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The Extent of Separation: Applications to Multicontact Systems

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Summary

The fundamental equations for calculating the extent of separation are given for four different types of multicontact separation systems: crosscurrent distribution with discrete equilibrium contacts, crosscurrent distribution with differential contact, countercurrent distribution with discrete equilibrium contacts (binomial distribution), and countercurrent distribution with differential contact (Poisson distribution). Optimum values for the number of contacts, tube cutoff point, extent of separation, and distribution coefficients are derived. A method for comparing all separation techniques on an equivalent basis is proposed.

INTRODUCTION

The goal of this series of articles is to demonstrate how a universal separation index—ξ, the extent of separation—can easily and effectively apply to all of the different classes of separation techniques. In this paper we will briefly summarize the equations for four simple multicontact systems: (a) crosscurrent distribution with discrete equilibrium contacts, (b) crosscurrent distribution with differential contact, (c) countercurrent distribution with discrete equilibrium contacts, and (d) countercurrent distribution with differential contact. The reader is referred to Rogers' excellent review (*1*) or Stene's classic article (*2*) for references and a more thorough treatment of details not covered in the following sections. Our purpose here is to illustrate the application of the extent of separation, not to provide an exhaustive treatment of all aspects of multicontact systems.

DEFINITIONS

We will continue to employ terminology developed in previous publications. The substance to be separated is called *component* i and is defined as one of the distinct atomic, molecular, ionic, or aggregative species composing a mixture. The substances in an equilibrium system that perform the separation are called the *environments* s. They can be phases or distinct molecules, ions, or aggregates of molecules. A *partition state* is the chemical state characterized by component i and environment s and is represented by the notation $\boxed{i{:}s}$ and by the subscript is. The physical region of space in which a component accumulates as it is separated is called a *region*.

SEGREGATION FRACTIONS

The segregation fraction, Y_{ij}, is defined as the ratio of the amount of component i in region j to the total amount of component i in the entire separation system,

$$Y_{ij} = \frac{n_{ij}}{\sum_j n_{ij}} \tag{1}$$

Another form of the segregation fraction, Y_{is}, is useful when we are describing the distribution of component i between a number of environments s,

$$Y_{is} = \frac{n_{is}}{\sum_s n_{is}} \tag{2}$$

Equation (2) simplifies to

$$Y_{is} = \frac{K_{is}}{\sum_s K_{is}} \tag{3}$$

when the definition for the distribution coefficient, K_{is},

$$K_{is} = \frac{n_{is}}{n_{i1}} \tag{4}$$

is employed. Environment 1 is a "reference" environment, so K_{i1} is identically equal to one,

$$K_{i1} = \frac{n_{i1}}{n_{i1}} \equiv 1 \tag{5}$$

For a binary separation system consisting of two components ($i = 1, 2$) and two phases ($s = 1, 2$), the quantities p_i and q_i are customarily employed instead of the more recently defined segregation fractions, Y_{is} (*1–6*),

$$p_i \equiv Y_{i2} \equiv \frac{K_i}{1 + K_i} \tag{6}$$

$$q_i \equiv Y_{i1} \equiv \frac{1}{1 + K_i} \tag{7}$$

In deference to tradition, these two parameters will be used throughout this paper. Note that the subscript $s = 2$ has been deleted in the definition of the distribution coefficient, K_i, for a binary system.

TYPES OF MULTICONTACT SYSTEMS

Multicontact systems can be respectively described as being either *countercurrent*, *cocurrent*, or *crosscurrent*, depending upon whether the contacting environments pass each other in parallel but opposite directions, parallel but similar directions (perhaps with different velocities), or transversely.

An additional distinction must be made between systems which employ *discrete equilibrium contacts* and those which employ *differential contact*. If the two partitioning environments ($s = 1, 2$) represent phases and if the total volume of the contacting phase is V_2^0, the optimum separation can be achieved when V_2^0 is subdivided (for multiple contacting) into n equal parts,

$$V_2 = \frac{V_2^0}{n} \tag{8}$$

The distribution coefficient, K_i, becomes

$$K_i = \kappa_{i2}\frac{V_2}{V_1} = \kappa_{i2}\frac{V_2^0}{nV_1} \tag{9}$$

where κ_{i2} is a partition coefficient,

$$\kappa_{i2} = \frac{c_{i2}}{c_{i1}} \tag{10}$$

The quantity n also represents the number of times the multiple contacting procedure is performed. In a system with discrete equilibrium contacts, n remains finite, whereas in a system with differential contact, n tends toward infinity as a limit.

CROSSCURRENT DISTRIBUTION WITH DISCRETE EQUILIBRIUM CONTACTS

Consider a single equilibrium stage in which two components ($i = 1, 2$) each distribute between two environments ($s = 1, 2$). Once the stage has reached equilibrium, partition state $\boxed{i{:}2}$ is decanted or removed from the system, fresh environment 2 is added, and the system re-equilibrated with the amount of i remaining in partition state $\boxed{i{:}1}$. This process is repeated n times and all of the "extracts" (i.e., partition states $\boxed{i{:}2}$) are pooled. If the same amount of environment 2 is employed for each distribution, the distribution coefficient K_i in Eqs. (6) and (7) remain constant and the segregation fractions given by Eq. (1) become

$$Y_{i1} = \left(\frac{1}{1 + K_i}\right)^n = q_i^n \tag{11}$$

$$Y_{i2} = 1 - \left(\frac{1}{1 + K_i}\right)^n = 1 - q_i^n \tag{12}$$

The extent of separation is therefore (7)

$$\xi = \text{abs}\,[Y_{11} - Y_{21}] = \text{abs}\left[\frac{1}{(1 + K_1)^n} - \frac{1}{(1 + K_2)^n}\right] \tag{13}$$

Equation (13) can be differentiated with respect to n and the result set equal to zero to yield the optimum number of contacts, n_{opt},

$$n_{\text{opt}} = \frac{\ln\left[\dfrac{\ln(1 + K_1)}{\ln(1 + K_2)}\right]}{\ln\left(\dfrac{1 + K_1}{1 + K_2}\right)} \tag{14}$$

and the optimum extent of separation, ξ_{opt},

$$\xi_{\text{opt}} = \left(\frac{1}{1 + K_1}\right)^{n_{\text{opt}}} \text{abs}\left[1 - \frac{\ln(1 + K_1)}{\ln(1 + K_2)}\right] \tag{15}$$

By employing the definition for the quotient of the distribution coefficients (7),

$$\alpha \equiv \frac{K_2}{K_1} \tag{16}$$

we can differentiate Eq. (13) with respect to K_1 at constant α, set the resulting derivative equal to zero, and obtain the optimum value of K_1,

$$K_1\Big|_{\text{opt}} = \frac{\alpha^{1/(n+1)} - 1}{\alpha - \alpha^{1/(n+1)}} \tag{17}$$

the optimum value of K_2,

$$K_2\Big|_{\text{opt}} = \frac{\alpha^{(n+2)/(n+1)} - \alpha}{\alpha - \alpha^{1/(n+1)}} \tag{18}$$

and the maximum value of the extent of separation, $\xi_{\max}$,

$$\xi_{\max} = \text{abs}\left[\frac{(\alpha^{n/(n+1)} - 1)^{n+1}}{(\alpha - 1)^n}\right] \tag{19}$$

Equations (14) and (17) have been previously reported by Treybal (*6*).

CROSSCURRENT DISTRIBUTION WITH DIFFERENTIAL CONTACT

We can now determine what happens when only a limited amount of fresh environment 2 is available for the multiple contacting process. We first define the quantity, K_i^0, as

$$K_i^0 = \kappa_{i2}\frac{V_2^0}{V_1} \tag{20}$$

and employ Eq. (9) to compute the following limit

$$\lim_{n\to\infty} q_i^n = \lim_{n\to\infty}\left(\frac{1}{1 + \frac{K_i^0}{n}}\right)^n = e^{-K_i^0} \tag{21}$$

The extent of separation therefore becomes

$$\xi = \text{abs}\,[e^{-K_1^0} - e^{-K_2^0}] \tag{22}$$

an equation which can be optimized with respect to K_1^0 at constant α,

$$\alpha \equiv \frac{K_2^0}{K_1^0} \tag{23}$$

to yield the optimum value of K_1^0,

$$K_1^0\Big|_{\text{opt}} = \frac{\ln \alpha}{\alpha - 1} \tag{24}$$

the optimum value of K_2^0,

$$K_2^0\Big|_{\text{opt}} = \frac{\alpha \ln \alpha}{\alpha - 1} \tag{25}$$

and the maximum value for the extent of separation,

$$\xi_{\max} = \alpha^{\alpha/(1-\alpha)} \text{ abs } [\alpha - 1] \tag{26}$$

COUNTERCURRENT DISTRIBUTION WITH DISCRETE EQUILIBRIUM CONTACTS (BINOMIAL DISTRIBUTION)

Rogers (*1*) and Sixma and Wynberg (*4*) have given excellent summaries of the Craig countercurrent apparatus, a notable example of a multiple contacting process that involves countercurrent distribution. In the nomenclature of Sixma and Wynberg, tubes are numbered starting with zero (0, 1, 2, . . . , r) and the number of cycles, n, is equal to the number of times that the mobile phase is transferred to the next tube. The separation system is again similar to that given for the single equilibrium stage, i.e., two components each distributing between two environments.

The fraction of component i in tube r after cycle n is equal to (*4*)

$$\begin{aligned} T_i(n,r) &= \frac{n!}{(n-r)!r!} p_i^r q_i^{n-r} \\ &= \frac{n!}{(n-r)!r!} \frac{K_i^r}{(1+K_i)^n} \end{aligned} \tag{27}$$

When two different components are present within the countercurrent apparatus, the extent of separation can be computed according to the formula,

$$\begin{aligned} \xi &= \sum_{r=0}^{r_c} \text{abs } [T_1(n,r) - T_2(n,r)] \\ &= \sum_{r=0}^{r_c} \frac{n!}{(n-r)!r!} \text{abs} \left[\frac{K_1^r}{(1+K_1)^n} - \frac{K_2^r}{(1+K_2)^n} \right] \end{aligned} \tag{28}$$

provided that a cutpoint (in this case, tube r_c) is chosen.

Since the quantities $T_i(n,r)$ and $T_i(n,r-1)$ are related by the equation,

$$T_i(n,r) = \frac{n-r+1}{r} K_i T_i(n,r-1) \tag{29}$$

it is useful to recast Eq. (28) into the following form,

$$\xi = \text{abs}\,[T_1(n,r_c) - T_2(n,r_c)] + \sum_{r=0}^{r_c-1} \text{abs}\,[T_1(n,r) - T_2(n,r)] \quad (30)$$

If we now employ Eq. (29) for $r = r_c$, differentiate Eq. (30) with respect to r_c, set the derivative equal to zero, and observe that

$$\frac{\partial}{\partial r_c}\left\{\sum_{r=0}^{r_c-1} \text{abs}\,[(T_1(n,r) - T_2(n,r)]\right\} = 0 \quad (31)$$

we can calculate the optimum tube cutoff point, r_{opt},

$$r_{\text{opt}} = n\,\frac{\ln \dfrac{1+K_2}{1+K_1}}{\ln \dfrac{K_2}{K_1}} \quad (32)$$

and the optimum extent of separation, ξ_{opt},

$$\xi_{\text{opt}} = \sum_{r=0}^{r_{\text{opt}}} \frac{n!}{(n-r)!r!}\,\text{abs}\left[\frac{K_1^r}{(1+K_1)^n} - \frac{K_2^r}{(1+K_2)^n}\right] \quad (33)$$

The standard deviation of the binomial distribution is

$$\sigma_i \equiv \sqrt{np_iq_i} \quad (34)$$

For a symmetrical distribution system, i.e., one in which

$$\sigma_1 = \sigma_2 = \sigma \quad (35)$$

we obtain

$$\sigma^2 = n\,\frac{\alpha^{1/2}}{(1+\alpha^{1/2})^2} \quad (36)$$

$$K_1|_{\text{opt}} = \alpha^{-1/2} \quad (37)$$

$$K_2|_{\text{opt}} = \alpha^{1/2} \quad (38)$$

$$r_{\text{opt}} = \frac{n}{2} \quad (39)$$

and

$$\xi_{\max} = \sum_{=0}^{n/2} \frac{n!}{(n-r)!r!}\,\frac{\text{abs}\,[\alpha^{(n-r)/2} - \alpha^{r/2}]}{(1+\alpha^{1/2})^n} \quad (40)$$

Equation (32) differs from the result obtained by Nichols (*8*).

COUNTERCURRENT DISTRIBUTION WITH DIFFERENTIAL CONTACT (POISSON DISTRIBUTION)

The Poisson distribution is obtained from Eq. (28) via a procedure similar to that employed in Eq. (21). The quantity $T_i(r)$ becomes

$$T_i(r) = \lim_{n\to\infty} T_i(n,r) = \lim_{n\to\infty} \frac{n!}{(n-r)!r!} \frac{\left[\frac{K_i^0}{n}\right]^r}{\left[1+\frac{K_i^0}{n}\right]^n}$$

$$= \frac{K_i^{0^r}}{r!} e^{-K_i^0} \tag{41}$$

Note that we can write a relationship similar to Eq. (29),

$$T_i(r) = \frac{K_i^0}{r} T_i(r-1) \tag{42}$$

The extent of separation for such a system,

$$\xi = \sum_{r=0}^{r_c} \frac{1}{r!} \operatorname{abs} [K_1^{0^r} e^{-K_1^0} - K_2^{0^r} e^{-K_2^0}]$$

$$= \operatorname{abs} [T_1(r_c) - T_2(r_c)] + \sum_{r=0}^{r_c-1} \operatorname{abs} [T_1(r) - T_2(r)] \tag{43}$$

can be differentiated with respect to r_c and the derivative set equal to zero to yield the optimum cutpoint, r_{opt},

$$r_{\text{opt}} = \frac{K_2^0 - K_1^0}{\ln \frac{K_2^0}{K_1^0}} \tag{44}$$

and the optimum extent of separation, ξ_{opt},

$$\xi_{\text{opt}} = \sum_{r=0}^{r_{\text{opt}}} \frac{1}{r!} \operatorname{abs} [K_1^{0^r} e^{-K_1^0} - K_2^{0^r} e^{-K_2^0}] \tag{45}$$

EXAMPLES

Several of the preceding equations have been programmed on a computer to demonstrate the application of the extent of separation to multicontact separation systems. Listings of the computer programs are available upon request. Figure 1 represents Eq. (13) for the following

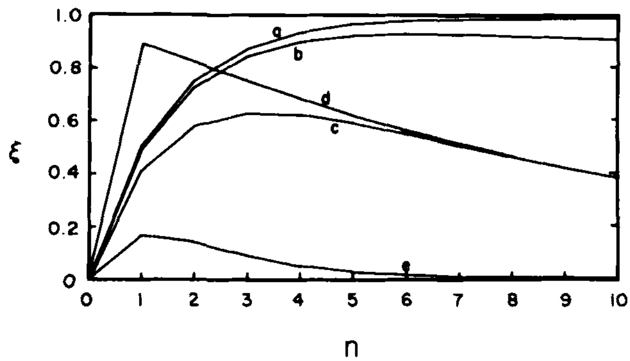

FIG. 1. The extent of separation, as a function of the number of discrete equilibrium contacts, for crosscurrent distribution. Equation (13) is plotted for the following pairs of values of the distribution coefficients K_1 and K_2, respectively: (a) 10^{-3}, 1; (b) 10^{-2}, 1; (c) 10^{-1}, 1; (d) 10^{-1}, 50; and (e) 1, 2.

pairs of values of the distribution coefficients, K_1 and K_2: (a) 10^{-3}, 1; (b) 10^{-2}, 1; (c) 10^{-1}, 1; (d) 10^{-1}, 50; and (e) 1, 2. The optimum extent of separation can be clearly seen in three of the curves. As a consequence of the existence of such an optimum, this type of multicontact separation technique is useful only for large α and small K_1.

Figure 2 represents Eq. (13) for the values of the distribution coefficients given by Eqs. (17) and (18) and by Eqs. (37) and (38). The curves are plotted for $n = 1$ and $n = 10$ [when $n = 1$, Eqs. (17) and (37) are identical]. Though repeated extractions do not produce a significant increase in ξ_{max} [Eq. (19)], the optimum values of the distribution coefficients must always be employed when $n > 1$ or else a significant decrease in separation efficiency results. A plot of ξ_{max} vs $\alpha - 1$ [Eq. (26)] can almost be superimposed upon curve b in Figure 2.

The curves shown in Figure 3 represent the extent of separation for systems exhibiting binomial or Poisson distributions. For low values of $\alpha - 1$, the maximum extent of separation increases as a function of the square root of n, the number of cycles. A similar square root dependence is observed for the Poisson distribution, only with K_1^0 as the argument of the square root rather than n.

DISCUSSION

The previous sections of this paper have demonstrated that the extent of separation can be easily and readily applied to most (and hopefully all)

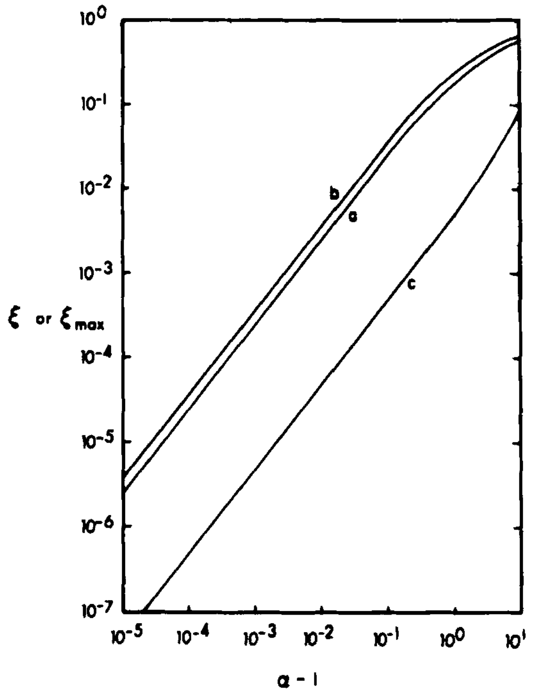

FIG. 2. The extent of separation, as a function of the quantity $\alpha - 1$, for crosscurrent distribution with discrete equilibrium contacts. Curve a corresponds to Eq. (19) with $n = 1$, curve b to Eq. (19) with $n = 10$, and curve c to Eq. (13) with $K_1 = \alpha^{-1/2}$ and $K_2 = \alpha^{1/2}$.

multicontact separation systems. For those systems in which the distribution coefficients are constant from stage to stage, simple theoretical expressions for the optimum number of contacts, the optimum stage cutoff point, and the optimum extent of separation can usually be derived. By differentiating the equation for the extent of separation with respect to K_1 and setting the derivative equal to zero, it is also frequently possible to calculate the optimum values of the distribution coefficients that would lead to the maximum value of the extent of separation. The experimental implications of a theoretical knowledge of such optima and maxima can be readily appreciated.

Figures 2 and 3 offer a very interesting clue as to how all separation techniques can be compared *on an equivalent basis.* For low values of the quantity $\alpha - 1$, it can be observed that the slope of each curve has a value of unity, or, in other words,

$$\lim_{\alpha \to 1} \frac{\partial \xi}{\partial(\alpha - 1)} = \text{function} \tag{46}$$

The function is dependent upon the physical parameters of the separation system. This type of relationship appears to hold for any type of separation process, provided only that the parameter α is properly defined. For example, in a rate-controlled single equilibrium stage (*9*), α would be equal to the ratio of the two rate constants,

$$\alpha = \frac{k_2}{k_1} \tag{47}$$

whereas for a diffusion-controlled stage (*9*), α would be equal to the ratio of the two diffusion coefficients,

$$\alpha = \frac{D_{22}}{D_{12}} \tag{48}$$

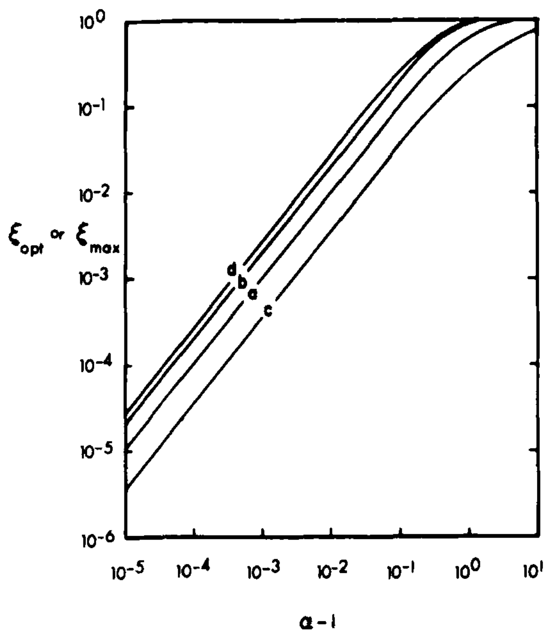

FIG. 3. The extent of separation, as a function of the quantity $\alpha - 1$, for countercurrent distribution with discrete equilibrium contacts (binomial distribution) and differential contact (Poisson distribution). Curve a corresponds to Eq. (40) with $n = 25$, curve b to Eq. (40) with $n = 100$, curve c to Eq. (45) with $K_1^0 = \alpha^{-1/2}$ and $K_2^0 = \alpha^{1/2}$, and curve d to Eq. (45) with $K_1 = 50$.

In each case, in the limit as α goes to 1, the extent of separation becomes directly proportional to $\alpha - 1$. We will elaborate upon this point in a subsequent paper.

List of Symbols

c	concentration (moles/cm^3)
D	diffusion coefficient (cm^2/sec)
k	rate constant (sec^{-1})
K	distribution coefficient (moles/moles)
K^0	distribution coefficient defined by Eq. (20) (moles/moles)
n	cycle number
p	dimensionless group defined by Eq. (6)
q	dimensionless group defined by Eq. (7)
r	tube number
T	term in binomial or Poisson expansion
V	volume of phase (cm^3)
V_2^0	total volume of contacting phase (cm^3)
Y	segregation fraction

Greek Letters

α	quotient of the distribution coefficients, rate constants, or diffusion coefficients
κ	partition coefficient (moles/cm^3:moles/cm^3)
ξ	extent of separation
σ	standard deviation

Subscripts

c	cutpoint
i	component i
ij	component i in region j
is	component i in environment s (i.e., partition state $\boxed{i:s}$)
max	maximum value
opt	optimum value
s	environment s
$i1$, $i2$, 12, 22	specific partition states

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