

Nonideal Phenomena in Countercurrent Distribution

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Summary

An equation is presented that predicts the number of inputs required to produce a step-function (frontal) output in countercurrent distribution (CCD). When a portion of both phases is transported during experiments, the published equations for CCD are inappropriate. Expressions have been derived that predict the properties of elution and frontal outputs when biphasic flow occurs. When phase volumes and partition coefficients vary during the course of the distribution, computer simulation of the process, using the appropriate ternary phase diagram becomes necessary for adequate prediction of solute profiles. Shifts in position, shape, and height of frontal outputs and the nature of excess lower phase in the effluent are predicted and compare well with experimental results.

A number of recent publications have pointed out that good separations have been effected by countercurrent distribution; however, theoretical calculations have not agreed with experimental results (1, 2). It is the purpose of this paper to consider some of the "nonideal phenomena" that are encountered in multistage extraction and the appropriate mathematical techniques for theoretical calculations. Some of these phenomena may occur in chromatographic systems.

The relationships between countercurrent distribution and chromatography have been described (3). In the former, large volumes of solvents are contained in each tube, which makes the tool particularly effective in preparative work. In this case, it is often desirable to use relatively high concentrations of material and the ideal equations, which have been published (4), may not be useful (5). Another ap-

proach involves the use of a large number of consecutive inputs, so that a considerable amount of solute can be distributed while the concentration in any tube is kept relatively low. If the number of inputs is very large, a step-function (or frontal) output is observed in the effluent at the end of the apparatus. It is worthwhile to consider some relationships in frontal countercurrent distribution at both low and high levels of solute concentration. The effluent profiles are similar to those observed in chromatographic systems and may have special significance in the analogous case of liquid-liquid chromatography.

In the usual terminology of countercurrent distribution:

$$V_R = V_{U_{tot}} + V_{L_{tot}}/K_D; n_R = V_R/V_T$$

$$K_D = \frac{\text{equilibrium concentration of solute in upper phase}}{\text{equilibrium concentration of solute in lower phase}}$$

$$V_R = \text{retention volume, the accumulated volume of effluent to the solute peak}$$

$$V_U = \text{volume of upper phase in a single tube}$$

$$V_L = \text{volume of lower phase in a single tube}$$

$$p = \text{number of tubes in the apparatus}$$

$$pV_U = V_{U_{tot}}$$

$$pV_L = V_{L_{tot}}$$

$$V_T = \text{volume transferred on each operation}$$

Mayer and Tompkins carried out a theoretical analysis of column separation processes assuming transfer of discrete volumes of mobile phase (6). Rieman and his students extended this treatment by approximating column effluents with Gaussian solute profiles (7). This treatment is especially well suited to the consideration of output profiles from countercurrent distributors if the number of transfer is large. If the discontinuous output is approximated with a smooth curve, Eq. (1) describes the output in ideal cases:

$$M = J \left(\frac{K_D}{2\pi V_L V_R} \right)^{1/2} \exp \left[- \left(\frac{V_R K_D}{2V_L} \right) \left(\frac{V - V_R}{V_R} \right)^2 \right] \quad (1)$$

where M is the molarity of solute in V_U milliliters of effluent, J is the number of millimoles (mM) of solute added to the instrument, and V is nV_T . This equation is a good approximation where a single input or a few inputs are introduced. If n increments of solute of concentration M_F^* are added to the instrument,

$$J = M_F^* V_T n = \int_{V=0}^V M_F^* dV \quad (2)$$

Then

$$Y = \frac{M}{M_F^*} = \left(\frac{K_D}{2\pi V_L V_R} \right)^{1/2} \int_{V=0}^V \exp \left[- \left(\frac{V_R K_D}{2V_L} \right) \left(\frac{V - V_R}{V_R} \right)^2 \right] dV \quad (3)$$

This expression is of the form

$$Y = \frac{1}{(2\pi)^{1/2}} \int_{V=0}^V \exp \left(\frac{-t^2}{2} \right) dt \quad (4)$$

where

$$t = (V - V_R)/\sigma \quad (5)$$

$$\sigma = \left(\frac{V_L V_R}{K_D} \right)^{1/2} \quad (6)$$

and

$$dt = dV/(V_L V_R/K_D)^{1/2} \quad (7)$$

When $V = 0$, $t = -(K_D V_R/V_L)^{1/2}$ and $-\infty < t < -(p)^{1/2}$. For the sake of integration to the accuracy of data in probability tables (8), t may be approximated as $-\infty$ for all reasonable values. Thus

$$Y = \frac{M}{M_F^*} = \frac{1}{(2\pi)^{1/2}} \int_{t=-\infty}^t \exp \left(\frac{-t^2}{2} \right) dt \quad (8)$$

This equation describes the frontal output if solute is successively fed into the instrument. If solute feeds are discontinued and eluent is fed into the apparatus, an amount of solute corresponding to that in the mobile phase will be eluted, after which the solute concentration will start to decline in the effluent. In ideal or near-ideal systems, the trailing profile, from V_3 to V_4 of Fig. 1, will be the mirror image of the leading profile from V_1 to V_2 . In this case, the volume of feed solution or number of inputs required to obtain a frontal output may be determined. Let V_1 in Fig. 1 be the volume of effluent where solute starts emerging from the instrument ($Y = 0.01$) and V_2 is the volume of effluent where the plateau is just reached, within 1% ($Y = 0.99$).

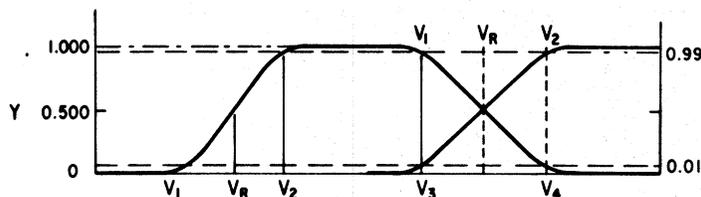


FIG. 1. Frontal output profile Y versus volume in ml.

These terms may be evaluated from Eqs. (9) and (10). If V_3 corresponds

$$V_1 = V_R + t_1(V_L V_R / K_D)^{1/2} \quad (9)$$

$$V_2 = V_R + t_2(V_L V_R / K_D)^{1/2} \quad (10)$$

to the volume when the plateau has just dropped to $Y = 0.99$ and V_4 is the volume, at the end of the frontal output, where $Y = 0.01$, superimposition of V_1 on V_3 and V_2 on V_4 results in a rectangle, of height $Y = 1$, the area of which corresponds to the amount of solute required to just achieve a frontal output. The value of V_F , the volume of feed solution required, can be determined from Eq. (11). If

$$V_F = V_2 - V_1 = (t_2 - t_1)(V_L V_R / K_D)^{1/2}$$

when $Y_1 = 0.01$ and $Y_2 = 0.99$, $t_2 = -t_1 = 2.33$, then

$$V_F = 4.66(V_L V_R / K_D)^{1/2} \quad (11)$$

When nonideal phenomena are important the aforementioned equations may become poor approximations.

In many cases some, but not all, of the two liquid phases may be transported out of tubes and through the instrument. In Fig. 2(a), under ideal conditions, everything above the transfer level and nothing below it would be transported to the tube of next higher serial number during the transfer stroke. Under real conditions some of the upper phase and dissolved solute will be retained on the wall of the vessel while some of the lower phase may be held at the air-liquid interface and transported. Figure 2(b) shows the case encountered when the lower phase exceeds the transfer level. This is commonly encountered when a cocurrent reservoir is used to feed the lower phase during an

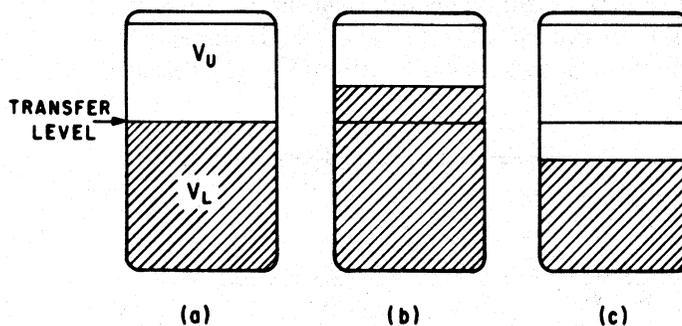


FIG. 2. Nonideal transfer effects. Lower solution: (a) at, (b) above, (c) below transfer level.

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experiment. In Fig. 2(c) some of the upper phase, in addition to that held on the wall, is retained. This may be a result of experimental design, phase equilibria, and/or surface effects. If significant quantities of solute are held back or transported due to these effects, the ideal equations must be modified. Let

$$z = V_{LT}/V_L \quad (12)$$

$$(1 - w) = V_{UT}/V_U \quad (13)$$

Here V_{UT} and V_{LT} are the volumes of upper and lower phases transported per operation. The mobile phase may be biphasic. The fraction of solute extracted into this mobile phase is denoted as $(1 - A)$ and

$$(1 - A) = \left(\frac{K_D}{K_D + V_L/V_U} \right) (1 - w - z) + z \quad (14)$$

Equation (1) must be modified in this case. If F is the number of millimoles of solute appearing in the effluent on operation n , then

$$F = \frac{J}{n_R} \left(\frac{p}{2\pi A} \right)^{1/2} \exp \left[- \frac{(1 - A)^2}{2Ap} (n - n_R)^2 \right] \quad (15)$$

The shape of the effluent curve is influenced by these phenomena, as is its position, since

$$n_R = \frac{p}{(1 - A)} \quad (16)$$

Consideration of Eqs. (12)–(16) indicates that w/z may be manipulated so that no change in n_R will occur. When the ratio is that given in Eq. (17), n_R and the elution profile will be identical to that found in an ideal case where both w and z are zero.

$$w/z = V_L/(V_U K_D) \quad (17)$$

In an experiment in which V_L and V_U are fixed, there is only one value of K_D at this w/z where n_R equals that for the ideal case. Solutes that emerge earlier than this hypothetical solute with this K_D value will have their retention number at a higher value than would be predicted in the ideal case. The effluent curve would be lower and broader than expected in the absence of these effects. The reverse would be true for solutes with retention numbers greater than that of the hypothetical solute. This is demonstrated in Fig. 3. Conditions were chosen such that the central peak was undisturbed by retention of upper phase and transport of some lower phase. The curves were determined from

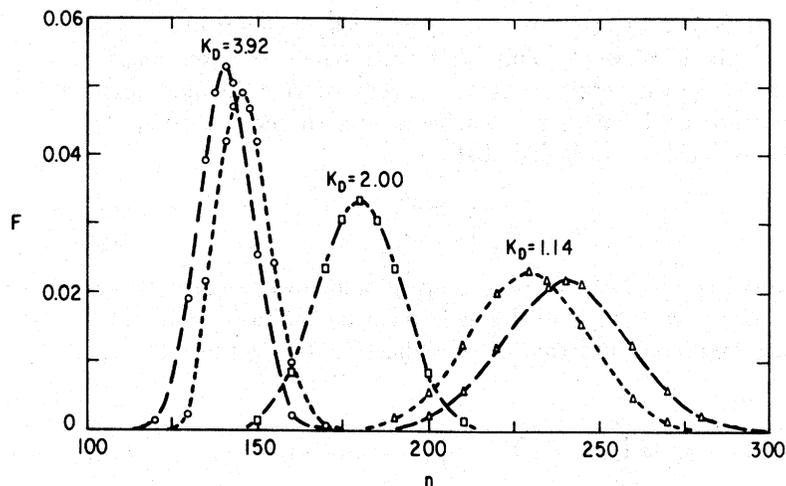


FIG. 3. Countercurrent distribution comparing output in the absence and presence of nonideal transfer effects. One millimole of each solute was distributed. The large dashes denote ideal conditions; the small dashes denote output when $z = 0.080$ and $w = 0.064$. The central curve is unaffected by nonideal transfer.

Eqs. (12)–(16). Recovery and purity of solute with $K_D = 2.00$ is considered in Table 1 under conditions where z and w are zero and where they are 0.080 and 0.064 respectively. Two fractions are considered, one where effluent from operations 158 to 205 is pooled and the other where effluent from operations 160 to 202 is combined. The data are given for the case where 1 mmole of each solute was utilized in the calculation. It is clear that less separation results in the nonideal case.

TABLE 1
Recovery of Solute

| K_D | Pooled fractions 158–205: mmole in fraction | | Pooled fractions 160–202: mmole in fraction | |
|-------|---|-----------------------|---|-----------------------|
| | Ideal | Nonideal ^a | Ideal | Nonideal ^a |
| 3.92 | 0.012 | 0.061 | 0.006 | 0.038 |
| 2.00 | 0.947 | 0.947 | 0.919 | 0.919 |
| 1.14 | 0.027 | 0.079 | 0.018 | 0.056 |

^a $z = 0.080$, $w = 0.064$.

With effects of this sort in mind, Eqs. (3) and (5) become Eqs. (18) and (19) respectively. The former is still of the form of Eq. (8). Finally

$$Y = \left(\frac{(1-A)^2}{2\pi pA} \right)^{1/2} \int_{n=0}^n \exp \left[- \frac{(1-A)^2}{2Ap} (n - n_R)^2 \right] dn \quad (18)$$

$$t = \frac{(1-A)}{(pA)^{1/2}} (n - n_R) \quad (19)$$

Equation (20) may be written, of which Eq. (11) is the analogue:

$$n_F = \frac{2t(pA)^{1/2}}{(1-A)} \quad (20)$$

Here n_F is the number of inputs required to just achieve a frontal output. In some cases further nonideal effects occur. For example, K_D , V_U , V_L , and the other terms may vary during the course of an experiment. Computer simulation becomes useful in such cases. Williams and Craig have prepared a computer program that is useful when the distribution coefficient varies while no other changes occur (9). It became desirable to prepare a computer simulation that is applicable when this as well as other nonideal phenomena (5) are encountered.

EXPERIMENTAL

Phase Equilibria

A ternary diagram was constructed for the methyl palmitate-acetonitrile-hexane system from solubility and tieline data at $25.0 \pm 0.1^\circ\text{C}$ (Fig. 4). A method for the mathematical description of a quaternary diagram, of which the above forms a face, has been reported (10). Equilibrium data of Brancker et al. (11) were used for the acetone-water-chloroform system (Fig. 5). The ternary diagrams are represented on rectangular rather than equilateral coordinates to facilitate computation.

Countercurrent Distribution

Distributions were carried out in a 200-tube Craig apparatus* at $25.0 \pm 0.5^\circ\text{C}$. A volume of lower phase (pre-equilibrated with other

* Mention of commercial items is for the convenience of the reader and does not imply an endorsement by the U. S. Department of Agriculture over others of a similar nature.

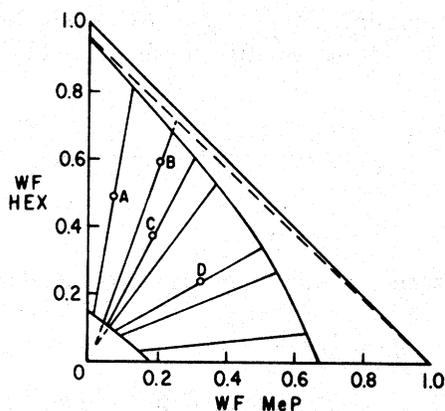


FIG. 4. Methyl palmitate-acetonitrile-hexane system at 25°C. Equation of upper curve: $WF\ Hex = 7.36X^5 + 9.32X^4 - 5.06X^3 + 1.14X^2 - 1.24X + 0.958$; equation of lower curve: $WF\ Hex = -1.21X^2 - 0.558X + 0.141$; $X = WF\ MeP$.

solvent) in excess of the cutoff volume was added to each distributor tube. Upper phase was added to the first few tubes to assure equilibrium and to coat the tube walls. Measured volumes of upper phase (pre-equilibrated with other solvent) containing known amounts of solute were dispensed from the "cocurrent reservoir" and combined

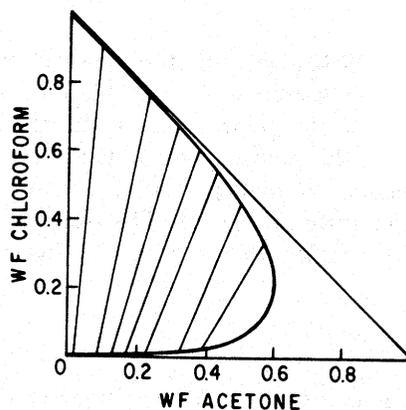


FIG. 5. Acetone-water-chloroform system at 25°C. Equation of upper curve to the last tieline: $WF\ chloroform = -1.50X^3 - 0.917X^2 - 1.16X + 0.994$; equation of lower curve to the last tieline: $WF\ chloroform = 1.09X^3 - 0.517X^2 + 0.090X + 0.006$; $X = WF\ acetone$.

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with measured volumes of upper phase emerging from the solvent reservoir. After the desired number of inputs were made, the "cocurrent reservoir" was disconnected, the volume of upper phase being dispensed from the solvent reservoir adjusted accordingly, and the distribution continued. In the case of the methyl-palmitate-containing system fractions were collected at the end of the apparatus. Their volumes and masses were measured, the solvent evaporated, and the solute weighed. Eleven equilibration strokes and a 3-min settling time were used. When the acetone-containing system was studied, the first ten tubes of the apparatus were utilized and effluent from the last of these was collected. Volumes and phase masses were measured and weight percent of solute was determined by gas chromatography. Fifteen equilibration strokes and a 3-min settling time were used. A commercial chromatograph equipped with a thermal conductivity detector was used for fraction analysis. The column was 9 ft \times 1/8 in. stainless steel packed with 40-80 mesh Poly-Pak #2; He flow rate 32 ml/min; column temperature 199°C. Correction factors were calculated from daily analysis of known mixtures.

In separate material balance experiments using individual tubes, it was determined that the average cutoff volume for tubes in the apparatus was 39.2 ml and that 0.8 ml of hexane phase or 1.3 ml of water phase was retained on the wall of each tube.

Computer Simulation

An IBM 1130 computer was employed to simulate countercurrent distributions using phase equilibria data. For this purpose, the solubility curves were described by empirical equations that were determined by the method of least squares utilizing the computer. Tielines were described by their slopes and Y -intercepts. Densities of the pure components and each phase at the ends of the tielines were determined. It was found that the density, ρ , of any phase could be expressed by Eq. (21). This equation assumes that no significant changes in partial molal volumes occurred. This is true within 1% in the systems studied. Here WFA denotes weight fraction of A and ρ_A is the density of pure A.

$$\frac{1}{\rho} = \frac{WFA}{\rho_A} + \frac{WFB}{\rho_B} + \frac{WFC}{\rho_C} \quad (21)$$

The steps involved in the simulation are as follows:

1. Initial conditions within the distributor and feed profiles are stated.
2. The weight and weight fraction of each component in each tube are determined.
3. The point describing the system is located on the ternary diagram and it is determined whether or not this point lies within the immiscible region and below the isopycnic tieline.
4. If this point does not fall on a tieline, a new tieline is found by interpolation.
5. The weight fractions of all components in each phase are determined.
6. Densities, masses, and volumes of both phases are determined.
7. All material above the cutoff arm, except for a predetermined amount that is held by the wall, is transferred to the next tube.

This process is repeated for as many transfers as are desired. The tieline interpolation is achieved by extrapolating the two tielines closest to point C (Fig. 4), the point in question. The equation of the line through this intersection and point C is determined. The intersection of this interpolated line and the solubility curves is determined. This operation can be performed algebraically for the second-degree equation, but for equations of order greater than two, a composite equation is formed and the root obtained by the Newton-Raphson method (12).

Phase volumes and compositions in all tubes at any point in the distribution may be printed out. Effluent information is printed out at the end of a run. Any feed profile and initial tube condition, as well as many types of phase diagrams, may be used.

RESULTS AND DISCUSSION

An important phenomenon that may occur in countercurrent distribution is variation in the distribution coefficient that renders the ideal equations invalid. This variation is depicted in Fig. 6 for the methyl-palmitate-containing system. In dilute solution variation of K_D is slight. As the amount of solute is increased, K_D changes markedly. When the weight percent of methyl ester is above about 3, the weight fraction of at least two components must be stated in order to define the system and K_D . The figure allows one to differentiate between the "analytical region," up to about 2% solute, and the "preparative region."

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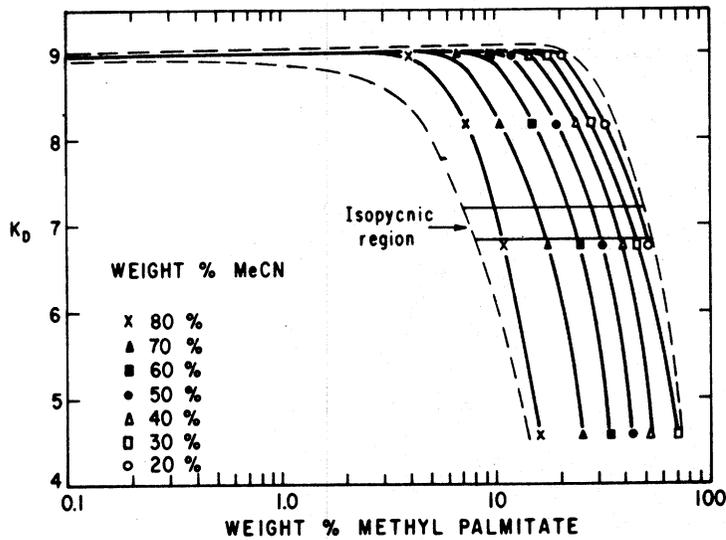


FIG. 6. Variation in partition coefficient as a function of methyl palmitate and acetonitrile composition.

The line on which point D lies (Fig. 4) was calculated to connect two phases of equal density in equilibrium and is referred to as the isopycnic tieline. Separation of the phases by settling is impossible here and was seen to be a slow process in the nearby composition region. At compositions below this line, phase inversion would occur. The value of K_D would be the reciprocal of that depicted in Fig. 6.

Results of an experiment in which a total of 50.0 g of methyl palmitate, dissolved in the upper phase, was fed into the instrument as 50 discrete inputs are shown in Fig. 7. These data are compared with the ideal case in which K_D is that in dilute solution and is invariant, and no volume reorganizations or other nonideal phenomena occur. Three important differences are noted: The experimental plateau does not reach $Y = 1.00$, the shapes of the leading and following edges are not identical, and lower phase appears in the effluent indicated by the curve on the lower left.

The two-phase effluent consists of about 1.5 ml of lower phase and 18.4 ml of upper phase at operation 240. Most of the lower phase is removed from tube 0 with some washed out of tubes 1 and 2. The computer simulated case has the following characteristics: The plateau does not reach $Y = 1.00$ and is identical with the plateau height of

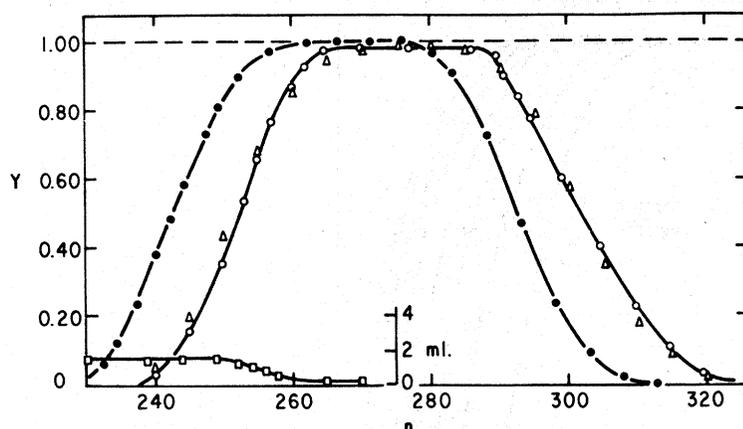


FIG. 7. Countercurrent distribution of methyl palmitate in hexane-acetonitrile. ●, output profile calculated from Eq. (3): $K_D = 8.9$, $V_U = 20$, $V_L = 39.2$; ○, experimental output; △, computer stimulated output; □, volume of lower phase in effluent.

the experimental curve; the shapes of the leading and trailing edges are more like those in the experimental curve than are those in the ideal case; and the lower phase is washed out of the instrument at a level of about 0.9 ml at operation 240. Most of the lower phase had been washed out of tube 0. In the experiment a total of 50 ml was washed out of tubes 0 through 2 and 51 ml of lower was collected in the effluent. Eleven strokes of the distributor had been used. When an experiment was carried out in which 98 strokes were utilized, it was found that 20.3 ml, 4.4 ml, and 4.2 ml were washed out of tubes 0, 1, and 2 respectively. Apparently the system was near but not at equilibrium when only 11 strokes were used.

The reasons for some of the observed effects are clear if Fig. 4 is consulted. In usual countercurrent operations the feed solution is made up by dissolving solute in a sample of mobile phase. The mobile phase has the composition denoted by intersection of the upper solubility curve with the hexane axis. Addition of methyl palmitate to this solution is the equivalent of moving along the dashed line. Consider the case when the composition of the feed solution is denoted by the intersection of the dashed line with an extension of the tieline, on which point B lies. It is clear that the solution with maximum weight fraction of solute that can be in equilibrium with stationary phase lies on the tieline at the solubility curve. This is at a value

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lower than the weight fraction of solute in the input. Thus the plateau must occur at a value of Y less than 1.00. When concentration is expressed on the molarity scale, density must also be considered, but the same conclusion is reached in this case. Use of this feed solution shifts the system composition toward the hexane-rich phase; for example, from point A to point B. The lever rule indicates that the mass of the hexane-rich upper phase increases at the expense of the lower phase. Use of Eq. (21) shows that the volume of lower phase decreases and the volume of upper phase increases. When a portion of the enlarged upper phase, relatively rich in solute, is passed into the next tube which contains stationary phase(s) at a lower weight fraction of solute, and the total solute weight fraction is lower than it was in the previous tube, volume reorganization may occur leading to an increase in the volume of lower phase. If this phase is now greater than the cutoff volume, a portion of lower phase will appear in the effluent. Toward the end of the experiment, as the concentration of solute in each tube drops from that at the plateau, the loss of solute from the stationary phase results in a decrease in volume in each tube of about 0.2 ml. This is much smaller than the volume effect observed on the leading edge, but examination of the instrument after an experiment indicates that this phenomenon does occur. In the usual discussions of countercurrent distribution (13), the volumes of the upper and lower phases are stated at the start of the operations and are assumed to be invariant.

If larger solute concentrations are used in the feed solution, the effects are magnified. This can be demonstrated by the extrapolation of the tielines of greater methyl palmitate weight fraction, to the dashed line in Fig. 4.

The results of a similar experiment using the acetone-containing system are shown in Fig. 8. Here the concentration profile of solute in the upper-phase effluent in the experimental case is compared with the leading edge for the ideal case when K_D is evaluated in very dilute solution. The experimental curve occurs at a much lower value of n and has a steeper slope than does the ideal curve. If the ideal equations are used and K_D is evaluated from the half-height (i.e., V_R) of the experimental curve, another frontal output may be drawn, as is shown in the figure. The K_D evaluated in this manner is a weighted average over the composition ranges encountered in the distribution. It is not of fundamental significance but is a curve-fitting parameter. Distribution coefficients, evaluated at infinite dilution, are widely

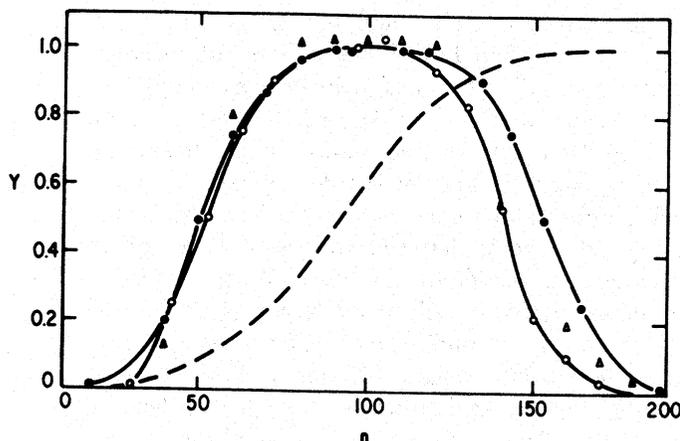


FIG. 8. Countercurrent distribution of acetone in water-chloroform. $Y = (\text{wt. acetone in upper/vol. upper})/(\text{wt. acetone per input/vol. of input})$. ●, output profile calculated from Eq. (3): $K_D = 0.24$, $V_L = 39.2$, $V_U = 19.4$, $p = 10$; ○, experimental; △, computer simulated output; ---, output profile calculated from Eq. (3): $K_D = 0.2$ (infinite dilution value).

used to calculate selectivities and separation requirements. Their use would be inappropriate at the concentration levels utilized in most of this study. The area under the curve is significantly larger than that for the experimental case. Dissolution of acetone in the chloroform phase increases the volume of this phase above the cutoff arm of the distribution tubes in the early part of the experiment. This causes transfer of some lower phase out of the instrument. The emerging lower phase is relatively rich in acetone. Volumes of lower phase eluted and the quantities of solute dissolved in these are shown in Figs. 9(a) and 9(b). Figure 10 shows experimental- and computer-effluent profiles determined for the total amount of solute in the effluent. The concordance is good in view of losses of acetone by evaporation during the experiment, except for tailing predicted by computer simulation.

After the plateau, as upper phase devoid of solute is added to the instrument, acetone is removed resulting in a shrinkage of the lower phase. The agreement between amount of lower phase present in each tube at the end of the experiment was good, except in the case of tube 1. Tube 0 was essentially depleted of lower phase, as was predicted, while tube 1 was also essentially depleted. Computer prediction indicated that about 13 ml of lower phase should remain in tube 1 at the conclusion of the experiment (Fig. 9(c)). Part of the discrepancy

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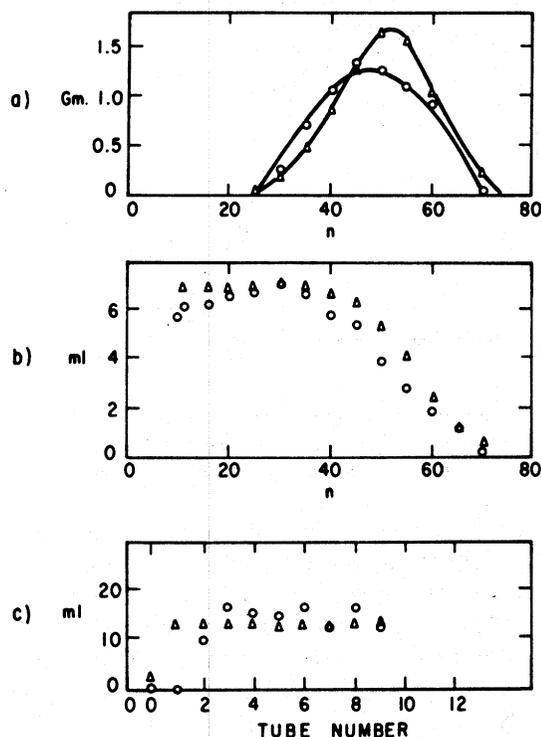


FIG. 9. Transport of lower phase in acetone-containing system: (a) weight of solute eluted in lower phase; (b) volume of lower phase eluted; (c) volume of lower phase remaining in distributor after 200 transfers. \circ , experimental; Δ , simulated.

lies in the suspension of about 0.1 ml of lower phase at the air-upper-phase interface. This is not predictable from the ternary diagram but tends to wash lower phase out of the instrument even when the lower phase lies beneath the cutoff arm. Similarly, if this phenomenon were considered in the simulation, the lengths of the extraction train and hence the trailing edge of the profile would be shortened.

In view of the large (1) deviations from ideality, (2) cumulative effects when small amounts of materials are transported out of the lower phase, and (3) number of transfers, the overall agreement of computer simulation with experimental evidence is good.

If automatic methods are used for the determination of solutes in effluents from liquid-liquid systems, the previously discussed phe-

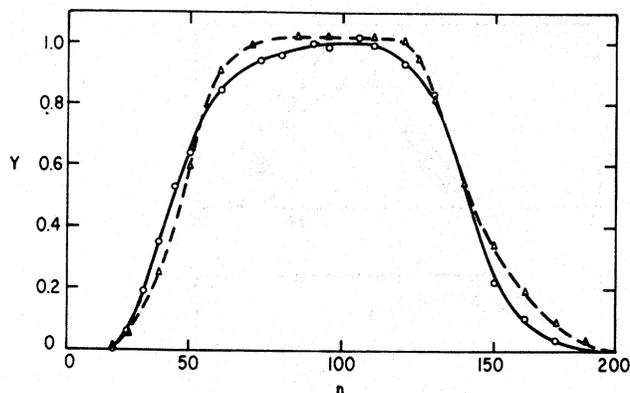


FIG. 10. Countercurrent distribution of acetone in water-chloroform. $Y =$ (wt. acetone in effluent fraction/vol. of fraction)/(wt. acetone per input/vol. of input). \circ , experimental; \triangle , computer simulated output.

nomena must be considered. If, for example, a flame-ionization monitor were usable, it would detect the total amount of solute in the effluent even when two phases are eluted. The curve would be related to that depicted in Fig. 10. Optical detectors could require special adaptation in the face of two-phase effluents. Refractive index monitors often require cooling of effluents to minimize gas desorption effects. Cooling an initially homogeneous effluent sample could lead to two phases. Furthermore, as the mobile-phase composition moves along the solubility curve in the ternary diagram, major changes in refractive index could occur that would not be related easily to solute concentration. Data obtained might be interpreted as "noise" or "baseline shifts," especially before and after the peak maximum or the plateau. In chromatographic studies, the equilibrium phenomena are very important driving forces, although equilibrium may not be reached. Changes in the volumes of intracolumn stationary and mobile phases may lead to changes in paths of flow and flow rates within the column. Although this may lead to loss of stationary phase by stripping, the phenomenon does not have to occur. Loss of stationary phase by solubilization in the mobile phase caused by the presence of the solute may be important.

Table 2 is a comparison of experimental, simulated, and calculated values of the number of inputs required to just achieve a frontal output. The first section of the table is concerned with ideal conditions where K_D is a constant and one phase is transported. The equations

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TABLE 2
Number of Inputs Required to Achieve a Frontal Output

| System | V_{UT} | V_T | V_U | V_L | p | n_R | n_F from: | | |
|--|----------|-------|-------|-------|-----|-------|-------------|----------|----------|
| | | | | | | | Data | Eq. (11) | Eq. (20) |
| $K_D = 9.29$ | 19.5 | 19.5 | 20.0 | 40.0 | 200 | 249 | 36 | 35 | 37 |
| $K_D = 3.92$ | 25.0 | 25.0 | 25.0 | 40.0 | 100 | 140 | 34 | 35 | 35 |
| $K_D = 2.00$ | 25.0 | 25.0 | 25.0 | 40.0 | 100 | 180 | 56 | 56 | 56 |
| $K_D = 2.00$ | 20.0 | 20.0 | 20.0 | 40.0 | 20 | 40 | 29 | 29 | 29 |
| $K_D = 1.14$ | 25.0 | 25.0 | 25.0 | 40.0 | 100 | 239 | 85 | 85 | 86 |
| $K_D = 0.1077$ | 20.0 | 20.0 | 20.0 | 40.0 | 200 | 3910 | 1270 | 1270 | 1270 |
| $K_D = 9.29 + 0.125 T_2^a$ | 19.5 | 19.5 | 20.0 | 40.0 | 200 | 249 | 35 | 34 | 36 |
| $K_D = 9.29 - 0.125 T_2$ | 19.5 | 19.5 | 20.0 | 40.0 | 200 | 250 | 36 | 35 | 37 |
| $K_D = 2.00 + 0.215 T_2$ | 20.0 | 20.0 | 20.0 | 40.0 | 20 | 37 | 25 | 26 | 26 |
| $K_D = 2.00 - 0.215 T_2$ | 20.0 | 20.0 | 20.0 | 40.0 | 20 | 46 | 45 | 35 | 35 |
| $K_D = 0.1077 + 0.0007 T_2$ | 20.0 | 20.0 | 20.0 | 40.0 | 200 | 3610 | 1140 | 1160 | 1160 |
| $K_D = 0.1077 - 0.0007 T_2$ | 20.0 | 20.0 | 20.0 | 40.0 | 200 | 4620 | 1970 | 1490 | 1490 |
| $K_D = 3.92$ | 23.4 | 26.6 | 25.0 | 40.0 | 100 | 145 | 38 | | 38 |
| $K_D = 2.00$ | 23.4 | 26.6 | 25.0 | 40.0 | 100 | 180 | 56 | | 56 |
| $K_D = 1.14$ | 23.4 | 26.6 | 25.0 | 40.0 | 100 | 228 | 80 | | 80 |
| Methyl palmitate (experimental; see text for details) | | | | | | | 30 | 35 | 33 |
| Methyl palmitate (simulated; see text for details) | | | | | | | 35 | | 38 |
| Acetone (experimental; see text for details) | | | | | | | 75 | | 70-150 |
| Acetone (simulated; see text for details) | | | | | | | 54 | | 58 |

^a T_2 is the total amount of solute in a tube.

agree exceptionally well with the data from computer simulation, pointing up the validity of the Gaussian approximation to the binomial distribution (14,15). When K_D is varied in a decreasing manner, the equations become less useful. When the output curve "heads" badly in these cases, the equations tend to seriously underestimate the number of inputs required. In the case of a sharpening front, the equations appear to give excellent agreement with simulations. Systems with biphasic flow and constant K_D are depicted in the third section of the table. There is excellent agreement between the predictions made from Eq. (20) and the simulation. Use of Eq. (11) would be

inappropriate under these conditions and Eqs. (12) through (20) are necessary to evaluate the output profile.

In the case of the methyl palmitate system, a number of nonideal phenomena occur. If the value of K_D in dilute solution and the initial phase volumes ($V_U = 20.7$, $V_L = 39.2$, $V_{UT} = 19.9$) are utilized in calculation of V_F by Eq. (11), it is found that 690 ml of solution or 35 inputs are required, while Eq. (20) predicts 33 inputs. If V_U is chosen to be 19.2, V_L is 40.7 (the conditions are similar to those at transfer 240), and K_D is 8.9 as above, n_F calculated by Eq. (20) is 40. Although it is difficult to discern from the experimental evidence when Y is at 99% of the plateau value, it appears that approximately 30 inputs were required. This is compared to 35 inputs indicated by computer simulation, and 38 inputs if the retention data from the simulation are used for calculation by Eq. (20).

Study of the acetone-containing system is quite challenging. The relatively large V_{LT} , and the quantity of solute therein dissolved, make it inappropriate to use the ideal equations. Even Eqs. (12) through (20) are of limited use since the amount of lower phase transported, as in the methyl palmitate study, varies somewhat at the start of the experiment and drops to zero at the plateau. If V_U is chosen to be 14.0, V_L 45.9, V_{UT} 12.7, V_{LT} 6.5, and K_D 0.2 (i.e., the volumes are essentially those in the last tube at transfer 33, while the K_D is that at infinite dilution), then n_F is 70. If the initial phase volumes, about 20 and 40 ml, and K_D at infinite dilution are used, n_F is 150 when z and w are both zero. But it must be remembered that the real case is much more complicated than the conditions for which the equations were set up. The solvent volumes throughout the apparatus varied appreciably during the course of the experiment while the partition coefficient, determined by computer simulation of the process, varied from 0.2 to 0.5. If the retention data from the computer simulation are utilized for calculation of n_F , 58 inputs are required.

CONCLUSION

The ideal equations are useful approximations to reality. When part of one or both phases is retained, the semi-ideal equations become more desirable. When phase volumes and partition coefficients vary during the course of an experiment, computer simulation using phase equilibria and transfer phenomena becomes necessary. The computer simulation has the added advantage of showing the nature of

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the aforementioned variations at any stage in the process. It is not restricted to either elution or frontal modes of operation and can accommodate any sort of input profile. Yet effective use of the computer requires some knowledge of the number of equilibrations and tubes. The equations discussed are useful for estimating these values, even in difficult cases, when the appropriate parameters can be determined from phase diagrams.

Computer programs for simulation of countercurrent distribution will be available from this Laboratory upon request (16).

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