

Mass Transfer Between Isobutanol and Water in Concurrent Flow Through a Packed Column

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Local and mean rates of transfer of isobutanol into the water-rich phase and of water into the isobutanol-rich phase were measured in concurrent upward flow through a column packed with glass spheres. The use of a two-component system permitted determination of the individual-phase coefficients. These are the first rate measurements for concurrent flow in a packed bed. Because the flow rates are not limited by flooding, much higher rates of transfer are attainable than in countercurrent flow.

Liquid-liquid extraction is carried out in industry principally in countercurrent flow through columns or in mixers and settlers. Mass transfer corresponding to a number of equilibrium stages may be accomplished in a single column, but the throughput is severely limited by the use of density difference as a driving force for one of the fluids. Mass transfer in a mixer-settler unit is limited to one equilibrium stage. A number of such units can be operated in series with countercurrent flow of raffinate and extract between the stages to provide a more complete extraction.

Mechanical agitators for mixer-settler units are generally bulky, inefficient, and expensive. On the other hand concurrent flow of the two liquid phases through a packed bed provides compact, efficient, and inexpensive mixing and dispersion. The power requirement for dispersion and mixing is supplied by the pressure drop across the bed. Since the flow rates are restricted only by the allowable pressure drop through the packed bed, rather than by density difference, very high throughputs are possible.

Most commercial applications of liquid-liquid extraction involve two relatively immiscible solvents and a distributed solute. The transfer process then involves three components, two transferring in one direction and the third in the opposite direction at any particular location. Colburn and Welsh (1) suggested that in fundamental investigations the solute be eliminated and transfer limited to two relatively immiscible solvents into one another. In a two-component system the equilibrium concentrations are functions of temperature and pressure only. Hence if the interface concentrations are assumed to be those of static equilibrium, the mass transfer coefficients for the individual phases can be determined from bulk concentrations.

This scheme has been utilized in a number of investigations of mass transfer in countercurrent flow through packed and spray columns and in other special types of contacting equipment (1, 2, 3, 4, 5, 6, 7, 8). No mention has been found in the literature of mass transfer rates in concurrent flow through a packed bed for either two- or three-component systems.

The isobutanol-water system was chosen for this investigation because of the prior work in other types of flow and because of experimental and analytical convenience. Transfer was investigated as a function of bed height and of the flow rates and inlet compositions of the individual phases in upward flow through a column packed with glass spheres.

PROCESS DESCRIPTION

The rate data were expressed in terms of volumetric coefficients for

mass transfer defined as follows:

$$\frac{d(Vy_a)}{dZ} = - \frac{d(Lx_a)}{dZ} = k_{aL} (c_{aL} - c_{aL}^*) = k_{aV} (c_{aV}^* - c_{aV}) \quad (1)$$

The interface concentrations are implied to be those of static equilibrium. Equation (1) further implies that longitudinal diffusion in the continuous phase and back mixing in both phases are negligible; therefore these effects will be incorporated in coefficients derived from Equation (1).

Mean coefficients over any segment of the column are defined by integrals

$$\bar{k}_{aV} = \frac{1}{\Delta Z} \int_{(Vy_a)_1}^{(Vy_a)_2} \frac{d(Vy_a)}{C_{aV}^* - C_{aV}} \quad (2)$$

A component and an over-all balance from the inlet to any height can be combined to give

$$V = \frac{(Vy_a + Lx_a)_0 - x_a(V + L)_0}{y_a - x_a} \quad (3)$$

It is apparent that both the local and mean coefficients can be determined from measurements of the composition as a function of height and the feed rates.

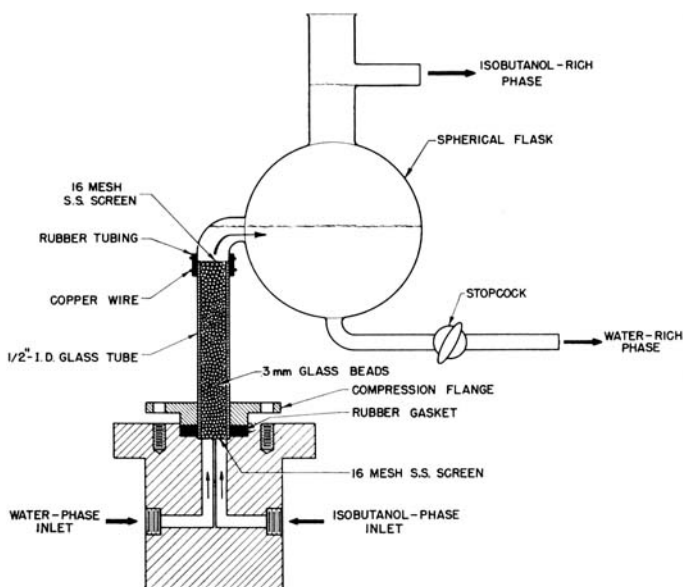


Fig. 1. Sketch of column and settler.

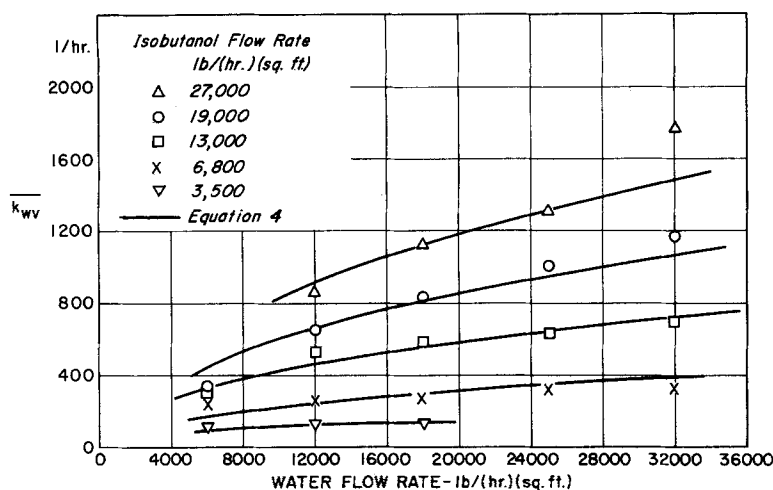


Fig. 2. Mean transfer coefficient for water in the isobutanol-rich phase.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental equipment consisted principally of feed reservoirs, proportioning pumps, a column inlet flange, several packed columns of different heights, and two settlers of different size. The reservoirs were calibrated, and the feed rates were determined by the change in level. Feed rates were controlled by adjusting the length of the pump strokes. Pulses were successfully dampened by air filled glass flasks in the discharge lines. The water rate was varied in five steps from approximately 6,000 to 32,000 lb./hr. (sq. ft. of column cross section) and the isobutanol rate in five steps from approximately 3,500 to 27,000 lb./hr. (sq. ft. of column cross section). The feed streams were maintained at $25.0 \pm 0.5^\circ\text{C}$. by passage through coils immersed in constant-temperature baths. The isobutanol and water passed separately through 15/64-in. channels in the aluminum inlet flange and entered the base of the packing at a center-to-center distance of 17/64 in. as shown in Figure 1. The columns were 1/2-in. I. D. gauge glass cut to the desired heights. The diameter of the column was chosen to permit high mass velocities without the use of an excessive amount of isobutanol. The packing consisted of 3-mm. glass spheres. The spheres were held in place by 16-mesh stainless steel screens at the top and bottom. Columns packed to heights of 1, 2, 4, and 6 in. were used. Round-bottom glass flasks with a short, hooked, side arm at the equator, as shown in Figure 1, were used as settlers. A 500-ml. flask was used for the higher flow rates and a 200-ml. flask for the lower rates. The level of the interface between the phases in the settler was maintained at the equator of the flask by manual adjustment of a stopcock in the outlet line at the base of the settler. The isobutanol-rich phase simply overflowed through the outlet at the top of the settler. Samples were taken at these two outlets.

Commercial grade isobutanol and distilled water were used. It was necessary to acidify the water to 0.0001 normal hydrochloric acid to avoid the formation

of emulsions in the packed column. The phases separated very quickly when acidified water was used. Under all of the conditions investigated an isobutanol-rich phase was dispersed in a continuous water-rich phase. The samples were analyzed by measuring the index of refraction to ± 0.00005 units with a precision refractometer. The uncertainty in the index of refraction is estimated to correspond to approximately ± 0.05 wt. % water in the water-rich phase and ± 0.15 wt. % water in the isobutanol-rich phase. Measured indices of the isobutanol and water agreed closely with the values in the literature. The small amount of hydrochloric acid did not change significantly the equilibrium compositions of 91.7 wt. % water in the water-rich phase and 16.7 wt. % water in the isobutanol-rich phase nor the indices of the refraction of either phase.

Preliminary tests revealed that the settler outlet compositions attained steady state values following a change after operating periods corresponding to four volumetric displacements of the settler. To be conservative samples were taken after seven displacements.

A water feed rate was established, and samples were taken for a series of five isobutanol feed rates. The flow rates for individual runs as determined by volumetric displacement did not correspond precisely to the five nominal values for

each phase owing to imprecision in the pump settings. The measured indices of refraction were corrected to the nominal isobutanol and water feed rates by translation parallel to curves through plots of the raw data vs. the flow rates. This procedure, as opposed to cross plotting, preserved the identity and scatter of the individual data points and, since the adjustments were small, introduced no appreciable error. The adjusted data were utilized in subsequent computations and correlations.

The flow rates of the individual phases change significantly as mass transfer takes place. All comparisons, plots, and correlations were made on the basis of the total isobutanol flow rate, that is the sum of the isobutanol flow rates in the two phases, and the corresponding total water flow rate. Pure water and pure isobutanol were fed to the column in most runs, and in this event the total flow rates of isobutanol and water were the same as the feed rates of the two phases. Details of the equipment, data, and processing of the data are given in reference 9.

MASS TRANSFER IN THE COLUMN OUTLET AND SETTLER

The degree of dispersion was visually very great in the packed column, and the phases separated very rapidly on leaving the packing. Mass transfer in the outlet line and settler would therefore be expected to be negligible compared with that in the packed column. This presumption was tested by several sets of experiments and analyses.

Differentiation of data for different feed compositions and packed heights yielded completely negligible values for the transfer outside the column. Outlet compositions obtained with the 500-ml. settler were undistinguishable from those obtained with the 200-ml. settler despite the 2 1/2 to 1 ratio of residence times and the approximately 2 to 1 ratio of settling areas. Extrapolation of outlet compositions to zero packed height and correlation of the raw data in terms of a coefficient for transfer in the separating system also both failed to indicate significant transfer outside the packed column.

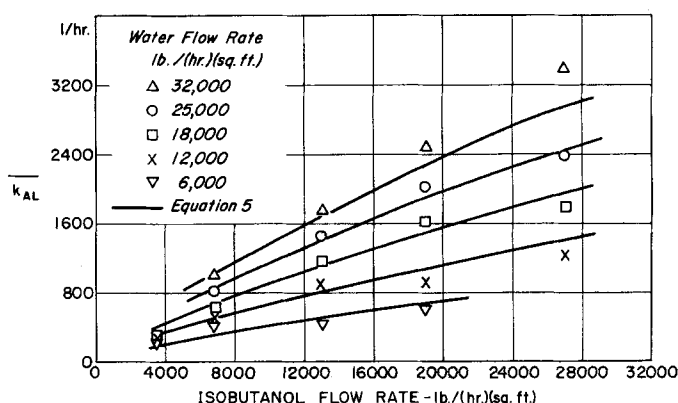


Fig. 3. Mean transfer coefficient for isobutanol in the water-rich phase.

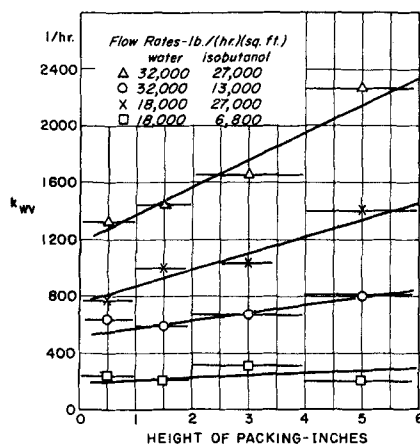


Fig. 4. Local transfer coefficient for water in the isobutanol-rich phase.

The compositions measured at the settler outlet were therefore subsequently treated as column outlet compositions.

RESULTS

Mean Coefficients

Mean transfer coefficients for the 6-in. packed column were computed from Equations (2) and (3) by graphical integration with the compositions for the several packed heights. These coefficients are exact as contrasted with coefficients based on external compositions only and the assumption of a logarithmic or other mean concentration difference.

The computed coefficients for water in the dispersed (isobutanol-rich) phase and for isobutanol in the continuous (water-rich) phase are plotted in Figures 2 and 3, respectively, as functions of the water and isobutanol flow rates. The curves in Figures 2 and 3 represent the equations

$$\bar{k}_{wv} = 0.00032 L^{1/2} V_o \quad (4)$$

and

$$\bar{k}_{AL} = 0.00057 L_o^{3/4} V_o^{3/4} \quad (5)$$

The even fractional exponents differ less than the standard errors from the exponents originally determined by bivariate, least square regression in logarithmic form. The coefficients of determination of the regression equations for Equations (4) and (5) are both 0.97.

It should be emphasized that the above coefficients are for a packed height of 6 in. and pure feed streams. However no effect of composition on the coefficients was discernable in experiments in which the feed composition was varied. The effect of packed height is considered in the next section.

Transfer coefficients for counter-current flow through packed columns have been correlated by expressions

similar to Equations (4) and (5) but with a variety of different exponents. The process of dispersion and mixing in either concurrent or countercurrent flow of two liquid phases through a packed column is insufficiently known to rationalize the observed values of the exponents of the flow rates in terms of mechanisms of transport with any assurance.

Owing to flooding, volumetric transfer coefficients for the isobutanol-water system are limited to about 100 (hr.)⁻¹ for countercurrent flow through any packing. As can be noted in Figure 3 coefficients as high as 3000 (hr.)⁻¹ were observed for concurrent flow. Even higher coefficients are apparently attainable with higher flow rates. Presumably, larger coefficients could be attained at the same flow rates with a smaller packing-to-column diameter ratio as found by Lewis, Pratt, and Jones (10) for countercurrent flow. Limited experiments in which the dampers were removed indicate that pulsations such as those produced by a reciprocating pump can be used to obtain still higher coefficients.

Both phases appeared to approach compositions corresponding to one equilibrium stage indicating that gross motion of one phase relative to the other was not a significant factor in the transfer process.

Local Coefficients

Average coefficients for the different segments of packed column were computed by dividing the incremental rate by the mean concentration difference over the increment. The variation in $(C^* - C)$ over the increments was so small that the computed coefficients were insensitive to the choice of a mean value.

These coefficients are plotted as bars in Figures 4 and 5 for representative combinations of water and isobutanol flow rates. The coefficient for water in the dispersed phase is observed to increase with distance through the column. This indicates that entrance effects (dispersion and/or mixing of the feed streams) persist throughout the entire 6 in. of packing. The variation of the coefficient for isobutanol with column height is obscured by the scatter in the data. This greater scatter is attributable to the smaller concentrations of isobutanol and the corresponding uncertainty in analysis.

The variation of the coefficients with distance through the column is of possible theoretical interest as an indication of mechanism but is of little practical interest because the coefficients are so large that equilibrium is approached closely in both phases in less than 6 in. under all conditions.

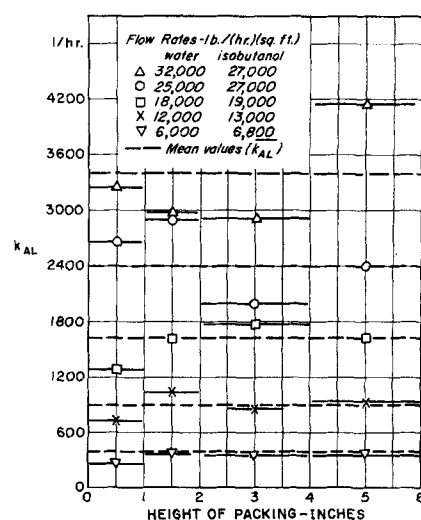


Fig. 5. Local transfer coefficient for isobutanol in the water-rich phase.

Coefficients for the Component-Rich Phase

Insofar as the interface concentration is equal to the equilibrium concentration the transfer rate is completely determined by the transfer coefficient for one of the two phases. The coefficients presented above are all for the phase in which the transferring component is the minor component. In principle the coefficients can also be computed for a component in the component-rich phase, for example for water in the water-rich (continuous) phase, as implied by Equation (1). However since the rate is fixed by the other phase, the difference between the bulk and equilibrium concentrations can independently and arbitrarily be made vanishingly small and the coefficient correspondingly large. Such anomalous values were indeed computed from the experimental data. These results indicate that the difference between the interface and equilibrium concentrations was significant in that phase under those conditions and hence suggest a method of determining the interface concentration and the interphase resistance.

CONCLUSIONS

Concurrent flow through a packed column is an effective means of obtaining high mass transfer coefficients in liquid-liquid systems. Near-equilibrium compositions can be attained in only a few inches of packing. The coefficients for both phases in the isobutanol-water system increase with the flow rates of both phases. Countercurrent flow rates and hence coefficients are severely limited by flooding, while concurrent flow rates and coefficients are limited only by the allowable pressure drop. This advantage must be

balanced against the necessity of multiple staging to obtain greater total transfer than one equilibrium stage in concurrent flow.

The assumption of an equilibrium composition at the interface is apparently not justifiable for a phase which approaches the equilibrium composition closely, while the rate of transfer into the other phase is still high.

ACKNOWLEDGMENT

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NOTATION

c = concentration, lb. mole/cu. ft.
 c^* = equilibrium concentration, lb. mole/cu. ft.
 k = local individual-phase coefficient for mass transfer based on packed volume, (hr.)⁻¹

$\bar{k}$ = mean individual-phase coefficient for mass transfer based on packed volume, (hr.)⁻¹
 L = flow rate of continuous (water-rich) phase, lb. mole/(hr.) (sq. ft. of column cross section)
 V = flow rate of dispersed (isobutanol-rich) phase, lb. mole/(hr.) (sq. ft. of column cross section)
 x = mole fraction of component in continuous (water-rich) phase
 y = mole fraction of component in dispersed (isobutanol-rich) phase
 Z = packed distance from inlet, ft.

Subscripts

A = isobutanol
 L = continuous (water-rich) phase
 o = at inlet to packing
 V = dispersed (isobutanol-rich) phase
 W = water
 α = any component

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Slow Compression Crushing of Single Particles of Glass

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Glass cylinders and spheres were crushed by slow compression in a hydraulic press. In all experiments the elastic energy stored in the specimen prior to fracture was measured. In some experiments the surface area of the resultant powder was measured by gas adsorption; in others the heat generation upon fracture was measured. The latter experiments show that considerable additional energy is fed into the fracturing specimen from the press. Local stress concentrations, and hence energy level at fracture, varied widely with particle shape. Calorimetric experiments suggest that real differences in crushing effectiveness, that is new surface per unit actual work done on the specimen, do occur. These differences are not due directly to the magnitude of the energy fed in from the press but rather to the effectiveness with which the stored or feed-in energy is used.

Single particles of glass spheres or cylinders, lying either on their flat or round side, were slowly compressed between the flat jaws of a hydraulic press until crushing occurred. Slow compression is defined here to be any form of compressive loading of a specimen at rates sufficiently slow to permit a static rather than dynamic analysis of the forces applied. The elastic energy stored in the specimen prior to fracture was calculated, and the sur-

face area of the resultant powder was determined by gas adsorption, or the heat generation in the sample was calorimetrically determined (1).

Axelson's (2,3) slow compression crushing experiments on quartz prisms showed that when a specimen happened to fail at low elastic energy concentration the surface area produced per unit stored elastic energy was as much as 17.6 times higher than when the specimen failed at high elastic energy concentration. Thus it appears that it might be possible to obtain more surface area production

from a given effort if crushing could somehow be induced at low-energy levels.

Particle shape and orientation were varied in the present work in order to attain a wide range in the stored elastic energy of the specimen at fracture.

GLASS SPECIMENS

Glass is isotropic, very nearly elastic to the point of fracture (7), has well-known properties, and furthermore flaws or strains can be observed either by ordinary or polarized light. Also the surface area of even small samples of glass can be measured by gas adsorption. Pyrex glass fabricated into small cylinders and spheres was used. Two sizes of cylinders and one size of spheres were used. The large glass cylinders were 0.5 in. high by 0.5 in. in diameter, and the small glass cylin-

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