

Effect of Wetting Characteristics of Packing on Efficiency of Packed Liquid-Liquid Extraction Columns

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PACKED TOWERS for extraction and stripping have been the subject of relatively extensive investigation. Methods have been suggested for correlating flooding data (4, 6); backmixing and holdup have been investigated (13, 20, 23, 24); the choice of the dispersed phase has been considered (1, 3, 9, 15, 21); flow rates have been studied (18); and the effect of chemical additives (5, 8) has been demonstrated.

In these investigations, and others, the wetting characteristics of the dispersed phase seemed particularly important. Appel and Elgin (1), Meisner and others (15), and Treybal (20, 21) showed that mass transfer coefficients are higher when the dispersed phase does not wet the packing, while Berg, Manders, and Switzer (3) found higher efficiencies with water dispersed regardless of the wetting characteristics of the packing. Appel and Elgin (1) and Sherwood, Evans, and Longcor (18) showed the column efficiency to depend almost entirely on the dispersed phase flow rate. Varteressian and Fenske (22) reported data on the extraction of dilute aqueous ethyl alcohol by benzene using nickel, copper, and aluminum Raschig rings; nickel rings gave the highest efficiency. Livingston (14) was granted a patent in 1940 on the selection of packings with correct wetting characteristics for higher contact efficiencies in packed towers.

A few investigations have been designed to test the effect of wettability in other types of equipment than packed columns. For example, Garner, Ellis, and Hill (7) carried out work on sieve plate columns in which plate wettability was one of the variables, while Sobotik and Himmelblau (19) studied wettability in pulse columns.

Most of the work related to the effect of wettability in packed columns has been of a qualitative nature. Because more information on the effects of packing wettability seemed desirable, it was decided to study the effect of a strong hydrophobic and a weak hydrophilic packing material on the efficiency of liquid extraction in a packed tower as a function of the flow rates in each phase, and to vary both the direction of solute transfer and the choice of the continuous phase. The water-acetic acid-methyl isobutyl ketone system was chosen for this investigation, since considerable equilibrium data were available (2, 10, 11,

16, 18) for this system. Ceramic and plastic Raschig rings (and mixtures of the two) and ceramic and plastic Berl saddles were selected as the hydrophilic and hydrophobic (more truthfully, organophobic and organophilic) materials, respectively.

DESCRIPTION OF APPARATUS

Extraction was carried out in a 3-inch borosilicate glass column constructed of a straight 4-foot section of pipe with a tee at the bottom and a double-tee overflow arrangement at the top. The bottom tee housed a liquid interface detector unit. The packing within the column was supported by a circular piece of 4-mesh wire cloth attached to and below the ketone distributor. A similar piece of wire cloth attached to and above the water distributor kept the plastic packing from floating when the water phase was continuous. Polyethylene tubing was used for all piping. Connections were made with nylon or stainless steel fittings. The flow of each phase to the column was indicated by rotameters. Four 40-gallon stainless steel tanks were used to contain the fresh and spent ketone and water phases.

The column was packed with $\frac{3}{8}$ -inch ceramic Raschig rings purchased from the Maurice A. Knight Co., $\frac{3}{8}$ -inch polyethylene Raschig rings made by cutting $\frac{3}{8}$ -inch polyethylene tubing into $\frac{3}{8}$ -inch pieces, mixtures of the two, $\frac{1}{2}$ -inch ceramic Berl saddles, and $\frac{1}{2}$ -inch polyethylene saddles specially molded to the pattern of the ceramic saddles by Dumond, Inc., San Angelo, Tex.

The methyl isobutyl ketone was supplied through the courtesy of the Union Carbide Chemicals Co., and was the equivalent of reagent grade. The acetic acid was also reagent grade. Distilled water was used for all runs.

PROCEDURE

Although the flow rates of both the continuous and discontinuous phases affect the efficiency of transfer, a more critical variable is the ratio of the two phase flow rates (21). For this investigation, the total flow rate (the sum of the flow rates for both phases) was held approximately

constant in the range of 3500 to 4300 pounds per hour per sq. foot, which was equivalent to 460 to 600 gallons per hour per sq. foot (the range in which the variation of HTU with total flow rate was found negligible), and the ratios of the flow rates were allowed to vary between 0.2 and 7.

For this system, data were taken with both phases dispersed. Only one system was considered; therefore the physical properties of the system were not variables. Runs were made with the direction of acid transfer both from the ketone to the water and from the water to the ketone phases. The interface was maintained as close as possible to the top, or bottom, of the packing, depending on the continuous phase, but not dipping into the packing on slight fluctuations.

The range of concentrations used in extraction affects both the required column height and the validity of the assumptions made to calculate the HTU values from the experimental data. If extraction is performed at low concentrations where the equilibrium line for the ternary is more nearly a straight line and arithmetic rather than log mean averages of the concentration change are acceptable, the equations used to calculate the results can be simplified considerably without introduction of appreciable error (21). In this work the raffinate inlet concentration of acetic acid was restricted to a maximum of approximately 10% by weight, and the outlet concentration to a minimum of approximately 1% by weight. The upper limit satisfied the assumptions of the equations used, while the lower limit was dictated by the analytical error introduced in titrating extremely low concentrations with a standard 50-ml. buret.

The samples taken during each run were analyzed for acetic acid by titrating with a standard sodium hydroxide solution in a semiethanolic medium. Both water and ketone were always mutually saturated in each other. Runs were made at $76 \pm 3^\circ$ F. Equilibrium data taken in this work agreed well with those of previous investigators.

CALCULATIONS OF RESULTS

Since a packed extraction column operates as a counter-current extractor with differential concentration changes throughout the height of the column, the efficiencies of various packings for this investigation were reported in terms of HTU, although the over-all mass transfer coefficient, Ka , might just as easily have been used. The equations used to calculate the number of transfer units were (2):

$$N_{tOE} = \int_{W_{E2}}^{W_{E1}} \frac{dW_E}{W_E^* - W_E} + \frac{1}{2} \ln \left(\frac{1 + rW_{E2}}{1 + rW_{E1}} \right) \quad (1)$$

$$N_{tOR} = \int_{W_{R2}}^{W_{R1}} \frac{dW_R}{W_R - W_R^*} + \frac{1}{2} \ln \left(\frac{1 + rW_{R2}}{1 + rW_{R1}} \right) \quad (2)$$

These equations are based on the assumptions of completely immiscible solvents and relatively dilute solutions. In the operation of the column used to obtain the data presented here, to approximate the condition of immiscibility, the water and ketone phases were mutually saturated with each other before the data were taken. The extract phase (E) refers to the phase into which the solute was being extracted and the raffinate phase (R) refers to the phase from which the solute was being extracted.

Various mathematical tricks resulting in errors in an "acceptable" range can be employed to integrate Equations 1 and 2 analytically, but graphical integration with a planimeter was used to calculate the integral term as follows. The equilibrium line was plotted as pounds of solute per pound of solute-free phase. The operating line for

Table I. Individual Film Coefficients for Ceramic and Plastic Raschig Rings

Type of Rings	Cont. Phase	Direction of Transfer	H_k , Inches	H_w , Inches
Ceramic	W	K \rightarrow W	11	5
	K	K \rightarrow W	6	16
	W	W \rightarrow K	10	0.25
	K	W \rightarrow K	8-11	9-11
Plastic	W	K \rightarrow W	6	6
	K	K \rightarrow W	0	16
	W	W \rightarrow K	9-12	11-20
	K	W \rightarrow K	8	25

the run under consideration was plotted on the same piece of graph paper and the concentration driving force terms, $(W_R - W_R^*)$ and $(W_E^* - W_E)$, were determined. On a second sheet of graph paper, W_E (or W_R) was plotted *vs.* $[1/(W_E^* - W_E)]$ or $[1/(W_R - W_R^*)]$ and the area under the curve from W_{E1} to W_{E2} (or W_{R1} to W_{R2}) was determined with the aid of the planimeter.

The height of the packing in the tower, which was long enough to minimize end effects, was obtained by measuring the distance between the lower packing support and the top of the packed bed. Although there is apparently no simple theoretical basis for correlating the data collected, data in the literature (21), as well as data collected in this investigation, have been shown to fall approximately on a straight

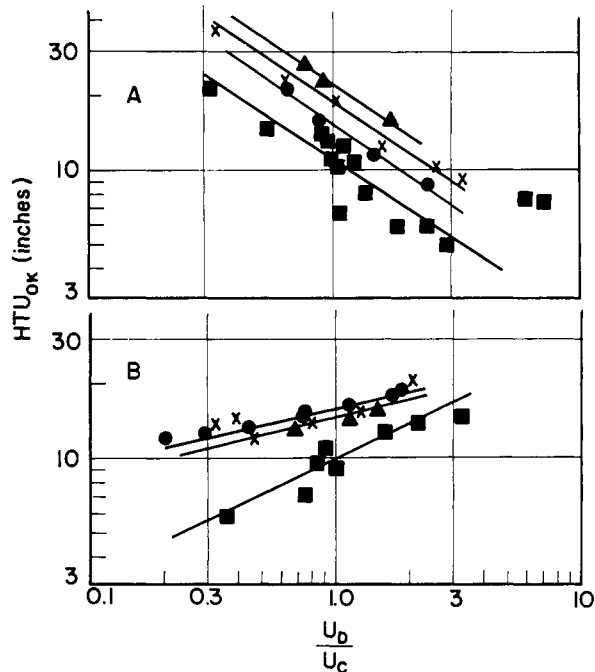


Figure 1. Extraction of acetic acid in column packed with Raschig rings

HTU shown for various combinations of rings
 Extraction direction ketone to water
 A Continuous phase ketone
 B Continuous phase water
 ■ Plastic Raschig rings
 X Ceramic Raschig rings
 ● Bottom half plastic, top half ceramic Raschig rings
 ▲ Random mixture of plastic and ceramic Raschig rings

line if log-log graph paper is used as in the accompanying figures.

To determine individual film resistances for the Raschig rings (the packing for which sufficient data were obtained), values of HTU_{OK} were plotted on arithmetic paper vs. the extraction factor $[M(U_{ketone}/U_{water})]$. According to the equation

$$HTU_{OK} = H_k + [M(U_{ketone}/U_{water})]H_w \quad (3)$$

which is valid only under the usual simplifying assumptions (21), the intercept of such a graph would be a measure of H_k while the slope would be H_w . Because of the restrictive nature of the conditions underlying Equation 3, the values of H_k and H_w in Table I can only be considered approximations, even though M varied only from 0.67 to 0.77 and the plots appeared in general to be reasonably well fitted by straight lines (with considerable scatter for about half the cases).

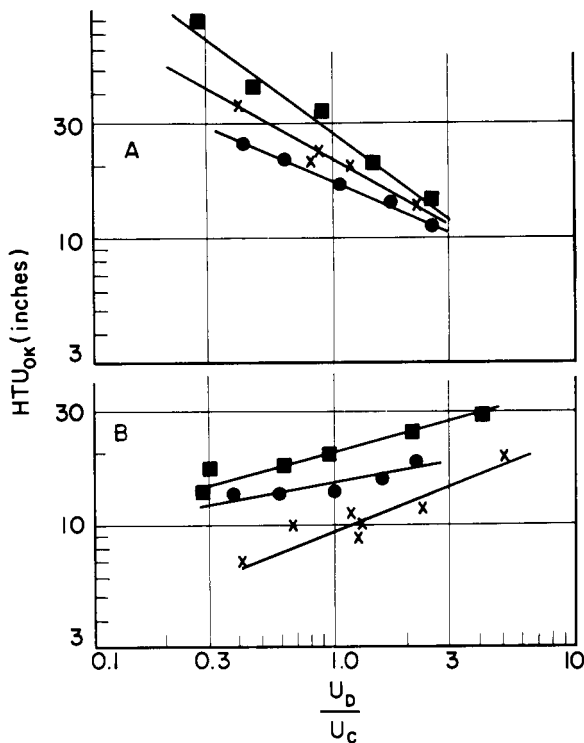


Figure 2. Extraction of acetic acid in column packed with Raschig rings

HTU shown for various combinations of rings
 Extraction direction water to ketone
 A. Continuous phase ketone
 B. Continuous phase water

RESULTS AND DISCUSSION

The data collected in the course of this investigation have been evaluated as HTU_{OK} and plotted vs. the ratio of the flow rates of the discontinuous phase to the continuous phase in Figures 1 and 2. The original data are available (17). It is difficult to estimate the error involved in the HTU_{OK} values. Duplicate runs gave variations in the neighborhood of 20% as a maximum; however, this was an extreme, and on the average the error was ± 5 to 10%. The material balance errors were all less than 6% and in 90% of the cases were within 2% accuracy.

Packing Materials. The influence of the packing material

surface roughness and wettability was apparently controlled to a greater extent than originally anticipated by the direction of solute transfer rather than by the nature of the continuous phase. For acid transfer direction from the ketone phase to the water phase, the polyethylene Raschig rings were appreciably more effective than the ceramic rings or mixtures of the two as shown in Figure 1, whether the water phase or the ketone phase was continuous.

For extraction in which the direction of transfer was from the water phase to the ketone phase (Figure 2), just the opposite effect held true; the plastic rings were decidedly less efficient than either the ceramic rings or mixtures of the two. As a general rule (for an exception examine Figure 2, A), when the column was packed with the bottom half filled with polyethylene rings and the top half filled with ceramic rings, the calculated efficiencies fell between the efficiencies of the all-ceramic and the all-plastic rings. Figure 1 also shows data taken for the column packed with a random mixture of the two rings for extraction from the ketone phase to the water phase. The efficiency of the mixed packing was either less than or approximately equal to the efficiency of the all-ceramic rings, and distinctly poorer than the efficiency of the all-plastic rings.

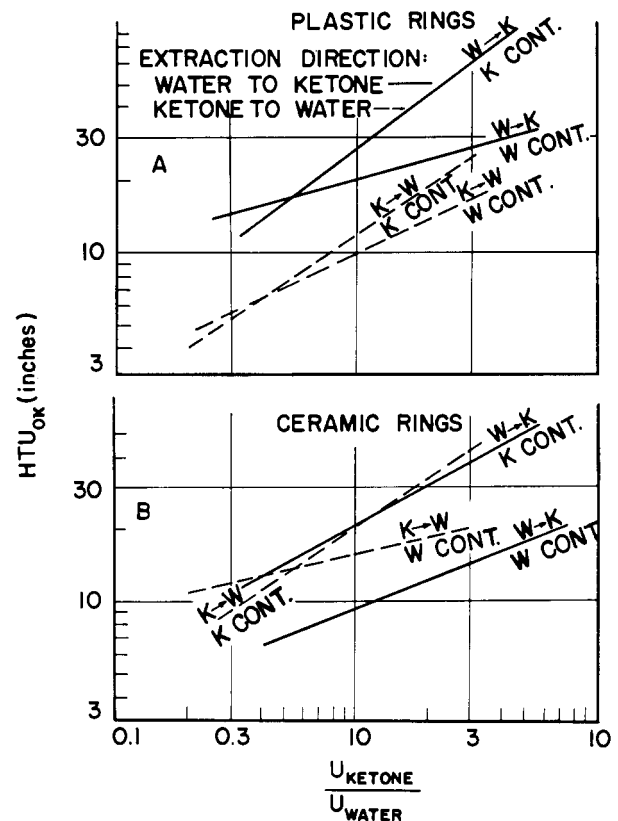


Figure 3. Influence of continuous phase on extraction in column packed with Raschig rings

We can conclude for a similar experimental setup that if acetic acid is to be extracted from methyl isobutyl ketone into water, plastic rings will give decisively lower values of HTU for any given flow ratio, no matter what the continuous phase is. A similar situation was true in pulse columns filled with plastic and stainless steel plates (19).

Choice of Continuous Phase. Should the continuous or the discontinuous phase wet the packing? In this system, for each type of packing, greater efficiencies were discovered when the water phase was continuous (except for U_{ketone}/U_{water} values greater than 2 in Figure 1) in contrast to Berg,

Manders, and Switzer (3). This can be seen by mentally imposing the reversed image of Figure 1, B, on 1, A, and Figure 2, B, on 2, A. If ceramic rings are available and the question of the continuous phase arises, Figure 3, B, shows that the water phase should be continuous if the transfer is from water to ketone; for transfer from ketone to water, in the higher range of $U_{\text{ketone}}/U_{\text{water}}$, water is the best continuous phase, while in a lower range, ketone becomes more effective. If plastic rings are available, the situation is a little more complex, and is shown in Figure 3, A, although in general water is still the best continuous phase.

In the case of ceramic rings, which are wet almost as well by the ketone as by the water, it was somewhat surprising to find water to be so clearly the more effective continuous

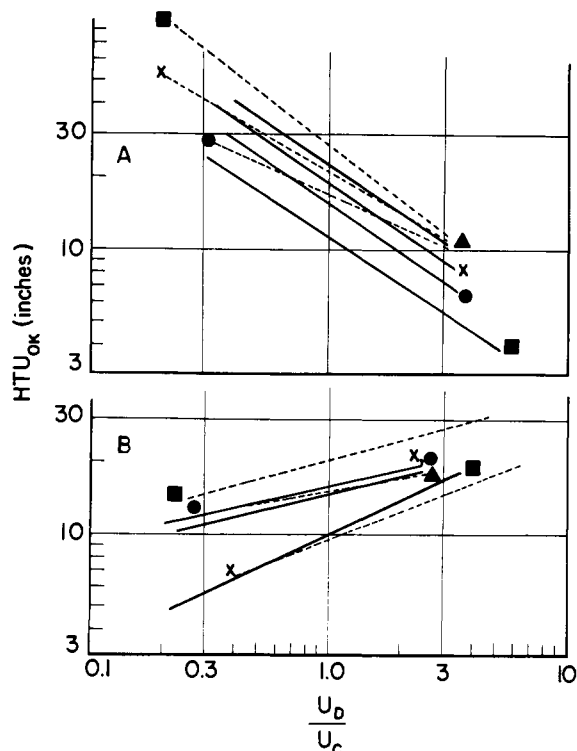


Figure 4. Effect of direction of transfer on extraction in column packed with Raschig rings

A. Continuous phase ketone
 B. Continuous phase water
 Extraction direction
 — Ketone to water
 --- Water to ketone

phase. It was also unexpected, in view of previous work (1, 15, 21), to find for the case of the plastic rings, which are definitely preferentially wet by the ketone, that having the ketone phase continuous was not clearly superior, and, in fact, was less effective, except for low $U_{\text{ketone}}/U_{\text{water}}$ ratios. It appeared therefore, that selection of water as the continuous phase was the most suitable, whether the packing was ceramic or plastic and was or was not wet by the water for this particular system.

Direction of Transfer. For each packing type, greater or equal efficiencies resulted when the extraction direction was from the ketone phase to the water phase (for either phase dispersed). For ceramic rings, when the ketone phase was continuous, and for a half and half mixture when the water phase was continuous, the direction of solute transfer had little if any effect. For all the other packings, the ketone to water transfer direction was markedly more efficient, in agreement with the work of Licht and Conway (12) and Sobotik and Himmelblau (19) among others. Figure 4 illustrates the effect of the direction of solute transfer. The

actual data points have not been shown, for the sake of clarity.

Effect of Flow Ratio. The effect of flow ratio is clearly shown in Figures 1 and 2, and as expected, has a distinct influence on the values found for HTU. The best HTU_{OK} values were obtained at $U_{\text{ketone}}/U_{\text{water}}$ flow ratios of about $1/4$, while the poorest values were at high flow ratios. The lines in Figure 1 and 2 indicate the estimated linear trend of the HTU values.

Comparison of Results with Others. It is difficult to find operating conditions reported in the literature directly comparable to these described here. The HTU_{OK} calculated from the data taken during this investigation are both higher and lower than those reported by Sherwood, Evans, and Longcor (18); however, Sherwood's results are calculated from data taken at more widely varying total flow rates and with slightly larger packing ($1/2$ -inch nominal size Raschig rings). These data are compared in Table II. The values shown in Figures 1 and 2 are about the same as those experienced for spray towers but higher than those found for pulse columns in the general range of corresponding flow rates.

Berl Saddles. Figure 5 illustrates the results obtained by using Berl saddles as the column packing. The trends just discussed for the rings apply equally well to the saddles. The slopes of the lines in Figure 5 are less than those of Figures 1 and 2, indicating that the flow ratio of the phases has less influence on the extraction efficiency in a column packed with saddles than with rings. The HTU values found in this work and those of Sherwood and others (18) are compared in Table II. The absolute values of the HTU for the saddles are higher than those for the rings, and consequently no data were collected for the various combinations of plastic and ceramic saddles. The results would be expected to follow the trends described for the rings.

Individual Film Coefficients. Keeping in mind that the individual film coefficients in Table I are only approximations, we can draw certain conclusions concerning the most effective type of packing and continuous phase for various levels of the extraction factor [$M(U_{\text{ketone}}/U_{\text{water}})$]

Table II. Comparison of HTU Values

U_D/U_C	Transfer direction. Water to ketone Continuous phase. Water	
	HTU, Inches	
	This invest. ^{a,b}	(18) ^{a,c}
	$3/8$ -inch ceramic rings	$1/2$ -inch carbon rings
4	13.2	27
2	11.4	16-20
1	9.2	10.5
0.57	7.7	7.5-10
	$1/2$ -inch ceramic saddles	$1/2$ -inch ceramic saddles
4	15	27
2	14	14.5
1	13	7.1
0.57	12	6.5

^a Interpolated values. ^b Total flow 60-80 cu. ft./ (hr.) (sq. ft.), equivalent to 3500 to 4300 lb./ (hr.) (sq. ft.). ^c Total flow 20-100 cu. ft./ (hr.) (sq. ft.).

in this work. For extraction from ketone to water with a low value of the extraction factor, the setup of plastic rings with ketone the continuous phase would give the lowest over-all HTU for this system, since H_k is negligible. On the other hand, at high values of the extraction factor the

plastic rings with water as the continuous phase would be a more appropriate arrangement. Similarly, with the extraction proceeding from water to ketone, at high extraction factors ceramic rings with water the continuous phase appears to be the best because of the low value of H_w . Arrangements for intermediate conditions and other situations can be similarly ascertained.

Effect of Wetting on Mass Transfer. Since it has been demonstrated that the wetting characteristics of the packing affect the mass transfer rates and consequently the extraction efficiencies in packed columns, an obvious question is:

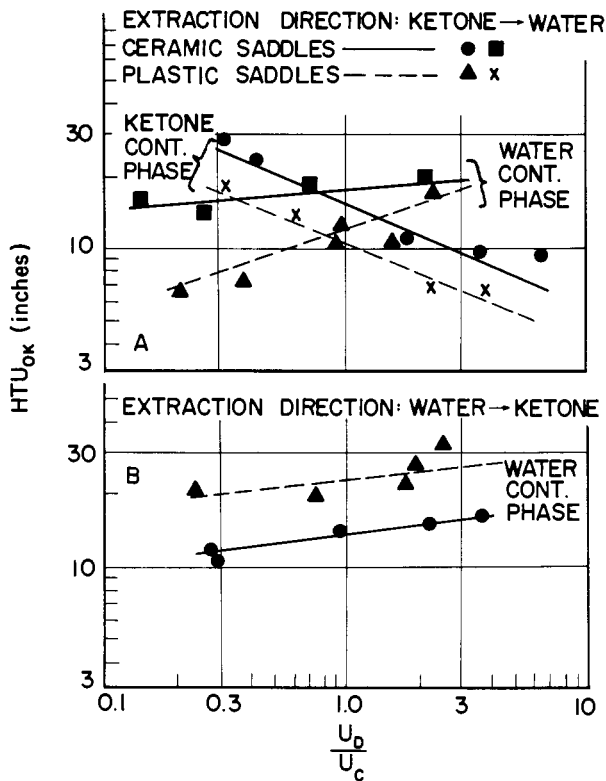


Figure 5. Extraction of acetic acid in column packed with Berl saddles

How or why does this effect take place? The controllable and measured quantities in a packed column have little to do with the basic factors which actually govern mass transfer in the column, such as hydrodynamic conditions and concentration gradients. Thus it is only possible to speculate concerning the influence of wettability of the packing rather than give a clear-cut answer based on concrete evidence. Whether or not the continuous phase wets the packings (or the discontinuous phase does not wet it) seems to have little to do with the over-all magnitude of the extraction efficiency. When the direction of transfer is from ketone to water, the plastic packing is the best; when it is water to ketone, it is the worst.

The influence of wetting on the individual film coefficients is a little clearer. For extraction from ketone to water, Table I shows for ceramic rings, which are wet almost as well by the ketone as by the water, that the resistance to transfer is higher in the discontinuous phase, whichever it is. For plastic rings, which are wet only by the ketone, the resistance is all in the water phase when the water is the discontinuous phase (being essentially zero for the continuous ketone phase), but when ketone is made the discontinuous phase, the wetting characteristics of ketone seem to prevent the value of H_k from exceeding that of the continuous water phase. For extraction from water to ketone using

ceramic rings and a continuous water phase, H_w was reduced materially. For the same conditions, changing to plastic rings increased H_w by a factor of 50 to 100. These wetting effects in the continuous phase significantly improved the effectiveness of transfer in that phase, probably through improved convective transfer, but an over-all improvement in transport for any given extraction factor did not necessarily result because of countervailing changes which tended to reduce transport in the discontinuous phase.

NOMENCLATURE

- H_k, H_w = height of transfer unit for individual film coefficients, ketone or water, respectively, inches
 HTU_{OK} = height of transfer unit based on over-all driving force and ketone phase, feet or inches
 M = slope (average) of phase equilibrium line, lb. acetic acid per lb. ketone acid-free divided by lb. acid per lb. water acid-free
 N_{tOE}, N_{OR} = number of transfer units based on over-all driving force and extract (E) or raffinate phase (R)
 r = ratio of molecular weight of solvent-free solute to molecular weight of solute
 U_C, U_D = mass flow of continuous (C) or discontinuous (D) phase, lb./hr.
 U_{ketone}, U_{water} = mass flow of ketone or water phases, lb./hr.
 W_E, W_R = concentration of solute in bulk extract (E) or raffinate (R) phase, lb. solute/lb. solute-free solvent
 W_E^*, W_R^* = hypothetical concentration in equilibrium with bulk concentration in opposite phase, lb. solute/lb. solute-free solvent

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