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A New Type of Continuous Countercurrent Extraction: An Extractor with Two Continuous Phases*

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Abstract

A continuous countercurrent extractor in which both solvent phases move as continuous streams was constructed and studied. Fibrous strands, e.g., cotton-rayon yarn, were utilized as "wall-less" tubings for the hydrophilic solvent (heavy phase) and the light phase mov d in a countercurrent manner through the annular spaces of the column. With the model system, caffeine–water–ethyl acetate, the highest efficiency demonstrated was HETS = 1.1 in. A mixture of caffeine and nicotinamide ($\beta = 4$) can be separated to a purity of 4000:1 or higher in the solvent system of ethyl acetate:water by the use of a specially designed feed stage located at the middle of the column. A colorful demonstration of this process utilized two dyes, Sudan black B (purple) and *p*-phenylazophenol (yellow) in the solvent system of toluene:*n*-hexane (1:3) vs methanol:water (4:1). The extractor is free of emulsion problems as demonstrated by the inclusion of Tween 80 in the heavy phase of the ethyl acetate–water system. The extractor can be run unattended indefinitely.

INTRODUCTION

Many types of continuous countercurrent extractors have been studied extensively (*1–6*). Those of simple construction are of low efficiency (HETS > 1 ft) whereas those of reasonably high efficiency (HETS = 2 to 5 in.) are provided with internal mixing mechanisms (*1*, *7*). All of these

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extractors are operated with a continuous solvent phase and a dispersed phase; consequently, they have the common disadvantage of loss of function whenever emulsion occurs. I wish to report that it is a rather simple matter to construct an extractor in which both solvent phases flow as continuous streams. Because of the absence of mechanical mixing between the two solvents, there is no danger of emulsification, as has been demonstrated by the inclusion of Tween 80 in one of the solvents.

It is well known that the driving force for the flow of liquids through a porous medium, i.e., capillaries, is surface tension. Since surface tension is only a special case of interfacial tension, one would expect that water would flow through a wick, e.g., cotton yarn, even if the yarn is immersed in a water-immiscible liquid like benzene. In fact, it can be easily demonstrated that a paper chromatogram for which water or aqueous methanol is used as the mobile solvent can be developed in a jar filled with either air or a lipophilic solvent like benzene or ethyl acetate. Based on this observation, the extractor reported here was designed and studied.

Essentially, a hydrophilic solvent, e.g., water or aqueous methanol (heavy phase), is allowed to flow downward through a number of fibrous strands, e.g., cotton-rayon yarn, packed loosely in a column. The column, i.e., the annular spaces, is filled with a lipophilic solvent, e.g., ethyl acetate or *n*-hexane (light phase), which is made to move upward under a slight hydrostatic head. The yarn strands behave as if they were "wall-less" tubings, and a highly efficient extraction process takes place. When a mixture of two compounds dissolved in the heavy solvent is fed to the middle of a column (center feeding) by means of a specially designed feed stage, the two components can be satisfactorily separated in a manner similar to the counter-double-current distribution (CDCD) of Post and Craig (*8*). Thus a highly efficient separation process can be realized with simple equipment.

CONSTRUCTION AND OPERATION OF THE EXTRACTOR

Figure 1 shows diagrammatically the extractor for end feeding. (All parts of the extractor are made of Pyrex glass, unless otherwise stated.) It is essentially a spray-tower type of extractor (*9*, *10*), except that the column is packed loosely with an assemblage of fibrous strands. Woolworth cotton (25%)-rayon (75%) yarn, No. 612 (diam = 3 mm when wet) was used. Unless otherwise stated, the column is packed with nine strands of the yarn per square centimeter of cross-sectional area.

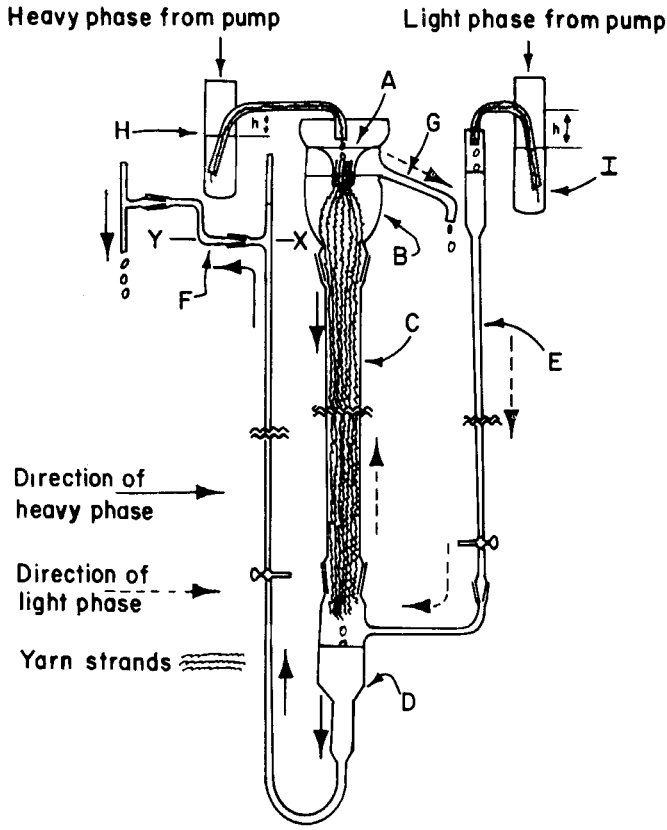

FIG. 1. Construction of extractor for end feeding. (A) Heavy-phase distributor, (B) light-phase collector, (C) column, (D) separator, (E) light-phase inlet tube, (F) heavy-phase exit tube, (G) light-phase exit tube, (H) flow rectifier (heavy phase), and (I) flow rectifier (light phase).

The two solvent phases are pumped by a Buchler micropump from their reservoirs into the two flow rectifiers, H and I. The micropump is a metered pump which runs at 2 cycles/min, i.e., it makes two deliveries every minute. The rectifiers are designed to convert this pulsating flow into continuous flow. The construction consists of an inverted U-tube sealed into a tube of 1 in. diameter, 4.5 in. long as shown. Inside the U-tube are placed two strands of the yarn, which act as a wick for continuous transfer of the liquid inside the 1-in. tubes to the inlets of the two solvents into the extractor. The flow rate through the yarn strands varies inversely with the

"hydrostatic head," h, as shown. The level of liquid inside the 1-in. tube remains constant as long as the pump rate remains constant.

The upper ends of the yarn strands in Column C are packed tightly into the short tubing of the heavy phase distributor, A, as shown. The short tubing has an inside diameter equal to 3/5 that of the column diameter. The heavy phase, after moving through this short tubing, distributes itself to the yarn strands, as can be demonstrated by allowing a colored solution, e.g., aqueous ammonical cupric sulfate, to flow down the yarn strands. The column (i.e., the annular spaces) is filled with the light solvent. As the light solvent is admitted continuously to the column through the inlet tube, E, it moves upward to the light phase collector, B, and thence overflows through the light phase exit tube, G. The heavy phase, after moving down through the "wall-less tubings" (yarn strands), collects at the bottom of the separator, D, and under the hydrostatic pressure of the light phase in the column, flows out through the heavy phase exit tube, F. Tube F is Z-shaped with ground glass joints at both ends. Turning the tube around XY as an axis permits raising or lowering of the elevation at which the heavy phase exits. This elevation controls the level of the interface in the separator, D.

To start the operation of the extractor, the entire extractor is filled with solute-free heavy phase by admitting the latter manually through the light phase inlet tube, E. The column is then drained by removing the Tube E. This is to insure that the yarn strands are saturated with the heavy phase. The column is then filled with the light phase by admitting the latter manually through its inlet tube, E. Both solvents are now pumped into Rectifiers H and I, which have been filled with the respective solvents. One of the solvents contains a solute (feed solution) and the other is solute-free (extractant). The position of the heavy phase exit tube, F, is adjusted so that the interface in the separator is in the middle and both exits deliver the effluents. The position of the interface fluctuates slightly during a run, usually only to 1 to 2 in. Adjustment of the elevation of Tube F to control the position of the interface is necessary during the first few hours of a run, but no further adjustment is needed after the extractor has been run overnight. In the present experimentation, the extractor was run completely unattended for 6 days.

To construct an extractor designed for center feeding, a "feed stage" is introduced to the middle of the column. The design of the feed stage is is shown in Fig. 2. Two columns are joined to the feed stage. The lower end of the upper column is joined to the feed stage at A, i.e., the feed stage replaces the Separator D, illustrated in Fig. 1. The top of the lower column

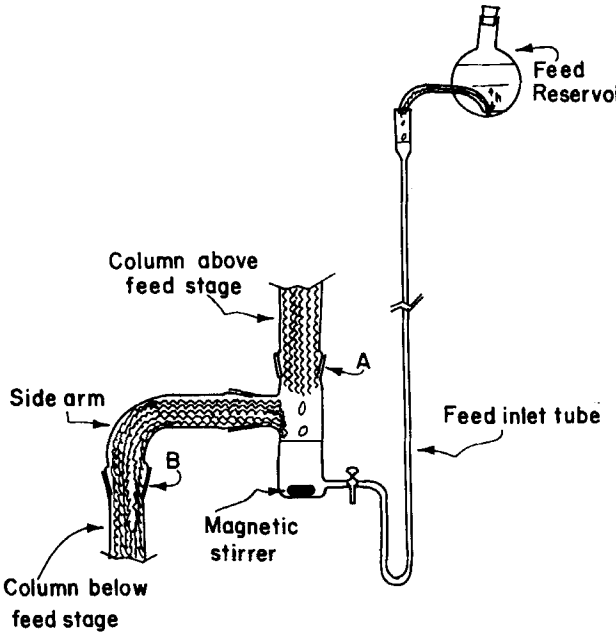

FIG. 2. Design of feed stage.

is joined to the feed stage at B, i.e., the side arm of the feed stage replaces the light phase collector and heavy phase distributor of the extractor illustrated in Fig. 1. The yarn strands of the lower column extend through the side arm into the upright container of the feed stage as shown. A tight-fitting polyethylene ring (not shown) serves to press the ends of the yarn strands against one side of the upright container. The feed inlet tube is U-shaped and is joined to the bottom of the upright container. Instead of using another metered pump to introduce the feed solution into the column, a specially designed feed reservoir was used for this purpose. It is a round-bottom flask with an arc-shaped tube sealed into it, as shown. A wick, i.e., a yarn strand, is placed inside the tube and the flask is tightly stoppered with a polyethylene stopper. As the feed solution flows out through the wick, air bubbles enter the flask through the same arc-shaped tube and rise into the air space above the liquid. The rate of flow is governed by the height, h, as shown in the figure and can be adjusted by changing the inclination of the flask. This device incorporates the principles of the flow rectifier (described above) and the Mariotte bottle. As the

heavy phase from the upper column drips to the bottom of the feed stage, it is mixed with the feed solution (also in the heavy phase) by a magnetic stirrer which rotates slowly. The yarn in the side arm acts as a wick to transfer the heavy phase to the lower column. Therefore, the entire extractor functions as one column with the feed stage at its middle.

DETERMINATION OF DISTRIBUTION COEFFICIENTS

Most of the experiments reported here dealt with extraction of caffeine from an aqueous solution into ethyl acetate. The distribution coefficient of caffeine between ethyl acetate and water was first determined. The distribution was carried out in separatory funnels at a room temperature of 23°C as well as in constant temperature rooms of 5 and 37°C. Aliquots of each phase were evaporated to dryness in a water bath at 60°C with the aid of a gentle current of air. The evaporation residues were dissolved in 95% ethanol, and the absorbance at 272 nm of the ethanolic solution was measured in a Beckmann Model DU spectrophotometer. The distribution isotherm at 23°C, shown in Fig. 3 (Curve A), is a straight line up to a concentration somewhat greater than 1.0 mg of caffeine/ml of aqueous

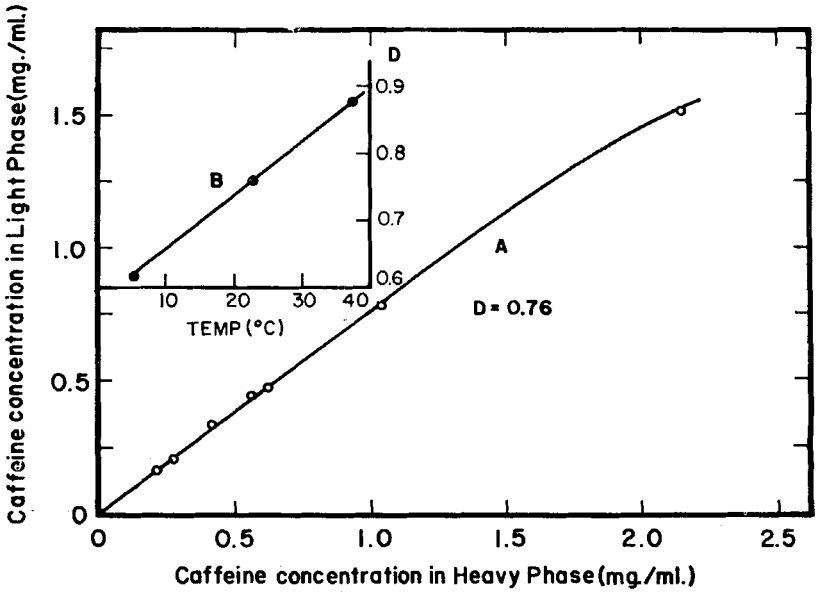

FIG. 3. Distribution of caffeine between ethyl acetate and water.

phase. From the slope of the straight line, one calculates the distribution coefficient,* D, to be 0.76, Curve B in the inset is a plot of D against temperature. Since most of the experiments reported here were run at a room temperature varying from 21.5 to 25°C, a value of 0.76 for D was used in all the calculations. The error introduced by variation in temperature is evidently not severe.

The distribution coefficient of nicotinamide between the same two solvents was similarly determined at 23°C; it was found to be 0.19.

MEASUREMENT OF FLOW RATES

Although the pumping rates were remarkably constant, the volumes of effluents were always smaller than those calculated from the pumping rates, especially that of the light phase, i.e., ethyl acetate. The difference is evidently due to the loss by evaporation from the liquid surfaces exposed to air and during dripping of the effluents from the exits. Although visible leakages can be eliminated easily, some invisible leakages (i.e., the rate of leaking is smaller than the rate of evaporation) is unavoidable. This can be easily demonstrated by the presence of caffeine crystals at the ground-glass joints when ethyl acetate containing caffeine as solute is used as the light phase. It is, therefore, more reliable to use the effluent volumes, corrected for evaporation loss, as a measure of the flow rates than to use the pumping rates.

For the light phase the evaporation loss from the surface of the light phase collector and during the dripping of liquid from the exit was determined by pumping ethyl acetate directly to the collector, which had been closed tightly at its bottom with a polyethylene stopper, and measuring the volume collected at the exit. This loss was found to average 40 ml/24 hr (or 1.7 ml/hr) at 21.5 to 25°C and at a flow rate of 30 ml/hr. This value was added to the volume of light phase effluent collected to give the L value (flow rate of the light phase). Losses due to evaporation at the surfaces in the flow rectifier† and the light phase inlet tube† and from the invisible leaks at all the ground-glass joints represent a volume of the light phase that did not enter the column and may, therefore, be ignored. The invisible leak at the joint of the upper end of the column with the light phase collector is usually negligible, as evidenced by the absence of caf-

*The definitions of terms used by Scheibel (*1*) are followed in the present report, and are given in the Symbols section. New terms introduced will be pointed out.

†All these openings were covered loosely with polyethylene stoppers to minimize evaporation.

feine crystals at the joint. This finding is understandable because this joint is under very little hydrostatic pressure.

There is very little evaporation loss of the heavy phase as compared with that of the light phase. The effluent volume collected often agreed with the pumping rate within 1.5%. Tests run by allowing the heavy phase to drip from a separatory funnel at a rate of 15 to 30 ml/hr showed that an evaporation loss of ~0.3 ml/hr occurred at 21.5 to 25°C. This value was also applied to the heavy phase effluent as a correction.

EVALUATION OF EXTRACTION EFFICIENCY

With the extractor shown in Fig. 1, experiments were run with ethyl acetate–saturated water containing caffeine at a concentration of 2 mg/ml (heavy phase) and solute-free water-saturated ethyl acetate (light phase). Equation (1) was used to evaluate the extraction efficiency:

$$\frac{x_n}{x_0} = \frac{E^{n+1} - 1}{E - 1} \quad \text{or} \quad n = \frac{\log\left[\frac{x_n}{x_0}(E - 1) + 1\right]}{\log E} - 1 \qquad (1)$$

where x_n = caffeine concentration in heavy phase entering the column at the top, mg/ml
x_0 = caffeine concentration in heavy phase leaving the column at the bottom after steady state has been reached, mg/ml
E = extraction factor = DR_v
D = distribution coefficient of caffeine
R_v = relative flow rate = L/H
L = volume flow rate of the light phase, ml/hr
H = volume flow rate of the heavy phase, ml/hr
n = number of theoretical stages

The height equivalent of a theoretical stage (HETS) is calculated by:

$$\text{HETS} = Z/n \qquad (2)$$

where Z = effective height of the column, in.

When a concentrated solution of caffeine in the heavy phase was fed to the feed stage of a column with n theoretical stages above and m theoretical stages below the feed stage and the column was run with both solvent phases free of solute at such a relative flow rate that caffeine was almost completely extracted into the light phase, the rejection ratio, R, was calculated from (*1*, *11*)

$$R = \frac{Ly_p}{H'x_B} = \frac{{E_1}^{n-1}(E_1 - 1)}{{E_1}^n - 1} \frac{[(E_1')^m - 1]E_1'}{E_1' - 1} \tag{3}$$

where H' = flow rate of heavy phase below the feed stage = $H + F$, ml/hr
F = flow rate of feed (feed is a solution in the heavy phase), ml/hr
E_1 = extraction factor of caffeine above the feed stage = $D_1(L/H)$
E_1' = extraction factor of caffeine below the feed stage = $D_1(L/H')$
D_1 = distribution coefficient of caffeine
y_p = caffeine concentration in the light phase effluent, mg/ml
x_B = caffeine concentration in the heavy phase effluent, mg/ml

When E_1 and E_1' are greater than 1, and m and n are large, Eq. (3) becomes Eq. (4) by approximation:

$$R = \frac{E_1 - 1}{E_1} \frac{(E_1')^{m+1}}{E_1' - 1} \tag{4}$$

When nicotinamide was fed to the feed stage and was almost completely extracted into the heavy phase, the retention ratio, R', was calculated from

$$R' = \frac{H'x_p}{Ly_B} = \frac{{E_2}^n - 1}{{E_2}^{n-1}(E_2 - 1)} \frac{E_2' - 1}{[(E_2')^m - 1]E_2'} \tag{5}$$

where E_2 = extraction factor of nicotinamide above the feed stage = $D_2(L/H)$
E_2' = extraction factor of nicotinamide below the feed stage = $D_2(L/H')$
D_2 = distribution coefficient of nicotinamide
x_p = nicotinamide concentration in the heavy phase effluent, mg/ml
y_B = nicotinamide concentration in the light phase effluent, mg/ml

When E_2 and E_2' are smaller than 1, and m and n are large, Eq. (5) becomes Eq. (6) by approximation:

$$R = \frac{1 - E_2'}{E_2'{E_2}^{n-1}(1 - E_2)} \tag{6}$$

RESULTS

An Example of Column Performance

Figure 4 shows the data for a typical run. A column of 15.7 mm (i.d.), and 19 in. high was used in this experiment. Ethyl acetate–saturated water

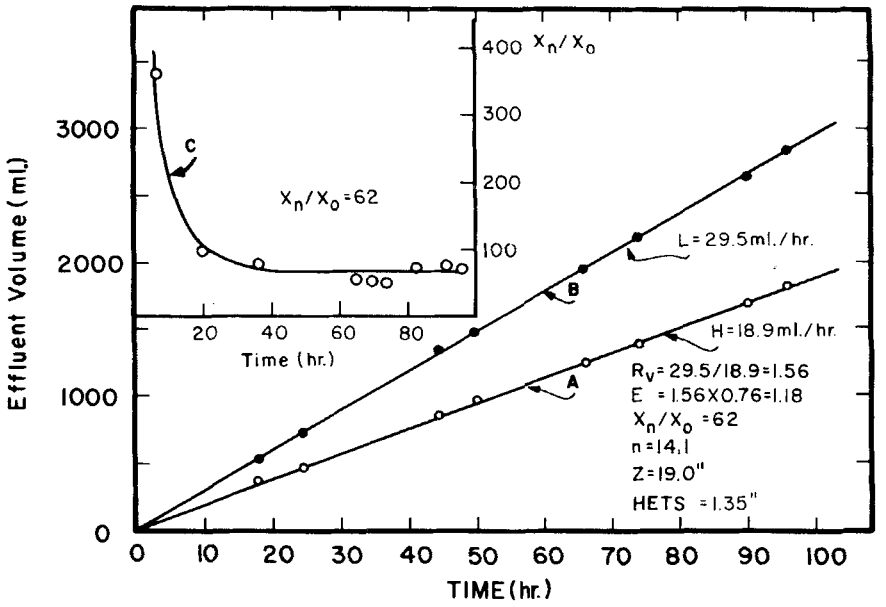

FIG. 4. Performance of extractor with end feeding.

containing 2 mg of caffeine/ml (x_n) was admitted to the top of the column as the heavy phase (feed solution). Solute-free water-saturated ethyl acetate was admitted to the bottom of the column as the light phase (extractant). The volumes of effluents (corrected for evaporation loss) are plotted against time in Curves A and B. They are straight lines, indicating constant flow rates. One may calculate H and L from the slopes, and then R_v and E. These values are also given in Fig. 4. The caffeine concentration in the heavy phase effluent (x_0) was periodically determined by measuring its absorbance at 272 nm. Curve C shows a plot of x_n/x_0 against time; this ratio decreased from infinity to a minimum in 20 to 30 hr. After that, only slight fluctuations occurred up to 100 hr, indicating clearly that, when a steady state has been reached, it will remain steady indefinitely. From the values for x_n/x_0 (62) and E (1.18), the n and HETS values, calculated from Eqs. (1) and (2), equaled 14.1 and 1.35 in., respectively.

The y_n value (caffeine concentration in the light phase effluent) averaged 1.22 mg/ml, giving a material balance of 95.5%.

Effect of Strand Concentration

Some of the essential parameters pertaining to the extractor described above were studied with the same procedure. The effect of the strand

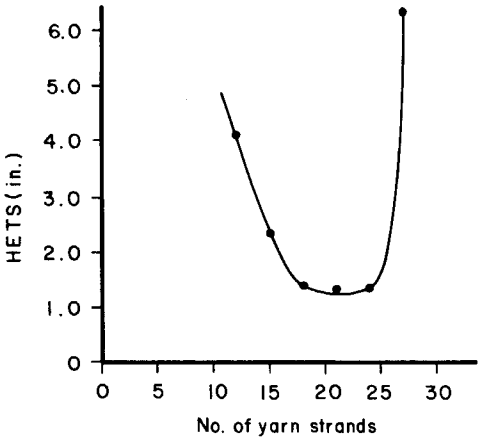

FIG. 5. Effect of strand concentration on extraction efficiency. Column, 15.7 mm (i.d.). $Z = 19$ in., $H = 18$ ml/hr, $L = 28$ ml/hr.

concentration, i.e., number of yarn strands used in the column described above ($d = 15.7$ mm, $A = 1.94$ sq cm), is shown in Fig. 5. The efficiency of the extractor dropped markedly when fewer than 18 strands were used, but strand concentration greater than 18, e.g., 21 and 24, did not increase the efficiency significantly. In fact, the efficiency decreased greatly when 27 strands were used. It should be noted that with 24 strands or fewer and at the flow rates indicated in Fig. 5, the level of ethyl acetate in its inlet tube, E (Fig. 1), was not significantly higher than that in the light phase collector, B. In the experiment with 27 strands, the level of ethyl acetate in Tube E was $\sim 1/4$ in. higher than that in B, indicating that a significant hydrostatic head was needed to force the light phase to go through the column. When 30 strands were used, the hydrostatic head amounted to more than 1 in. and both the light and the heavy phases emerged from the light phase exit, G. This state must be equivalent to the flooding stage of a spray tower.

In the experiments reported below, 18 strands (i.e., 9 strands/cm^2 of cross-sectional area) were used.

Effect of Flow Rates

Figure 6 shows the effect of flow rates and, consequently, of the R_v value on the HETS value. The column just described was used here, too. Curve A is a plot of the HETS value against L, i.e., the flow rate of the light phase, with the R_v value kept constant at ~ 1.5. In other words, the

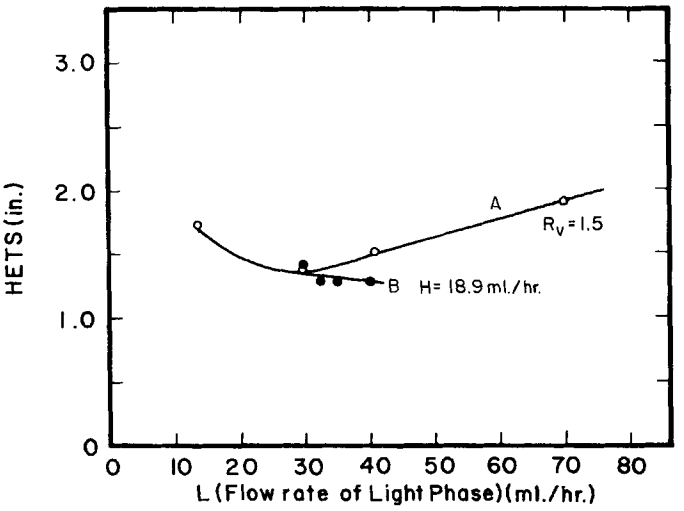

FIG. 6. Effect of flow rate on extraction efficiency. Column, 15.7 mm (i.d.). Z = 19 in. Number of yarn strands = 18.

H value, the flow rate of the heavy phase, was varied proportionally. Curve B is a plot of the HETS value against L, with H kept constant at 18.9 ml/hr.

It can be seen that when R_v was kept constant, there was an optimum flow rate of L = 25 to 30 ml/hr (Curve A). Although an increase in the flow rates caused a moderate increase in the HETS value, a decrease in the flow rates caused a marked decrease in efficiency.

The data in Curve B show that, with H kept constant, an increase in L (consequently, in E) decreased the HETS value slightly. Since the test range was rather narrow, one cannot be sure whether such an effect is actually significant.

Effect of Column Height

Table 1 shows the variation of the HETS value with changes in the effective height of the column, Z. An increase in Z increases the number of theoretical, stages, n, but the increase is not proportional to Z. As a result, the HETS value also increases, i.e., the efficiency drops somewhat. As will be discussed in a later section, this observation is explained on the basis of "channeling" of solvents as they flow through the column.

TABLE 1

Efficiency of Extraction in Columns of Different Heights[a]

Effective height of column (Z) (in.)	Number of theoretical stages (n)	Height equivalent of stage (HETS) (in.)
8.5	7.3	1.16
19.0	14.1	1.35
27.0	19.1	1.41
36.5	21.6	1.69

[a]Column 15.7 mm (i.d.), H = 18 ml/hr. L = 28 ml/hr. Number of yarn strands = 18.

Effect of Column Diameter

Data obtained in columns with different diameters are summarized in Table 2. Although a column with a diameter of 10.7 mm (i.d.) showed no better performance than did one of 15.7 mm (i.d.), the performance of a column with 25.2 mm (i.d.) was noticeably poorer than that of either. The HETS value for the latter was 2.28 in. as compared with 1.41 in. for a 15.7 mm (i.d.) column of the same height (27 in.). As will be discussed later, a channeling effect is also believed to be the explanation of this observation.

Extraction of Caffeine from Ethyl Acetate with Water

Water-saturated ethyl acetate in which caffeine had been dissolved at

TABLE 2

Efficiency of Extraction in Columns of Different Diameters[a]

Inside diameter of column (d) (mm)	Effective height of column (Z) (in.)	Number of theoretical stages (n)	Height equivalent of theoretical stage (HETS) (in.)
10.7	16.3	12.2	1.33
15.7	19.0	14.1	1.35
15.7	27.0	19.1	1.41
25.2	27.0	11.8	2.28

[a]Nine yarn strands per sq cm cross-sectional area. H/A = 9 ml/(sq cm) (hr). L/A = 14 ml/(sq cm) (hr).

a concentration of 1.2 mg/ml (y_n) was admitted to the extractor as the light phase (feed solution) at a flow rate of 19.3 ml/hr (L). Solute-free ethyl acetate–saturated water was used as the heavy phase (extractant) at a flow rate of 17.3 ml/hr (H) in a column of 15.7 mm (i.d.) with an effective height of 19.0 in. The caffeine concentration in the light phase effluent (y_0) reached a plateau of 0.0114 mg/ml in $\sim$30 hr as expected. By using y_n/y_0 (105) and $1/E$ (1.180) in place of x_n/x_0 and E, respectively, the n and HETS values for this experiment, calculated from Eqs. (1) and (2), equaled 17.0 and 1.12 in., respectively. This efficiency is somewhat higher than that given in Fig. 4 (HETS = 1.35 in.). Because the difference is, however, not large, it is safe to conclude that caffeine can be extracted from either solvent phase to the other with approximately the same efficiency.

Separation of Caffeine and Nicotimamide

To illustrate that the continuous countercurrent extractor with center feeding can be used to spearate two compounds from a mixture, caffeine and nicotinamide in the solvent system of ethyl acetate and water were chosen. As stated earlier, the distribution coefficient of caffeine (D_1) is 0.76 and that of nicotinamide (D_2) is 0.19, giving a β value of 0.76/0.19 = 4.0.

Caffeine alone, dissolved in the heavy phase at a concentration of 12 mg/ml, was first fed to the feed stage at a rate of 1.5 ml/hr (F). The extractor was of 15.7 mm (i.d.) and of effective heights 19.0 in. below and 19.0 in. above the feed stage. Solute-free water-saturated ethyl acetate was admitted to the extractor as the light phase at a flow rate of 46.0 ml/hr (L), and solute-free ethyl acetate–saturated water, at a flow rate of 17.5 ml/hr (H), was used as the heavy phase. The R_v value below the feed stage was 46.0/19.0 = 2.42, and that above the feed stage was 46.0/17.5 = 2.63 ($1/\sqrt{D_1 D_2} = 2.63$). The experiment was run for 6 days. The x_B and y_p values, determined every 24 hr, were, on average (after the first 24 hr), 0.0002 mg/ml (this concentration was too low to be measured accurately) and 0.39 mg/ml, respectively. The rejection ratio (R) was calculated from Eq. (3) as $2.42 \times 0.39/0.0002 = 4700$. When calculated from Eq. (4) on the basis of $n = m = 14$, i.e., 14 theoretical stages above and 14 below the feed stage (cf. Fig. 4), this value is equal to 5700, agreeing well with experimental data in view of the low accuracy of the x_B value.

The same experiment was repeated with a solution of nicotinamide in the heavy phase, 12 mg/ml as the feed. The experiment was run for 6 days, and the nicotinamide concentrations in the heavy and light phase ef-

fluents were determined every 24 hr. After the first 24 hr the x_p and y_B values averaged 0.95 mg/ml and < 0.0001 mg/ml, respectively, giving a retention ratio of $R' > 0.95/(0.0001 \times 2.42)$, i.e., > 4000 (Eq. 5). The R' value, calculated from Eq. (6) on the basis of $n = m = 14$, was 19,000.

After it had been established that the extractor with center feeding did work as expected, the same experiment was repeated, this time with a mixture of caffeine and nicotinamide dissolved in the heavy phase, 12 mg of each compound/ml, as the feed. The experiments was run for 5 days. After the first 24 hr the heavy and light phase effluents were tested on a thin-layer chromatogram. A mixture of ethyl acetate, methanol, and water (50:5:1) was used to develop the chromatogram on a Brinkmann silica-gel F–254 plate. Only a single caffeine spot was found in the light phase effluent ($R_f = 0.58$) and only a nicotinamide spot was found in the heavy phase effluent ($R_f = 0.50$). The UV spectra of both effluents were also determined in a Perkin-Elmer Model 402 spectrophotometer. The light phase effluent showed a spectrum identical to that of pure caffeine, with λ_{max} at 273 nm, and that of the heavy phase was identical to that of pure nicotinamide, with λ_{max} at 257 nm (sh), 264 nm, and 271 nm (sh). These data demonstrated that the continuous countercurrent extractor, when operated with center feeding, satisfactorily separates a mixture of two compounds of different distribution coefficients.

A Colorful Demonstration of the Continuous Countercurrent Extraction Process

As a colorful demonstration of the function of the extractor, two dyes, Sudan black B (purple) and *p*-phenylazophenol (yellow), were separated by the use of the appartus reported here. The heavy solvent was a 4:1 (by volume) mixture of methanol and water, and the light solvent was a 1:3 (by volume) mixture of toluene and *n*-hexane. The distribution coefficient of Sudan black B (D_1) is $\sim$3.0 and that of *p*-phenylazophenol (D_2) is $\sim$0.3, giving a β value of $\sim$10.

The extractor, as used, consisted of 13 in. above and 13 in. below the feed stage. The flow rate of the light phase was 23 ml/hr (L) and that of the heavy phase was 22 ml/hr (H), giving an R_v value of 1.05 ($1/\sqrt{D_1 D_2} = \sim 0.95$). A solution of these two dyes in the heavy phase, at concentrations of 0.25 mg/ml for Sudan black B and 10 mg/ml for *p*-phenylazophenol, was fed to the feed stage at a rate of 2.0 ml/hr. This mixture appeared dark green. After the first 24 hr the heavy phase effluent was bright yellow, no different from a solution of 1 mg of *p*-phenylazophenol/ml of the heavy phase, and the light phase effluent appeared purple, no different from a

solution of 0.02 mg of Sudan black B/ml of the light phase. It was also interesting to observe the color change along the column. From the feed stage on down, the color of the original mixture gradually gave way to pure yellow, and for 1 to 2 in. just above the separator the color was completely yellow. A similar situation existed above the feed stage; the color of the mixture gradually gave way to pure purple.

Extraction in the Presence of an Emulsifying Agent

When a solution of Tween 80 in water at a concentration of 1 mg/ml is layered with ethyl acetate in a test tube and the latter is inverted 20 to 30 times, an emulsion is formed. This emulsion remains unchanged for at least 24 hr. When centrifuged, the emulsion disappears to give a clear ethyl acetate phase and an aqueous phase that appears slightly milky. To demonstrate that no such emulsion would be formed during the use of the extractor, the experiment described above for center feeding was repeated with a solution of Tween 80 in the heavy phase, 15 mg/ml, as the feed. The extractor ran just as if no Tween 80 had been introduced. The light phase effluent was clear and the heavy phase effluent was slightly milky, just as the heavy phase had appeared after the emulsion had been broken by centrifugation. The milky appearance disappeared after 1 hr. Since there is no mechanical mixing in the extractor, one does not expect emulsification to occur, even in the presence of an emulsifying agent.

DISCUSSION AND CONCLUSIONS

An ideal extraction process with two continuous phases can be treated mathematically as follows. Let us consider first an ideal partition process involving two exceedingly thin layers of solvents in which the bulk concentration of a solute in each layer remains very low and uniform (i.e., no concentration gradient exists). As illustrated in Fig. 7a, we can write, according to the mass action law:

$$v_1 = k_1 y; \qquad v_2 = k_2 x \tag{7}$$

where y = solute concentration in the light phase, mg/ml
x = solute concentration in the heavy phase, mg/ml
v_1 = rate of interface crossing from light to heavy phase, mg/(sq cm) (sec)
v_2 = rate of interface crossing from heavy to light phase, mg/(sq cm) (sec)

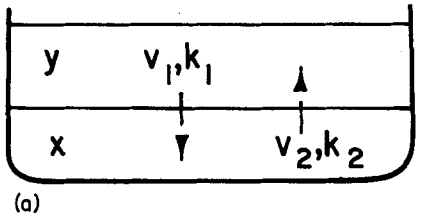

FIG. 7a. Illustration of an ideal partition process.

k_1 = kinetic constant for interface crossing from light to heavy phase, cm/sec

k_2 = kinetic constant for interface crossing from heavy to light phase, cm/sec

When equilibrium has been reached, $v_1 = v_2$, and

$$k_1\bar{y} = k_2\bar{x} \qquad \text{or} \qquad \bar{y}/\bar{x} = k_2/k_1 = D \tag{8}$$

where $\bar{y}$ and $\bar{x}$ indicate solute concentrations at equilibrium. The distribution coefficient, D, is, therefore, equal to the ratio k_2/k_1.

Now let us imagine a rectangular trough in which a very thin stream of a dilute solution of a solute in a heavy solvent flows from right to left at the bottom, at a rate of H ml/sec, and a very thin stream of a light solvent (solute free) flows from left to right atop the heavy solvent, at a rate of L ml/sec as shown in Fig. 7b. Let us designate the width of the trough w and the length Z. Then, by material balance across the section, dz, we have

$$(k_2x - k_1y)w\,dz = H\,dx \tag{9}$$

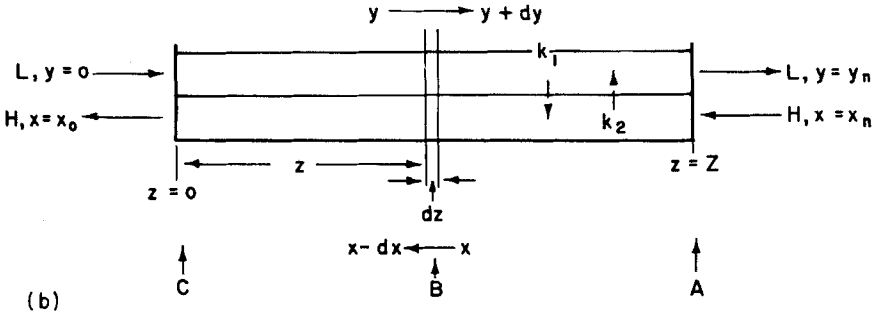

FIG. 7b. Illustration of an ideal continuous countercurrent extraction process.

By material balance across the section BC, when steady-state has been reached,

$$Ly = H(x - x_0) \tag{10}$$

Substitute Eq. (10) in Eq. (9) and rearrange:

$$w\,dz = \frac{dx}{\left(\frac{k_2}{H} - \frac{k_1}{L}\right)x + \frac{k_1}{L}x_0} \tag{11}$$

Integrate between $z = 0$, $x = x_0$, and $z = Z$, $x = x_n$, simplify, and solve for x_n/x_0,

$$\frac{x_n}{x_0} = \frac{\frac{k_2}{H}\exp\left[wZ\left(\frac{k_2}{H} - \frac{k_1}{L}\right)\right] - \frac{k_1}{L}}{\frac{k_2}{H} - \frac{k_1}{L}} = \frac{\frac{k_2L}{k_1H}\exp\left[wZ\frac{k_1}{L}\left(\frac{k_2L}{k_1H} - 1\right)\right] - 1}{\frac{k_2L}{k_1H} - 1} \tag{12}$$

Since $k_2/k_1 = D$, $L/H = R_v$, and $DR_v = E$, Eq. (12) becomes:

$$\frac{x_n}{x_0} = \frac{E\exp\left[\frac{k_1wZ}{L}(E - 1)\right] - 1}{E - 1} \tag{13}$$

Comparing Eq. (13) with Eq. (1), we have:

$$E\exp\left[\frac{k_1wZ}{L}(E - 1)\right] = E^{n+1} \tag{14}$$

Therefore

$$n = \frac{k_1wZ(E - 1)}{L\ln E} \tag{15}$$

and

$$\text{HETS} = \frac{Z}{n} = \frac{L\ln E}{k_1w(E - 1)} \tag{16}$$

of, in terms of k_2 and H,

$$\text{HETS} = \frac{HE\ln E}{k_2w(E - 1)} \tag{17}$$

Equation (16) or (17) holds, of course, only for an ideal case in which

diffusion and channeling effects are negligible and the thickness of each solvent phase is exceedingly small. One would not expect that the performance of an extractor like the one described in this report could be predicted by these equations. However, data presented above are in partial agreement with these equations. For example, Curve A in Fig. 6 shows that an increase in L above 20 ml/hr, with E kept constant, increases the HETS value even though these two values are not in the direct proportion demanded by Eq. (16). The increase in HETS value when L decreases below 20 ml/hr can be explained on the basis that the smaller the flow rate, the greater will be the effect of diffusion, resulting in a decrease in the extraction efficiency.

The effect of the number of yarn strands per unit cross-sectional area can also be judged by considering Eq. (16) or (17). The HETS value should be inversely proportional to w, the width of the imaginary trough. The number of yarn strands evidently means the width of the trough. Figure 5 shows that the HETS value does decrease with an increase in the number of yarn strands in the same column run with the same L and E values. However, the response is again not in full agreement with Eq. (16) or (17); the HETS value reaches a minimum at $\sim$10 yarn strands/cm^2 of cross-sectional area and then increases with any further increase in the number of yarn strands. This observation can be explained on the basis that when the column is too crowded with yarn strands, some of the annular spaces would disappear, thus actually decreasing the width of the imaginary trough.

The effects of varying L with H kept constant, i.e., a variation in E with H kept constant, can be judged by Eq. (17). The HETS value should be proportional to $E \ln E/(E-1)$. Curve B of Fig. 6 shows that HETS decreases slightly with an increase in E, whereas the value for $E \ln E/(E-1)$ increases slightly with an increase in E over the same range of E values. Since the range tested was rather narrow, it is by no means surprising to observe such a discrepancy between theory and experimental data. Other factors, e.g., diffusion and channeling, could easily mask the slight effect of $E \ln E/(E-1)$.

According to Eq. (16) or (17), the HETS value should be independent of Z and of the diameter of the column, d. Tables 1 and 2 show that HETS actually increased somewhat with an increase in either Z or d. This observation is explained on the basis that the flow of both solvent phases is by no means uniform. By using colored solutions, e.g., ammonical cupric sulfate in water or Sudan III in ethyl acetate, one observes that the advance of the color front is always faster on one side of the column than

on the other, especially with the light phase. After all, the extractor is not a chromatographic column; a great deal of channeling would be expected to occur. The longer the column or the larger the cross-sectional area, the worse may be the channeling effect.

Equation (16) or (17) shows that the HETS value varies inversely with the kinetic constant k_1 or k_2. Although there is no known method to measure k_1 or k_2, one would expect that k_1 or k_2 must vary with temperature. The temperature, therefore, affects not only E but also k_1 and k_2 and thus the HETS value. In the present study the experiments were not carried out in a constant-temperature room. The temperature effect must constitute a major source of inaccuracies in the data obtained. The temperature, of course, also affects the evaporation loss, especially that of the light phase. The latter causes inaccuracies in the measurement of the flow rates, H and L, and thus in the calculation of the HETS value. Therefore, although the present study showed conclusively that it is possible to construct a highly efficient continuous countercurrent extractor by utilizing fibrous strands as wall-less conduits for a hydrophilic solvent, the quantitative accuracy of the HETS values should not be overemphasized.

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SYMBOLS

A	cross-sectional area of column, sq cm
d	diameter of column, mm
D	distribution coefficient = $\dfrac{\text{solute concentration in light phase at equilibrium}}{\text{solute concentration in heavy phase at equilibrium}}$
E	extraction factor = DR_v
F	flow rate of feed solution, ml/hr in column with center feeding
H	flow rate of heavy phase, ml/hr or ml/sec in Eqs. (9)–(17)
HETS	height equivalent of a theoretical stage, in.
k_1 or k_2	kinetic constant of interface crossing, cm/sec
L	flow rate of light phase, ml/hr or ml/sec in Eqs. (9)–(17)
m	feed stage number, counting from bottom of column
n	feed stage number, counting from top of column, or total number of stages in a column with end feeding.

R rejection ratio $= \dfrac{\text{quantity of solute in light phase effluent}}{\text{quantity of solute in heavy phase effluent}}$

R' retention ratio $= \dfrac{\text{quantity of solute in heavy phase effluent}}{\text{quantity of solute in light phase effluent}}$

R_v relative flow rate $= L/H$

v_1 or v_2 rate of interface crossing, mg/(sq cm) (sec)

w width of the imaginary trough, cm

x concentration of solute in heavy phase, mg/ml

$\bar{x}$ or $\bar{y}$ concentration of solute in equilibrium with each other, mg/ml

x_B or y_B concentration of solute in the solute-poor effluent leaving the column with center feeding, mg/ml

x_n or y_n concentration of solute in the feed solutions entering the column or in the extract leaving the column with end feeding, mg/ml

x_p or y_p concentration of solute in the solute-rich extract leaving the column with center feeding, mg/ml

x_0 or y_0 concentration of solute in the raffinate leaving the column with end-feeding, mg/ml

y concentration of solute in light phase, mg/ml

z distance from solute-poor end to any point of the imaginary trough, cm

Z effective column height, in., or length of the imaginary trough, cm

β relative distribution $= D_1/D_2$

Subscripts

1 refers to the solute of higher distribution coefficient or to interface crossing from light to heavy phase

2 refers to the solute of lower distribution coefficient or to interface crossing from heavy to light phase

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