original Lewis cell[1] was modified by Bulicka and Prochazka,[2] who incorporated vertical baffles and a cylindrical perforated grid in the design in order to achieve greater turbulence together with increased stability of the interface. A brief review of various stirred cells is given by Lo, *et al.*[3]

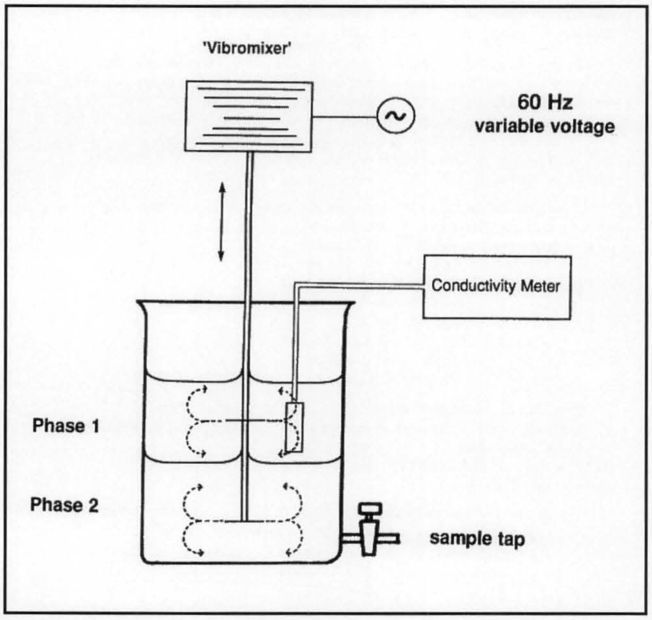

Figure 1. The apparatus.

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The objective of this experiment is to introduce chemical engineering students to a simple technique of predicting mass transfer coefficients using equipment with a well-defined interfacial area.

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THEORY

Solvent extraction of acetic acid from an organic phase into an aqueous phase is taken as an example because it is a non-reacting system. The concentration increase of acetic acid in water is followed with time. The rate of acetic acid transfer is assumed to be first order with respect to the difference between the final ($C_{a\infty}$) and the actual (C_a) solute concentration. For a volume V_a of the aqueous phase, the rate of change of solute concentration (dC_a / dt) can be expressed by

$$V_a \frac{dC_a}{dt} = k_a A \left(C_{a_\infty} - C_a \right) \tag{1}$$

which can be integrated as

$$\int_{C_{a_i}}^{C_a} \frac{dC_a}{\left(C_{a_\infty} - C_a \right)} = \frac{k_a A}{V_a} \int_0^t dt \tag{2}$$

yielding

$$\ell n \left(C_{a_\infty} - C_a \right) = \ell n \left(C_{a_\infty} - C_{a_i} \right) - \frac{k_a A}{V_a} t \tag{3}$$

where

C_{a_i}	initial concentration of acetic acid in water (generally zero)
C_a	acid concentration in water at time t
k_a	local aqueous phase mass transfer coefficient
A	interfacial area that is kept constant during the experiment
C_{a_∞}	aqueous phase acetic acid concentration at equilibrium

Equation (3) indicates that by plotting $\ell n \left(C_{a_\infty} - C_a \right)$ versus t, a linear line of negative slope ($-k_a A / V_a$) is obtained, from which k_a can be calculated.

The objective of this experiment is to introduce chemical engineering students to a simple technique of predicting mass transfer coefficients using equipment with a well-defined interfacial area.

APPARATUS

A sketch of the apparatus is shown in Figure 1. It is a modification of the Lewis cell.[4] A 1-liter glass beaker is used as the extraction cell. The cell has a sample draw-off tap at the bottom that is installed by glass blowing. Agitation is achieved by a single-phase Chemapec Inc. Vibro Mixer Model El-11043 operating at standard 60-Hz frequency and powered through a Variac to change the amplitude of vibration (degree of agitation). Mixing is provided by two 4.6-cm diameter stainless steel agitator discs mounted on the shaft of the Vibro Mixer. The liquid streams outward from the edges of the vibrating discs and circulates as shown in the figure. Mixing within the phases can also be achieved by a small impeller agitator provided the interface stays flat.

EXPERIMENTAL PROCEDURE

The organic phase may be either lighter (such as kerosene as Phase 1) or denser (such as carbon tetrachloride as Phase 2) than water. The concentration of acetic acid in the aqueous phase at any time may be determined by either titrating a small sample of solution or by monitoring the conductivity of the aqueous phase, which would eliminate the need for removal of aqueous samples for titration. Sample removal has some effect on the value of V_a, which is assumed to remain constant during the integration of Eq. (2). Although the present data have been obtained with carbon tetrachloride, the use of a relatively non-toxic organic phase denser than water (such as methylene chloride, CH_2Cl_2) is recommended. When using a lighter organic phase, the conductivity probe should be submerged in the aqueous phase before adding the organic phase in the cell.

On the other hand, when a denser organic phase is used, it should be added to the cell first, then the water, and then the conductivity probe should be placed in the top aqueous layer. A calibration curve can be drawn for $[CH_3COOH]$ versus con-

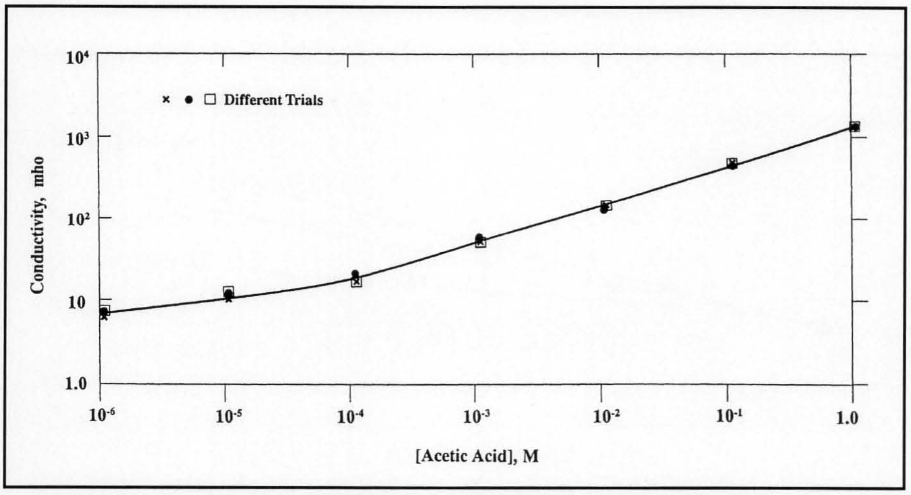

Figure 2. *A typical calibration curve.*

ductivity to facilitate analysis of results. A typical calibration curve is plotted in Figure 2 that indicates excellent reproducibility and linearity in the [H$^+$] range of 10^{-4} to 1 M. The data plotted in Figure 3 indicate that the results obtained with titrations versus conductivity measurements are within ±5% of each other.

Based on the experimental investigations followed for this study, the following procedure is recommended for the setup using CCl_4 and conductivity measurements:

1. Take 3 L of CCl_4 and add about 26 mL of glacial acetic acid. Mix well and use it as a stock solution. Titrate a 10-mL sample to determine the exact acid concentration. Adding 10 mL of water before titration is recommended.
2. Take 450-500 mL of the stock solution in the extraction cell.
3. Adjust the Vibro Mixer so that the agitator discs would be in the middle of each phase.
4. Take the same volume (450-500 mL) of water and add it quickly to the cell, pouring it over the top disc rather than directly into the organic phase. This will keep the transfer of acetic acid during start-up to a minimum.
5. Place the conductivity probe in the aqueous phase and start the agitator at a fixed voltage setting on the Variac (fixed amplitude).
6. Start conductivity measurements immediately, initially using one-minute intervals and later at longer intervals. Discontinue measurements when conductivity changes are insignificant over a ten-minute period.
7. Mix the two phases vigorously, preferably in a separatory funnel, to establish equilibrium. Measure the conductivity of the aqueous phase at equilibrium to determine $C_{a\infty}$.
8. Using the predrawn calibration curve (Figure 2), obtain the concentration values corresponding to the recorded conductivity values.
9. Take a sample of each phase and titrate to determine the acid content. Use these values to verify the mass balance and the concentration values obtained from the calibration curve.
10. Repeat twice more, each time with a fresh batch of CCl_4 stock solution, but a different Variac setting.
11. Plot $-\ell n\left(C_{a_\infty} - C_a\right)$ versus t for each of the three cases and determine k_a values from the slopes.

TYPICAL RESULTS AND DISCUSSION

Figure 4 is a plot of $-\ell n\left(C_{a_\infty} - C_a\right)$ versus t for three different agitation rates. The plots are linear, conforming to Eq. (3), and indicate that the slope (and hence the mass transfer coefficient) in each case increases with the increase in rate of

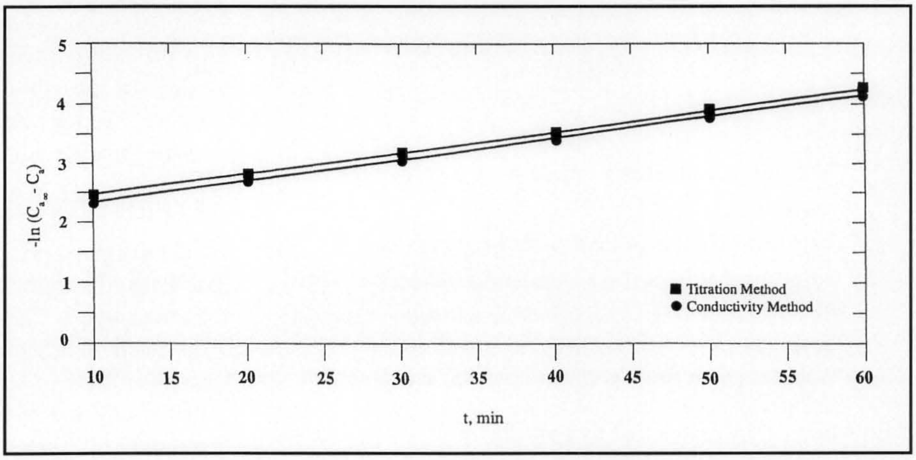

Figure 3. *Comparison of conductivity versus titration measurements for obtaining acid concentrations.*

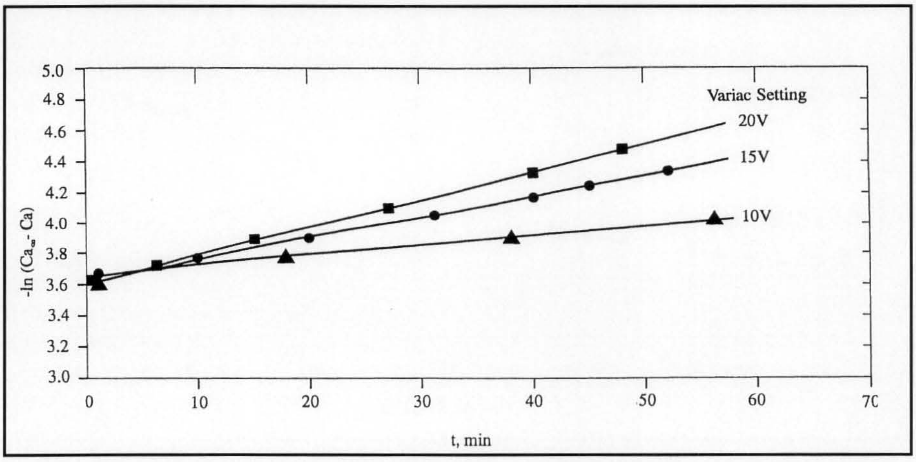

Figure 4. *Typical* $-\ell n\left(C_{a_\infty} - C_a\right)$ *vs. t plots.*

agitation. This is also depicted by the data (k_a versus Variac setting) plotted in Figure 5.

Figure 6 is a plot of k_a versus the aqueous phase viscosity. The changes in the phase viscosity were achieved by dissolving varying amounts of sucrose in water. The plot clearly indicates the adverse effect an increase in the viscosity has on the mass transfer coefficient.

CONCLUSIONS

- The class should be divided into various groups.
- Each group should follow steps 1 through 11 above.
- Various groups should use aqueous or organic phases of varying viscosities (the organic phase viscosity may be changed by adding various amounts of heavy mineral oil to the organic phase) and submit a formal report containing discussion on:
  - Comparison of $\ell n\left(C_{a_\infty} - C_a\right)$ versus t curves for various Variac settings
  - Dependence of k_a on liquid viscosity

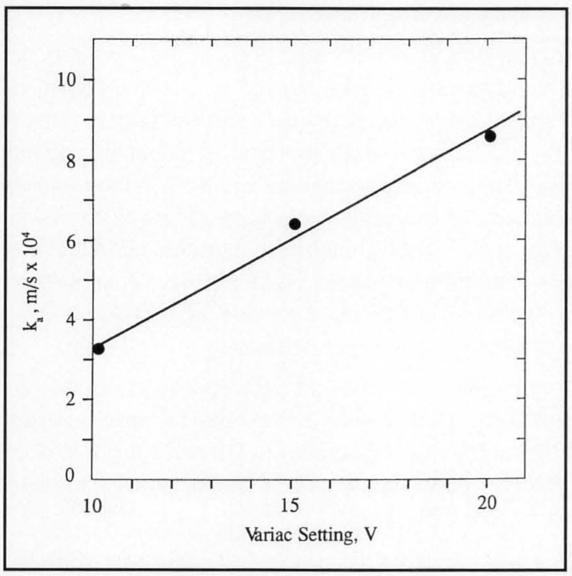

***Figure 5.** Dependence of k_a on degree of agitation.*

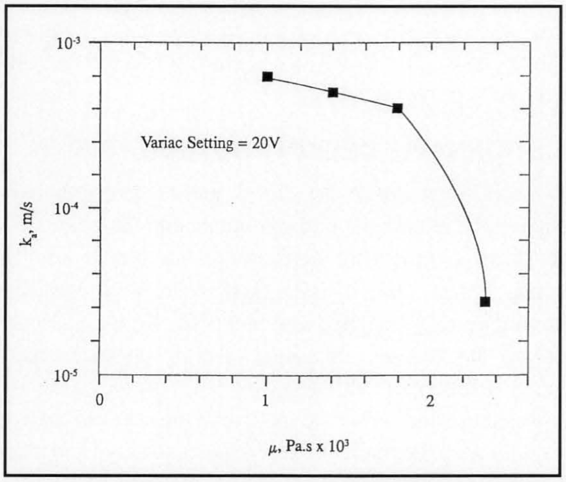

***Figure 6.** Dependence of k_a on viscosity of aqueous phase.*

POSSIBLE FUTURE PROJECTS

In future years the experiments may include investigation of a) the dependence of k_a on temperature, and b) the analysis based on the changes in acid concentration in the organic phase rather than the aqueous phase, *e.g.,* from the following equations:

$$V_o \frac{dC_o}{dt} = k_o A\left(C_o - C_{o_\infty}\right) \qquad (4)$$

NOMENCLATURE

A interfacial area (cross-sectional area of the beaker)
C bulk phase concentration of acetic acid at any time
k local mass transfer coefficient
t time
V phase volume

Subscripts

a aqueous phase
i initial
o organic phase
∞ equilibrium, final

ACKNOWLEDGMENTS

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ERRATUM

In the book review, *Chemical Thermodynamics: Basic Theory and Methods,* 5th ed., by Irving M. Lkotz and Robert M. Rosenberg, reviewed by Pablo G. Debenedetti in *Chemical Engineering Education,* **30**(1), 69 (1996), the sixth sentence of the fifth paragraph should read

> Similarly, the definition of an ideal gas as one satisfying PV = RT and, in addition, having a volume-independent energy is redundant.