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T. S. Buys[a][b]; K. De Clerk[a]
[a] DEPARTMENT OF PHYSICAL AND THEORETICAL CHEMISTRY, CHROMATOGRAPHIC RESEARCH UNIT OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, UNIVERSITY OF PRETORIA, PRETORIA, REPUBLIC OF SOUTH AFRICA [b] Department of Chemistry, University of South Africa, Pretoria, Republic of South Africa

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Resolution and Impurity in Skewed Peak Analysis

T. S. BUYS* and K. DE CLERK

CHROMATOGRAPHIC RESEARCH UNIT OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH
DEPARTMENT OF PHYSICAL AND THEORETICAL CHEMISTRY
UNIVERSITY OF PRETORIA
PRETORIA, REPUBLIC OF SOUTH AFRICA

Abstract

The resolution function based on the impurity ratio of the smaller of two overlapping peaks has been analytically approximated for the general case (molar ratio $m \neq 1$, peak width ratio $s \neq 1$) of both symmetric and asymmetric peaks. In principle this allows the computation of the additional column length required for the separation of two arbitrary peaks to the same efficiency as the Gaussian $m = s = 1$ case.

The impurity ratios of overlapping solute pairs are recognized as providing a suitable basis for measuring the analytical efficiency of a chromatographic separation (*1–3*). Since an impurity ratio is not easily determined experimentally, attempts have been made to relate it to an easily measured function, termed the resolution function (e.g., Ref. *2*). In the case of peaks of an equimolar solute mixture, an exact relationship exists between the impurity ratios and the peak resolution function proposed by the IUPAC committee (*4*).

The extension of the theory to a nonequimolar mixture is troublesome in the sense that an exact analytical relationship cannot in general be

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* Present address: Department of Chemistry, University of South Africa, Pretoria, Republic of South Africa.

obtained. Various criteria and approximations have been used. Glueckauf's original criterion (*1*) was based on a cut point which divided the two peaks into two fractions of equal impurity ratios. Haarhoff (*2*) pointed out that a more realistic description results when the impurity ratio of the smaller peak is taken as criterion with the cut point defined

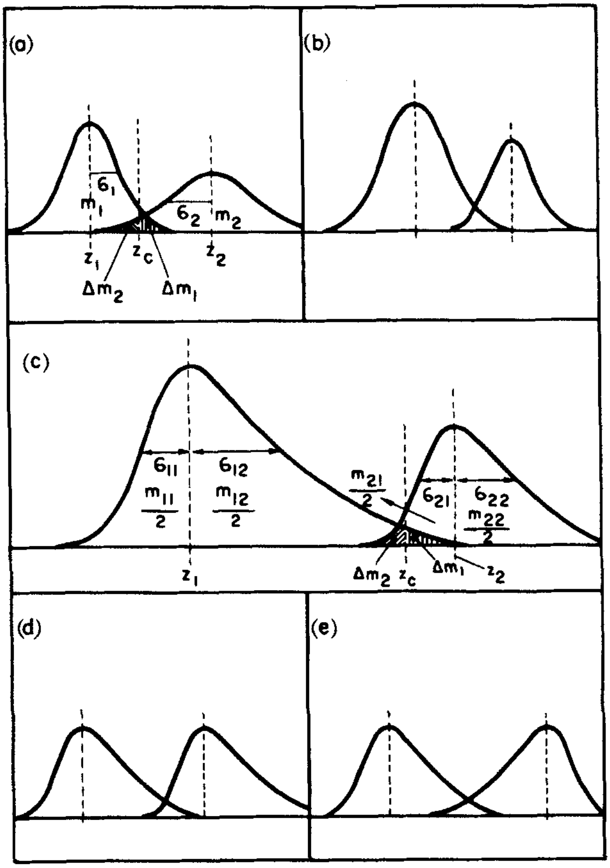

FIG. 1. Component concentration curves for two peaks illustrating various peak combinations and the parameters involved. (a) Symmetrical peaks $m = 1$, $s \neq 1$. (b) Symmetrical peaks $m \neq 1$, $s \neq 1$. (c) Asymmetrical peaks $m_a \neq 1$, $s_a \neq 1$. (d) Identical asymmetrical peaks $m_a = s_a = 1$; peaks skewed in the same direction. (e) Identical asymmetrical peaks $m_a = s_a = 1$; peaks skewed in opposite directions.

by the condition of equal minor portions of the two fractions. This ensures a superior separation of the larger peak.

The present study is an extension of this theory to an analysis of the separation of asymmetrical peaks. The mathematical approximations developed by Haarhoff will be used extensively. Some of the main assumptions which underlie the present treatment are the following:

(1) Symmetrical and asymmetrical peaks are assumed to be Gaussian and bi-Gaussian (*5*), respectively.

(2) The cut point will always be determined by the condition of equal minor portions (see Fig. 1), i.e.,

$$\Delta m_1 = \Delta m_2$$

(3) In the case of a nonequimolar mixture, an attempt will be made to relate a resolution function to the purity specification of the smaller peak. (The larger and smaller peaks will be referred to as peaks 1 and 2, respectively, and the notation for peak parameters adjusted accordingly.)

(4) In cases where the extent of separation of two pairs of peaks are compared, an additional restriction

$$\eta_2(\text{actual system}) = \eta_2(\text{reference system})$$

will be imposed.

A number of cases will now be considered; the first two on symmetrical peaks are included to facilitate the interpretation of the asymmetrical case.

Symmetrical Peaks $m = 1,\ s \neq 1$ [Fig. 1(a)]

Let

$$m = m_2/m_1 = 1$$

and

$$s = \sigma_2/\sigma_1 \neq 1$$

represent the molar and peak width ratios, respectively. The resolution function (*4*)

$$R_{1s} = \frac{z_2 - z_1}{2(\sigma_1 + \sigma_2)} \tag{1}$$

is exactly related to the impurity fraction

$$\eta = \frac{\Delta m_2}{m_1 - \Delta m_1} = \frac{\Delta m_1}{m_2 - \Delta m_2} \tag{2}$$

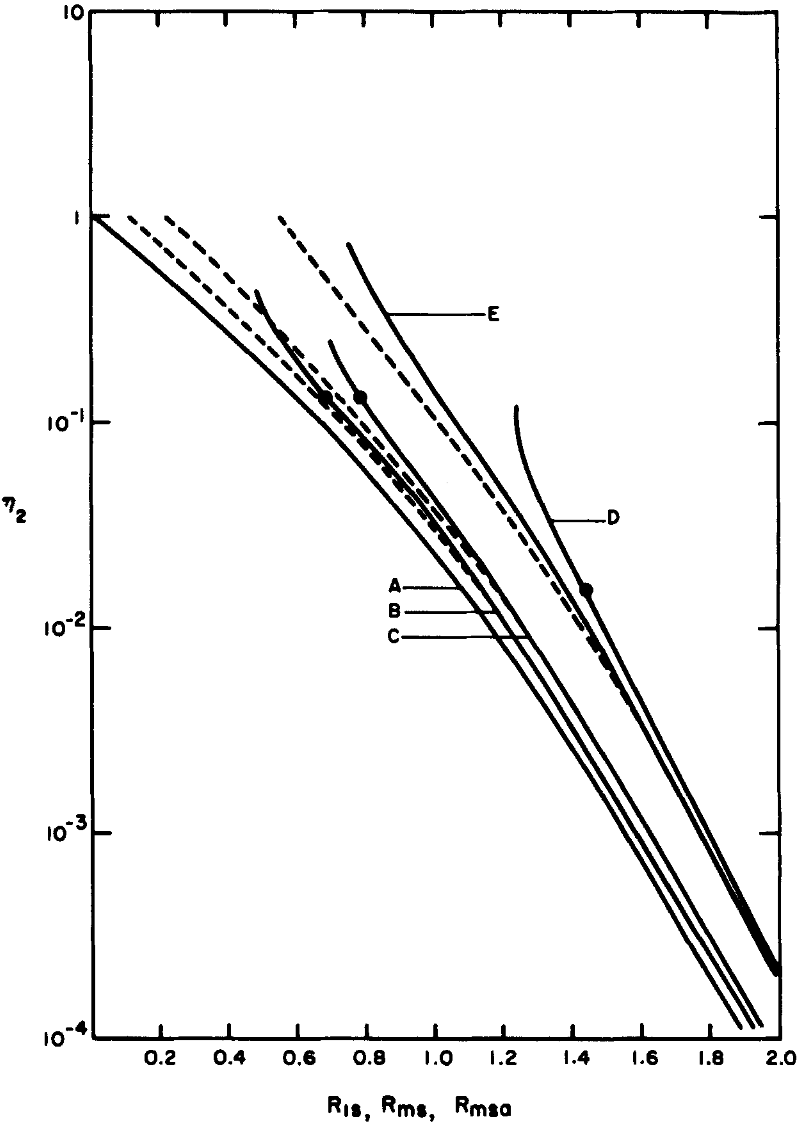

FIG. 2. Impurity ratio of smaller peak (η_2) vs. resolution function. A: η_2 vs. R_{1s} ($m = 1$, all s), Eq. (3). B: η_2 vs. R_{ms} ($m = 0.5$, $s = 2$), Eqs. (3) and (7); or η_{2a} vs. R_{msa} ($m_p = 0.5$, $s_p = 2$, $s_{2a} = 1$), Eqs. (3) and (24). C: η_2 vs. R_{ms} ($m = 0.5$, $s = 0.5$), Eqs. (3) and (7); or η_{2a} vs. R_{msa} ($m_p = 0.5$, $s_p = 0.5$, $s_{2a} = 1$), Eqs. (3) and (24). D: η_2 vs. R_{ms} ($m = 0.1$, $s = 0.5$), Eqs. (3) and (7); or η_{2a} vs. R_{msa} ($m_p = 0.1$, $s_p = 0.5$, $s_{2a} = 1$), Eqs. (3) and (24). E: η_2 vs. R_{ms} ($m = 0.1$, $s = 0.5$), Eqs. (3) and (8). (- -) Exact relationship between η_2 and R_{ms}. (●) Points corresponding to $R_{1s} = [\frac{1}{2} \ln (1/m)]^{1/2}$.

by (e.g., Ref. *2*)

$$\eta = \frac{1 - Z^*(2R_{1s})}{Z^*(2R_{1s})} \tag{3}$$

where

$$Z^*(x) = \tfrac{1}{2}\{1 + \operatorname{erf}[x/(2)^{1/2}]\}$$

Equation (3) is graphically represented in Fig. 2, Curve A, where η is plotted as a function of R_{1s}.

R_{1s} can be rewritten in terms of R_{11}, the resolution function for the case $m = s = 1$, to yield

$$R_{1s} = 2R_{11}/(1 + s) \tag{4}$$

where

$$R_{11} = \frac{z_2 - z_1}{4\sigma_1}$$

Symmetrical Peaks $m \neq 1$, $s \neq 1$ [Fig. 1(b)] (Referred to Symmetrical Peaks $m = 1$, $s \neq 1$)

The molar and peak width ratios are

$$m = m_2/m_1 < 1$$

$$s = \sigma_2/\sigma_1 \neq 1$$

The resolution function, R_{ms}, to be related to the impurity fraction

$$\eta_2 = \frac{\Delta m_1}{m_2 - \Delta m_2}$$

of the smaller peak is defined by

$$R_{ms} = \frac{z_2 - z_1}{2(\sigma_1 + \sigma_2)} \tag{5}$$

Both reference ($m = 1$, $s \neq 1$) and actual ($m \neq 1$, $s \neq 1$) systems obey the condition $\Delta m_1 = \Delta m_2$. The reference system is, however, constructed in such a way that the extra condition

$$(\eta_2)(m \neq 1) = (\eta_2)(m = 1) \tag{6}$$

is satisfied. It may now be shown that R_{ms} is approximately related to

R_{1s} by (see Appendix A)

$$R_{ms} = R_{1s} + \frac{1}{4(1+s)R_{1s}} \ln (1/m) \tag{7}$$

R_{ms} is thus related to the impurity ratio, η_2, of the smaller peak through Eqs. (3), (6), and (7). This is shown graphically in Fig. 2, Curves B, C, and D, for different values of m and s. The dotted lines represent the exact relationship (see Appendix A) between R_{ms} and η_2. Inspection of these curves reveals deviations of Eq. (7) from the actual relationship at small values of R_{ms} and especially at small values of m (Curve D). This originates in the assumption of large R_{1s} in the derivation of Eq. (7) (see Appendix A). A better quantitative approximation is (see Appendix A(2))

$$R_{ms} = \frac{1}{1+s} \{sR_{1s} + [R_{1s}^2 + \tfrac{1}{2} \ln (1/m)]^{1/2}\} \tag{8}$$

which reduces to Eq. (7) for

$$R_{1s} \gg [\tfrac{1}{2} \ln (1/m)]^{1/2}$$

The improvement obtained by using Eq. (8) instead of Eq. (7) can be judged by comparing Curve E (Eqs. 3, 6, and 8) with Curve D (Eqs. 3, 6, and 7) in Fig. 2. The circles on the curves in Fig. 2 correspond to $R_{1s} = [\tfrac{1}{2} \ln (1/m)]^{1/2}$.

Asymmetrical Peaks, $m \neq 1$, $s \neq 1$ [Fig. 1(c)]

(In this section a subscript a will be used to denote quantities referring to asymmetrical peaks while it is omitted in the symmetrical case.)

For symmetrical peaks the resolution required to separate a non-equimolar mixture to the same degree of purity as the equimolar mixture is given by Eq. (7). The aim of this section is to obtain the corresponding expression for the case of asymmetrical peaks. The asymmetrical peaks are characterized by the following parameters:

(1) The molar ratio

$$m_a = m_{2a}/m_{1a} < 1$$

where

$$\begin{aligned} m_{1a} &= \tfrac{1}{2}(m_{11} + m_{12}) \\ m_{2a} &= \tfrac{1}{2}(m_{21} + m_{22}) \end{aligned} \tag{9}$$

denote the numbers of moles of peaks 1 and 2, respectively.

(2) The width ratio

$$s_a = \sigma_{2a}/\sigma_{1a} \neq 1$$

with the standard deviations of peaks 1 and 2 approximated by

$$\sigma_{1a} = \tfrac{1}{2}(\sigma_{11} + \sigma_{12})$$

and

$$\sigma_{2a} = \tfrac{1}{2}(\sigma_{21} + \sigma_{22})$$

(3) Other peak parameters are

$$s_{1a} = \sigma_{12}/\sigma_{11}$$

$$s_{2a} = \sigma_{22}/\sigma_{21}$$

and, since the peaks are bi-Gaussian,

$$s_{1a} = m_{12}/m_{11}$$

and

$$s_{2a} = m_{22}/m_{21}$$

The discussion is simplified by taking as reference the nonequimolar symmetrical case ($m \neq 1$, $s \neq 1$). It is now assumed that the nonequimolar asymmetrical case ($m_a \neq 1$, $s_a \neq 1$) may be obtained from the reference case by skewing the peaks without changing their areas (numbers of moles), i.e.,

$$m_{1a} = m_1 \tag{10}$$

$$m_{2a} = m_2$$

so that

$$m_a = m_{2a}/m_{1a} = m = m_2/m_1$$

The condition of equal minor portions is satisfied for both symmetrical and asymmetrical cases, i.e.,

$$\Delta m_1 = \Delta m_2 \tag{11}$$

$$\Delta m_{1a} = \Delta m_{2a}$$

while, for comparative purposes, the condition

$$\eta_{2a} = \eta_2 \tag{12}$$

is imposed.

From Eqs. (9), (11), and (12) it follows that

$$\Delta m_{1a} = \Delta m_1 = \Delta m_2 \tag{13}$$

$$\Delta m_{2a} = \Delta m_1 = \Delta m_2$$

The resolution function, R_{msa}, to be related to η_{2a}, is defined by (see Fig. 1)

$$R_{msa} = \frac{z_2 - z_1}{2(\sigma_{12} + \sigma_{21})}$$

$$= \frac{s_p X_2 + X_1}{2(1 + s_p)} \tag{14}$$

where

$$X_1 = (z_c - z_1)/\sigma_{12} \tag{15}$$

$$X_2 = (z_2 - z_c)/\sigma_{21} \tag{16}$$

and

$$s_p = \sigma_{21}/\sigma_{12}$$

Δm_{1a} and Δm_{2a} are given by

$$\Delta m_{1a} = m_{12}[1 - Z^*(X_1)] \tag{17}$$

and

$$\Delta m_{2a} = m_{21}[1 - Z^*(X_2)] \tag{18}$$

while it may easily be shown that the minor portions for the case $m = 1$, $s \neq 1$ are given by (see also Ref. 2)

$$\Delta m_1 = \Delta m_2 = m_2[1 - Z^*(2R_{1s})] \tag{19}$$

From Eqs. (13), (17), and (19) it follows that

$$1 - Z^*(X_1) = \frac{m_2}{m_{12}}[1 - Z^*(2R_{1s})] \tag{20}$$

which has the approximate solution (see Appendix A)

$$X_1 = 2R_{1s} + \frac{1}{2R_{1s}} \ln (m_{12}/m_2) \tag{21}$$

The corresponding solution for X_2 follows as

$$X_2 = 2R_{1s} + \frac{1}{2R_{1s}} \ln (m_{21}/m_2) \tag{22}$$

Substitution from Eqs. (21) and (22) into Eq. (14) gives

$$R_{msa} = R_{1s} + \frac{1}{4(1 + s_p)R_{1s}} \{s_p \ln (m_{21}/m_2) + \ln (m_{12}/m_2)\}$$

Let

$$m_p = m_{21}/m_{12}$$

then

$$R_{msa} = R_{1s} + \frac{1}{4R_{1s}} \ln (m_{21}/m_2) + \frac{1}{4(1 + s_p)R_{1s}} \ln (1/m_p) \qquad (23)$$

From Eqs. (9) and (10) it follows that

$$m_2 = m_{2a} = \tfrac{1}{2}(m_{21} + m_{22})$$

so that

$$R_{msa} = R_{1s} + \frac{1}{4R_{1s}} \ln \left(\frac{2}{1 + s_{2a}}\right) + \frac{1}{4(1 + s_p)R_{1s}} \ln (1/m_p) \qquad (24)$$

Equation (24) directly relates the resolution required to separate two asymmetrical peaks ($m_a \neq 1$, $s_a \neq 1$) to that required to separate two symmetrical peaks to the same degree of purity (η_2). It should be noted that, since R_{msa} is defined as containing parameters only of the overlapping halves of the peaks, the overall width and molar ratios s_a and m_a do not appear in Eq. (24). To avoid confusion, it should be kept in mind that the asymmetrical case $m_a = 1$, $s_a = 1$ (i.e., the case corresponding to R_{11a}) here relates to two identical skewed peaks and that a distinction should be made between the following two possibilities.

Peaks Skewed in the Same Direction [*Fig.* 1(*d*)]. R_{11a} is given by

$$R_{11a} = R_{1s} + \frac{1}{4R_{1s}} \ln \left(\frac{2}{1 + s_{2a}}\right) + \frac{1}{4(1 + 1/s_{2a})R_{1s}} \ln s_{2a} \qquad (25)$$

so that (from Eqs. 24 and 25 or by independent derivation)

$$R_{msa} = R_{11a} + \frac{1}{4(1 + s_p)R_{1s}} \ln (1/m_p) + \frac{1}{4(1 + 1/s_{2a})R_{1s}} \ln (1/s_{2a})$$

From the above equation it follows that $R_{msa} = R_{11a}$ only if $m_p = s_p = 1/s_{2a}$

Peaks Skewed in Opposite Directions [*Fig.* 1(*e*)]. R_{11a} is given by

$$R_{11a} = R_{1s} + \frac{1}{4R_{1s}} \ln \left(\frac{2}{1 + s_{2a}}\right)$$

so that

$$R_{msa} = R_{11a} + \frac{1}{4(1 + s_p)R_{1s}} \ln (1/m_p)$$

In this case $R_{msa} = R_{11a}$ corresponds to

$$m_p = 1 \ (s_p = 1)$$

A graph of η_{2a} vs. R_{msa}, for given (s_p, m_p, s_{2a}), may be constructed by using Eqs. (3) and (24). This allows a correlation between experimentally measured R_{msa} values and the efficiency of the separation. (Figure 2 represents the cases for which $s_{2a} = 1$.)

CONCLUSIONS

The results obtained above may be applied to calculate the additional number of theoretical plates required to separate skewed nonequimolar peaks with the same efficiency as in the symmetrical equimolar case. The efficiency criterion is taken as the impurity ratio of the smaller peak. The principles of such an analysis are outlined below. For convenience the generalization can be visualized as taking place in consecutive stages, viz.:

(1) Symmetrical peaks, $m = 1, s = 1$.
(2) Symmetrical peaks, $m = 1, s \neq 1$.
(3) Symmetrical peaks, $m \neq 1, s \neq 1$.
(4) Asymmetrical peaks, $m_a \neq 1, s_a \neq 1$.

For the symmetrical case, $m = s = 1$, R_{11}^2 is known to be related to the column length, l, and the plate height, H, by (e.g., Ref. *2*)

$$R_{11}^2 = \frac{(\alpha - 1)^2}{16} \frac{k^2}{(1 + k)^2} \frac{l}{H}$$

so that the ratio R_{ms}^2/R_{11}^2 given by (Eqs. 4 and 7)

$$R_{ms}^2/R_{11}^2 = \left[\frac{2}{1 + s} + \frac{1}{8R_{11}^2} \ln (1/m)\right]^2$$

is, for instance, proportional to the ratio of column lengths required to separate the $m \neq 1, s \neq 1$ case with the same efficiency as the $m = 1$, $s = 1$ case. The column length adjustment required to compensate for skewness may also be assessed by analysis of Eq. (24) in the form

$$R_{msa}^2/R_{11}^2 = \left[\frac{2}{1 + s} + \frac{1 + s}{8R_{11}^2} \ln \left(\frac{2}{1 + s_{2a}}\right) + \frac{1 + s}{8(1 + s_p)R_{11}^2} \ln (1/m_p)\right]^2$$

To complete the analogy with the symmetrical case, it will be required to relate the σ_{21} and σ_{12} (see Eq. 14) to column length. This may always be effected empirically by writing these widths in the form of a power series in l and by determining the coefficients experimentally. The theoretical evaluation depends on the specific mechanism responsible for the peak skewing and cannot be formulated in general terms. The case of skewing due to nonlinear distribution isotherms has been analyzed elsewhere (*6*) where an approximate relationship to column length ratios has been established.

APPENDIX A

Derivation of Eqs. (7) and (8)

The mathematical procedure used in this section was originally developed by Haarhoff (*2*).

R_{ms} is given by

$$R_{ms} = \frac{X_2 s + X_1}{2(1+s)} \tag{A-1}$$

where

$$X_1 = \frac{z_c - z_1}{\sigma_1}$$

and

$$X_2 = \frac{z_2 - z_c}{\sigma_2}$$

while the impurity ratio of the second peak is given by

$$\eta_2 = \frac{\Delta m_2}{m_2 - \Delta m_2}$$

$$= \frac{1 - Z^*(X_2)}{Z^*(X_2)} \tag{A-2}$$

where

$$Z^*(X_2) = \tfrac{1}{2}\{1 + \operatorname{erf}[X_2/(2)^{1/2}]\}$$

From Eqs. (3), (6), and (A-2) it follows that

$$X_2 = 2R_{1s} \tag{A-3}$$

so that the equation determining the cut point ($\Delta m_1 = \Delta m_2$) is

$$1 - Z^*(X_1) = m[1 - Z^*(2R_{1s})] \tag{A-4}$$

The exact solution of this equation will be very complex; an approximate solution for X_1 may, however, be obtained in the limit of large R_{1s}. This solution is found to be unexpectedly good even for small values of R_{1s}. Since at large values of R_{1s}, X_1 also becomes large, this equation may be approximated by (7)

$$\frac{1}{X_1} \exp\left(-\frac{X_1^2}{2}\right) = \frac{m}{2R_{1s}} \exp(-2R_{1s}^2) \tag{A-5}$$

Let the solution be of the form

$$X_1 = 2R_{1s} + b/R_{1s} \tag{A-6}$$

Equation (A-5) now becomes

$$\frac{1}{(1 + b/2R_{1s}^2)} \exp(-2b - b^2/2R_{1s}^2) = m \tag{A-7}$$

This assumption of large R_{1s} allows both of the terms $b/2R_{1s}^2$ and $b^2/2R_{1s}^2$ to be neglected. This gives

$$b = b_1 = \tfrac{1}{2} \ln\left(\frac{1}{m}\right) \tag{A-8}$$

From Eqs. (A-1), (A-3), (A-6), and (A-8), Eq. (7) is obtained.

If m becomes small, however, b increases sharply as is shown in Fig. 3 where the approximation (A-8) is represented graphically. A better approximation, which takes this into account, may be formulated by rewriting Eq. (A-7) in the form

$$\frac{1}{(1 + b/2R_{1s}^2)} \exp[-2b(1 + b/4R_{1s}^2)] = m \tag{A-9}$$

and neglecting, relative to unity, only the smaller term $b/4R_{1s}^2$. The solution for b is now

$$b = -2R_{1s}^2 + 2R_{1s}[R_{1s}^2 + \tfrac{1}{2} \ln(1/m)]^{1/2} \tag{A-10}$$

which results in Eq. (8).

The exact relationship between R_{ms} and η_2 (dotted lines, Fig. 2) is obtained by deriving (graphically or from numerical tables) from Eq.

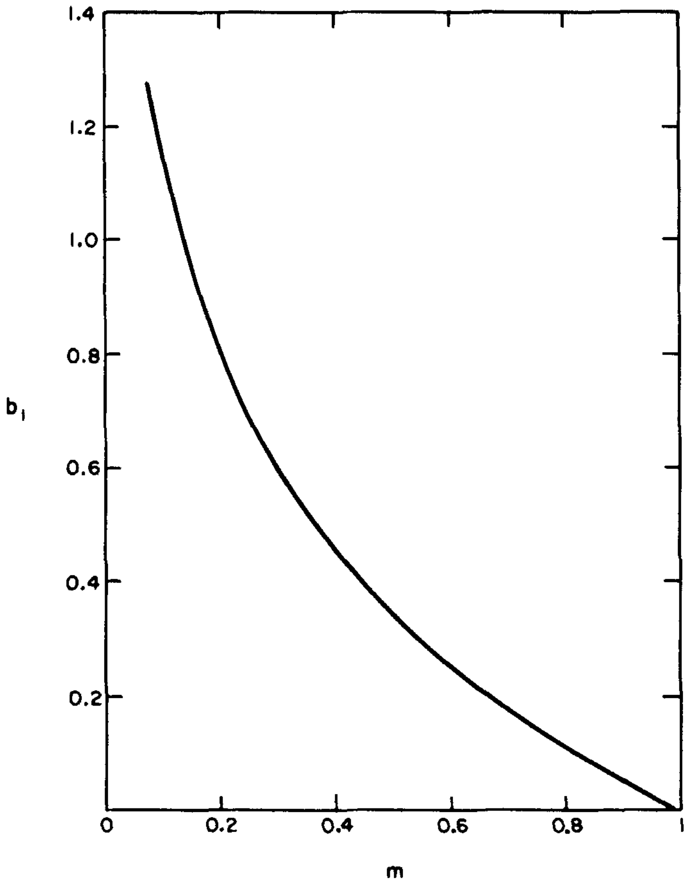

FIG. 3. The parameter b_1 as a function of m, Eq. (A-8).

(A-4), for given m and R_{1s}, a value for X_1. This is then used together with Eq. (A-3) to calculate R_{ms} from Eq. (A-1). η_2 follows from Eq. (3)

SYMBOLS

b	convenient parameter, Eq. (A-6)
b_1	convenient parameter, Eq. (A-8)
H	plate height
k	mass distribution coefficient

l	column length
m	molar ratio, symmetrical peaks
m_a	molar ratio, asymmetrical peaks
m_i	$(i = 1, 2)$ number of moles of component i, symmetrical peaks
m_p	$= m_{21}/m_{12}$, convenient parameter
m_{ia}	$(i = 1, 2)$ number of moles of component i, asymmetrical peaks
m_{ij}	$(i = 1, 2; j = 1, 2)$ peak parameters, asymmetrical peaks (see Eq. 9 and Fig. 1c)
Δm_i	$(i = 1, 2)$ minor portion of component i, symmetrical peaks
Δm_{ia}	$(i = 1, 2)$ minor portion of component i, asymmetrical peaks
R_{11}	resolution function for the case $m = s = 1$, symmetrical peaks
R_{1s}	resolution function for the case $m = 1$, $s \neq 1$, symmetrical peaks
R_{ms}	resolution function for the case $m \neq 1$, $s \neq 1$, symmetrical peaks
R_{11a}	resolution function for the case of two identical asymmetrical peaks
R_{msa}	resolution function for the case $m_a \neq 1$, $s_a \neq 1$, asymmetrical peaks
s	$= \sigma_2/\sigma_1$, peak width ratio, symmetrical peaks
s_a	$= \sigma_{2a}/\sigma_{1a}$, peak width ratio, asymmetrical peaks
s_{ia}	$= \sigma_{i1}/\sigma_{i2}$, $(i = 1, 2)$ skewness parameter of (bi-Gaussian) peak i
s_p	$= \sigma_{21}/\sigma_{12}$, convenient parameter
X_1	$= (z_c - z_1)/\sigma_{12}$, convenient parameter, Eq. (15)
X_2	$= (z_2 - z_c)/\sigma_{21}$, convenient parameter, Eq. (16)
z_i	$(i = 1, 2)$ position of peak maximum of peak i
z_c	position of cut point between peaks

Letters

α	relative retention
η	impurity fraction
η_i	$(i = 1, 2)$ impurity fraction of component i, symmetrical peaks
η_{ia}	$(i = 1, 2)$ impurity fraction of component i, asymmetrical peaks
σ_i	$(i = 1, 2)$ standard deviation of peak i, symmetrical peaks
σ_{ia}	$(i = 1, 2)$ standard deviation of peak i, asymmetrical peaks
σ_{ij}	$(i = 1, 2; j = 1, 2)$ peak standard deviation parameters, asymmetrical (bi-Gaussian) peaks (see Fig. 1-c)

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