952. *Preliminary Studies of Moving-bed Chromatography.*

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A process is described whereby mixtures of close-boiling volatile liquids (diethyl ether, dichloromethane, and dimethoxymethane) are separated continuously into two products; the binary mixtures can be separated into two pure components. This process, " moving-bed chromatography," involves the motion of a bed of solvent-impregnated solid particles countercurrent to a stream of inert gas. Separation depends on the differing extents of partition of the components between the two fluid phases, and on the ratio of rate of flow of inert gas to the rate of movement of the non-volatile solvent. The necessary operating conditions for separation can be predicted approximately from observations made on the behaviour of similar systems in an analytical gas–liquid chromatography column. A mathematical model is proposed in which the process is treated as a series of equilibrium stages or theoretical plates. The results are insufficient for full evaluation of the model but some examples provide simple approximations to the quantitative behaviour of the process.

In gas–liquid chromatography the efficiency of separation is due to the high area : volume ratio of the two fluid phases, which facilitates phase equilibration, and therefore gives a low height of equivalent theoretical plate (HETP). The non-volatile solvent often increases the relative volatility of a given pair of volatile components, which facilitates the separation. Both advantages can be retained, and the process converted into a continuous one, if the solid bed is moved countercurrent to the carrier gas. Although it might be claimed that such a process would not be chromatography since there would be no stationary phase, the behaviour of a binary mixture in such a countercurrent process can be largely predicted from its behaviour in a static-bed column, since the physicochemical principles of separation are almost identical; we therefore suggest the term " moving-bed chromatography " for a process in which separation is effected by causing a bed of solid particles to move countercurrent to a moving fluid phase which consists mainly of an inert component.

Moving-bed chromatography (gas–solid), under the name of " hypersorption," has been described in the patent and scientific literature [1] of the past decade. The gas–liquid variant is of more recent origin. Scott [2] outlined the principles of the process and achieved some success experimentally. Pichler and Schulz [3] published a more detailed description of a moving-bed process in which they partially separated mixtures of C_4 hydrocarbons by using dibutyl phthalate as a non-volatile solvent, and they outlined a theory based on retention factors. Barker and Critcher [4] successfully separated benzene and cyclohexane in a moving-bed chromatographic column involving a polyglycol derivative, and stated, in terms of partition coefficients, the general conditions for separation of a binary mixture. Somewhat similar processes in the patent literature [5] include the continuous separation of benzene–cyclohexane [5b] at the rate of 225 ml./min. in a column of 6 in. diameter and 10 ft. length.

The basic principle of gas–liquid moving-bed chromatography is illustrated in Fig. 1. A continuous feed of volatile components, combined with a continuous stream of carrier gas, produces two exit streams containing the top and the bottom product, as in

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[1] *E.g.*, U.S.P. 2,539,006/1951; 2,545,067/1951; Freund, Benedek, and Szepesy, " Vapour Phase Chromatography " (edited by Desty), Butterworths Scientific Publns., London, 1957, p. 359.

[2] Scott, " Gas Chromatography," ed. Desty, Butterworths Scientific Publns., London, 1958, p. 287; Scott, personal communication.

[3] Pichler and Schulz, *Brennstoff-Chem.*, 1958, **39**, 148.

[4] Barker and Critcher, *Chem. Eng. Sci.*, 1960, **13**, 82.

[5] (*a*) B.P. 810,767/1959; U.S.P. 2,893,955/1959; (*b*) U.S.P. 2,869,672/1959

a continuous distillation; and, in the use of a non-volatile component to improve the relative volatility, the process is analogous to extractive distillation. However, the true HETP of an extractive-distillation packed column is generally considerably greater than that of a normal fractionation (the true HETP must be calculated on the basis of relative volatility in the ternary system involving the solvent); and the control of product quality is not always easy in extractive distillation. It would be expected that moving-bed chromatography should give much lower HETP values, and that the use of carrier gas should give a greater flexibility in control of the separation.

As a first approximation, the principles of stagewise countercurrent liquid–liquid extraction give a better practical insight to moving-bed chromatography than do those of extractive distillation. Liquid–liquid extraction is often treated in terms of extraction factors and such functions can be used for the present process.

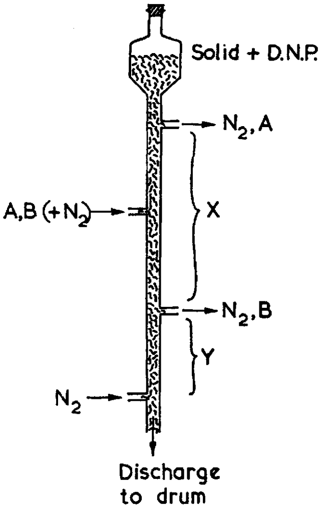

FIG. 1. General principle of the column: X = absorbing section, at t_1°; Y = stripping section, at t_2°; DNP = dinonyl phthalate.

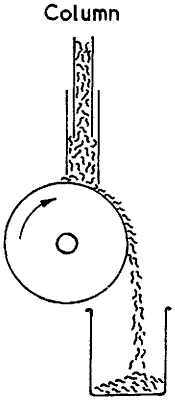

FIG. 2. Discharge on to rotating drum.

For any one volatile component at constant temperature in a given section of the column, the following quantities are defined: extraction factor (for one equilibrium extraction stage), E = ratio of the masses of the components passing into (*a*) the liquid and (*b*) the gas phase. Partition coefficient, K = ratio of the equilibrium masses of the components per unit vol. of (*a*) the solvent and (*b*) the carrier gas.

If V_L is the volume flow rate of the solvent and V_G that of the carrier gas, then the flow ratio $\phi = V_G/V_L$, and

$$E = K(V_L/V_G) = K/\phi.$$

Consider the desired separation in the absorber (at t_1°): for component A to move with the carrier gas, E_A must be <1, so that $\phi > K_A$; and for component B to move with the solvent, E_B must be >1, and $\phi < K_B$. Therefore, provided a sufficient number of equilibrium stages are present, complete separation will occur if $K_A < \phi < K_B$, at temperature t_1. This essential operating condition for separation was also stated by Barker and Critcher[4] who deduced it from the rate of linear movement of a component in a static-bed column.

The solvent leaving the bottom of the absorber should, if separation has occurred, contain only component B. In order to vaporise B into the bottom exit-gas stream, it is necessary in the stripper that $\phi > K_B$ at temperature t_2. This is readily achieved with a suitable temperature difference, $t_2 > t_1$.

In theory, the ease of separation of A and B will be determined by the partition ratio, K_B/K_A, which is comparable with the reciprocal of relative volatility in a distillation process. In practice, the difference between the partition coefficients, $K_B - K_A$, might also be significant, since this determines the degree of precision necessary in control of the flow ratio.

As a preliminary study of moving-bed chromatography, the separation of three close-boiling liquids (diethyl ether, dichloromethane, and dimethoxymethane) was studied. These components were chosen as having boiling points low enough for the absorbing section of the column to be operated at room temperature without excessively large gas flows. Negative azeotropes are known to be formed at atmospheric pressure for diethyl ether–dichloromethane and dimethoxymethane–dichloromethane. No studies were attempted of the most suitable solvent for separation of these mixtures; dinonyl phthalate was used because of its common occurrence in gas–liquid chromatography.

EXPERIMENTAL

The column was of 20-mm. glass tubing, the absorber being 4 ft. long with a central feed-point; the heated stripping section was 2 ft. long. The main stream of carrier gas (nitrogen) entered at the bottom of the stripper, and top and bottom exit streams led through simple momentum traps (for any solid displaced) to cold traps at −78° for collection of the products. Gas flows were measured with capillary flowmeters, the inlet gas being slightly above, and the exit streams slightly below, atmospheric pressure (3 cm. pressure drop across the column).

The solid was Celite (44—60 BSS mesh sieve) impregnated with 20% w/w of dinonyl phthalate and was fed by gravity from a closed hopper at the top of the column. The rate of movement of the solid bed was controlled by feeding it from the base of the column on to a

(1) Diethyl ether (X); dichloromethane (Y). $K_X = 145$, $K_Y = 359$. $K_Y/K_X = 2{\cdot}48$.

ϕ, upper	350	335	295	245	210	250	205
lower	285	275	220	165	170	125	145
Product, top	X, 3% Y	X	X	X	X	X	X
bottom	Y	Y	Y	Y	Y	Y, 7% X	Y, 12% X

Limits of flow ratio for complete separation: expected, 145—359; observed, 160—345.

(2) Dichloromethane (Y); dimethoxymethane (Z). $K_Y = 359$, $K_Z = 221$. $K_Y/K_Z = 1{\cdot}62$.

ϕ, upper	370	335	330	330	325	295
lower	275	260	250	245	235	205
Product, top	Z, 15% Y	Z	Z	Z	Z	Z
bottom	Y	Y	Y	Y, 1% Z	Y, 3% Z	Y, 22% Z

Limits of flow ratio for complete separation: expected, 221—359; observed, 250—360.

(3) Diethyl ether (X); dimethoxymethane (Z). $K_X = 145$, $K_Z = 221$. $K_Z/K_X = 1{\cdot}52$.

ϕ, upper	225	215	210	200
lower	180	175	165	160
Product, top	X, 11% Z	X, 4% Z	X	X
bottom	Z	Z, 1% X	Z, 20% X	Z, 43% X

Limits of flow ratio for complete separation: expected, 145—221; estimated experimental range, 180—210. Complete separation was not observed with this mixture, the differing flow ratios in the two halves of the absorber being a disadvantage (see Discussion).

(4) Diethyl ether (X); dichloromethane (Y); dimethoxymethane (Z).

ϕ, upper	335	290	195	200
lower	275	235	170	155
Product, top	X, Z	X, Z	X, Z	X
bottom	Y	Y	Y, Z	Y, Z, X

The effect of flow ratio on the distribution of components between the top and the bottom product was largely in accordance with the results of separations of the binary mixtures.

drum driven at slow constant speed (Fig. 2). A slight tendency for hold-up and sticking of the bed was eradicated by vibration of the column. The use of a 10-mm. column was abandoned owing to lack of uniformity of flow of the solid, and it seems likely that moving-bed chromatography in columns of small diameter will be impracticable.

The feed components entered the column in a secondary stream of nitrogen which had passed through a saturator containing the mixed liquids. This secondary stream produced a greater flow of gas in the upper half than in the lower half of the absorber.

Partition coefficients were measured, and products analysed, in a 4-mm. 6-ft. analytical gas–liquid chromatographic column packed with Celite (100—120 mesh) with 20% of dinonyl phthalate. Partition coefficients were measured at room temperature, and the usual corrections applied for dead-space volume and pressure-drop ratio. Analysis was carried out at 56°, the sensitivity limit being 0·5%.

Range of Operating Conditions for the Moving-bed Chromatographic Column.—The rate of feed of the volatile mixture was 3—5 ml. of liquid per hr. Nitrogen flows were, at the main inlet 150—200 and at the secondary inlet 15—30 ml./min., at the top exit 80—100, and at the bottom exit 60—80 ml./min. Hence V_G values (in ml./min.) were: upper half absorber, 80—100; lower half absorber, 50—85; and stripper, 110—165. The solid flow was 1·2—2 g./min., giving $V_L = 0{\cdot}25$—$0{\cdot}4$ ml./min. The temperature of the absorber was 17—20° and of the stripper 76—85°.

Results of Separations.—In the Tables flow ratios (ϕ) are given for the two halves of the absorber, the degree of accuracy being ± 10. In the stripper, ϕ exceeds 275 in all runs, which was adequate for complete stripping. Indication of only one component in the product implies at least 99·5% purity.

DISCUSSION

Method of Introducing the Feed.—Introducing the feed in a secondary stream of carrier gas is convenient, but suffers from the disadvantage of causing different flow rates, and hence different extraction factors, in the two halves of the absorber. For a mixture where the permissible range of flow ratio is relatively small (low value of $K_A - K_B$), this can prevent complete separation, as with mixture (3). This difficulty can be obviated by injecting the mixture directly into the column as was done by Barker and Critcher.[4] An alternative procedure, which would retain the advantage of the vaporising carrier gas, would be to keep the lower half of the absorber at a slightly higher temperature than the upper; the partition coefficients could then be modified in the same proportion as the flow ratios, in order to equalise the extraction factors throughout the absorber.

Theoretical-plate Treatment.—An exact treatment of a continuous countercurrent process requires consideration of both equilibrium and mass-transfer factors. A semi-empirical model often used for correlation of results is that of a series of equivalent equilibrium stages or theoretical plates, the number of such stages under given conditions being found by experiment.

If we assume the absorbing section in a moving-bed chromatographic column to comprise $2n$ equilibrium stages with central feedpoint, then by taking a mass balance over each stage, as in Alders's treatment [6] of liquid–liquid extraction, it can be shown that:

$$\frac{\text{Mass of a volatile component in the top product}}{\text{Mass of the same component in the feed}} \cdot \chi$$

$$= \frac{(E_2{}^n - 1)(E_1 - 1)}{E_1E_2{}^{n-1}(E_2 - 1)(E_1{}^n - 1) + (E_2{}^n - 1)(E_1 - 1)},$$

where E_1 and E_2 are the extraction factors for the component in the upper and lower portions of the absorber.

If $E_1 = E_2 = E$, then $\chi = 1/(E^n + 1)$.

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[6] Alders, " Liquid–Liquid Extraction," Elsevier, Amsterdam, 1955, Chap. V.

Consider components A and B under conditions such that $E_A < 1 < E_B$: then, if $n \gg 1$, the simple relation emerges that $\chi_A = 1 - E_A{}^n$, and $\chi_B = E_B{}^{-n}$. For a 1 : 1 feed composition and equal purity of top and bottom products, $\chi_A = 1 - \chi_B$, $E_A E_B = 1$, and hence the desired flow ratio is $(K_A K_B)^{\frac{1}{2}}$. For other feed compositions and specified purities of product, the flow ratio can be changed accordingly, which illustrates the flexibility of control of moving-bed chromatography.

The permitted range of flow ratio for a specified purity of products will depend on the number of equivalent theoretical plates, the range becoming narrower as the number of plates decreases. Consider a minimum purity of products of a % from a 1 : 1 feed; then, $\log \phi_{\text{max.}} = \log K_B + (1/n) \log (1 - a/100)$, and $\log \phi_{\text{min.}} = \log K_A - (1/n) \log (1 - a/100)$, where $\phi_{\text{max.}}$ and $\phi_{\text{min.}}$ are the upper and the lower limits, respectively, of flow ratio for this specified purity. If we put $K_A = 200$, $K_B = 300$, and $a = 99{\cdot}9$, then for $n = 100$ the limits of flow ratio are 214—280, but for $n = 50$ the limits are 230—261.

An exact calculation of the number of theoretical plates from the experimental results is not possible owing to ignorance of the precise values of partition coefficients at finite concentrations (see below). A very approximate estimate can be made from the equation $\log (\phi_{\text{max.}}/\phi_{\text{min.}}) = \log (K_B/K_A) + (2/n) \log (1 - a/100)$, since the ratio K_B/K_A is likely to vary less than the individual values of partition coefficients. Application of this equation to our experimental observations leads to the conclusion that the 4-ft. absorbing section is equivalent to at least 80 equilibrium stages, giving a maximum estimate of HETP of 0·6 in. This may be compared with a height of transfer unit of 0·9 in. in Barker and Critcher's column [4] in which coarser particles were used. HETP values in extractive-distillation packed columns used under laboratory conditions are about 4—6 in.[7] Values in static-bed gas–liquid chromatographic columns are not comparable with those in continuous countercurrent processes.

Correction of Partition Coefficients for Finite Concentrations.—A partition coefficient calculated from the retention time in an analytical gas–liquid chromatographic column is defined in terms of unit volumes of the inert components (non-volatile solvent and carrier gas), and, under the conditions used, the liquid phase is assumed to approximate to an infinitely dilute solution of volatile component. The value of such a partition coefficient would be expected to vary with composition of the liquid phase.

A thermodynamic partition coefficient should be defined in terms of the ratio of thermodynamic activities of the component in the two phases, activities being normally expressed on a mole fraction basis in the case of liquid–vapour equilibrium. Thus consider the following system, in which the gas phase is treated as an ideal gas: N^G moles of gas phase composed of $n^G{}_A$ moles of component A + n_G moles of carrier gas; and N^L moles of liquid phase composed of $n^L{}_A$ moles of component A + n_L moles of solvent. The volume of n_G moles of carrier gas (at 1 atm.) $= n_G \boldsymbol{R}T$, and the volume of n_L moles of solvent (of molecular weight M and density $\rho) = n_L M/\rho$. The thermodynamic partition coefficient,

$$K_a = \frac{\gamma_A n^L{}_A}{N^L} \cdot \frac{N^G}{n^G{}_B},$$

where γ_A is the rational activity coefficient of component A in the liquid phase. The partition coefficient in terms of concentrations, as previously defined, is given by

$$K_c = \frac{n^L{}_A \rho}{n_L M} \cdot \frac{n_G \boldsymbol{R}T}{n^G{}_A}$$

the carrier-gas volume being corrected to 1 atm. Combining these two expressions gives $K_c = (K_a/\gamma_A)(N^L n_G/N^G n_L)(\boldsymbol{R}T\rho/M)$. Putting $n_L/N^L = x_L$ (the mole fraction of solvent in the liquid phase), and $n_G/N^G = x_G$ (the mole fraction of carrier gas in the gas phase), we

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[7] Dicks and Carlson, *Trans. Amer. Inst. Chem. Engrs.*, 1946, **42**, 789; Colburn and Schoenborn, *ibid.*, p. 421.

have $K_c = (K_a/\gamma_A)(x_G/x_L)(\boldsymbol{R}T\rho/M)$. At infinite dilution, $x_G = x_L = 1$, and $K^\infty{}_c = (K_a/\gamma^\infty{}_A)(\boldsymbol{R}T\rho/M)$, where the superscripts refer to the values of the quantities at infinite dilution. The value of the partition coefficient in terms of concentration, at finite concentration, will be related to its value at infinite dilution, $K_c = K^\infty{}_c(\gamma_A{}^\infty/\gamma_A)(x_G/x_L)$.

Under the operating conditions of moving-bed chromatography, it is estimated that (x_G/x_L) varies from 1·2 to 1·6. Estimation of the activity coefficient ratio is more difficult. All three volatile components show appreciable negative deviations from Raoult's law, as can be calculated from the values of partition coefficients. Therefore, the activity coefficient would increase with increasing concentration and $(\gamma^\infty{}_A/\gamma^c{}_A) < 1$. As a result of these two opposing factors, the effect of change of concentration on the partition coefficients should not be excessively large, and the experimental results can be interpreted in terms of a slight increase (see below).

For an exact solution of the problem, measurements are required of activity coefficients in the ternary system, component A + component B + solvent. Considerable studies have been made of ternary systems such as C_4 hydrocarbons–furfuraldehyde,[8] and the results of the ternary and binary systems have been correlated by using the Margules and van Laar equations. No such measurements have been made of ternary systems involving gas–liquid chromatographic solvents where, as Ashworth and Everett [9] have shown for binary systems, the big difference in molecular sizes produces an added complication.

Flow Ratios Required for Separations by Moving-bed Chromatography.—The possible variation of partition coefficients with composition, coupled with the limited number of theoretical plates in the column, provides a possible explanation of the discrepancies between the observed flow ratios and those "expected." The "expected" range of flow ratios, as stated, corresponds to: $K_A < \phi < K_B$. This can only be true for infinitely dilute solution and an infinite number of theoretical plates. If it is assumed that, at finite concentration, both partition coefficients increase, then it would be expected for infinite plates, that the observed range would be $(K_A + \delta_A) < \phi < (K_B + \delta_B)$. The effect of a finite number of plates is to narrow the range over which separation occurs, giving an observed range $(K_A + \delta_A + \delta_{A'}) < \phi < (K_B + \delta_B - \delta_{B'})$. Thus, the lower limit of flow ratio is increased to a relatively greater extent than the change in the upper limit. This is in agreement with the experimental results.

The theoretical-plate concept in distillation theory is known to be a crude but useful model of the behaviour of a packed column, and the transfer-unit concept is an attempt at a more realistic approach.[10] The limitations of the former model apply equally to the simple treatment outlined above and, at high values of flow ratio, it would be expected that the HETP of a moving-bed chromatographic column would increase, resulting in a further reduction in the upper limit of flow ratio.

The Relative Merits of Moving-bed Chromatography for the Separation of Volatile Liquids.—The use of a solid-supported liquid phase results in lower HETP values than are normally achieved in countercurrent processes in which the liquid flows over a stationary column packing. Herein lies the advantage of moving-bed chromatography over extractive distillation or similar processes. Its advantages over orthodox preparative gas–liquid chromatography seem to be in the merits of a continuous process and in the possibility of increased throughputs. Whereas our column was operated at a rate of only 5 ml./hr. Barker and Critcher [4] used a rate of feed of 30 ml./hr. in a 1-inch column, and much higher relative rates are described in some patents.[5b]

The physical limitation on throughput in a moving-bed chromatographic column, operating ideally, is the maximum rate of gas flow before incipient fluidisation of the solid

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[8] See, *e.g.*, Gerster, Mertes, and Colburn, *Ind. Eng. Chem.*, 1947, **39**, 797; McMillin, Kobe, McKetta, and van Winkle, *Ind. Eng. Chem., Chem. Eng. Data Ser.*, 1958, **3**, 96.

[9] Ashworth and Everett, *Trans. Faraday Soc.*, 1960, **56**, 1609.

[10] *E.g.*, "Chemical Engineering Practice," ed. Cremer and Davies, Butterworths Scientific Publns., London, 1958, Vol. 5, pp. 606–611.

bed occurs (comparable to " flooding " of a distillation column). For a given gas flow, in a given system, there is likely to be some optimum temperature, which is not necessarily room temperature. Studies are proceeding on the influence of temperature on separations by this method.

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