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Separation of Close Species by Displacement Development on Ion Exchangers. III. Enrichment Variation While Approaching the Steady State

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Abstract

A very simple relation giving band enrichment vs displacement in the displacement development of a binary mixture of close species on ion exchangers is proposed. Comparison is made with true values obtained by computer simulation in numerous cases and shows the approximation is quite good. It is then possible to calculate the necessary displacement to reach steady state with a given difference. The classical relation of the steady state ($l = l_0/\varepsilon$, $l =$ displacement length; $l_0 =$ band length; $\varepsilon = k - 1$) is discussed, and this yields a precise difference between the so-called steady experimental front and the true steady state.

INTRODUCTION

It has been shown in a previous paper (*1*) that when separating close species by displacement development, the evolution of a system after sampling and injecting the original mixture could be predicted if the band total enrichment E while approaching the steady state was known (i.e., before taking the first sample). Indeed we have shown that marginal enrichment does not depend on the band front shape, but only on its total enrichment.

Knowledge of the equation of the curve $E = f(t)$, representing the variation of total enrichment E vs the number of plates t by which the band has been displaced, is thus fundamental. The shape of the curve can be obtained very precisely by simulating the displacement on a computer. However, this process is tedious, and it is clear that a rough estimation of the curve $E = f(t)$ would be preferred, and it is that type of equation we give here.

ENRICHMENT VARIATION ALONG DISPLACEMENT

We use the previously defined notations:

k = $1 + \varepsilon$ (exchange constant)
x = the molar fraction in any plate of the more retained species in the mixture
x_0 = the molar fraction of the more retained species in the original mixture
$E = \dfrac{x - x_0}{x_0(1 - x_0)\varepsilon}$, the reduced relative enrichment more simply called enrichment (see Ref. *1* for considerations about the choice of E)
$E_N = \sum_N \dfrac{x - x_0}{x_0(1 - x_0)\varepsilon}$, total enrichment of a N plates zone
p = band plate abcissa, the origin being taken at the point where $x = x_0$, the positive side being the one of increasing x
P = total number of band plates.
M = middle of the band abcissa, which is then ranging from plate $M - (P/2)$ to plate $M + (P/2)$
t = plates number corresponding to the band displacement

TOTAL LIMIT ENRICHMENT CALCULATION

Enrichment of the rich zone ($x > x_0$, $p > 0$) when the stationary state is reached (band displaced of an infinite number of plates, with no sampling) will be called total limit enrichment E_l. When stationary state is reached, the isochrone shape is given by (*2*)

$$x = \frac{1}{1 + \dfrac{1 - x_0}{x_0}\exp(-2p\varepsilon)} \tag{1}$$

M, the abcissa of the band middle, is then given by

$$M = \frac{1}{2\varepsilon}\ln\frac{1 - x_0}{x_0}\,\frac{sh\varepsilon Px_0}{sh\varepsilon P(1 - x_0)}$$

[which can be deduced from relation proposed in Ref. *2* by multiplying both numerator and denominator by exp $(-p\varepsilon x_0)$ and which has the advantage of being much more symmetrical].

Band enrichment between two plates i and j is given by

$$E_i^j = \int_i^j \frac{x - x_0}{x_0(1 - x_0)\varepsilon}\,dp$$

Replacing x by its value as a function of p as defined by Eq. (1) yields

$$E_i^j = \frac{j - i}{x_0\varepsilon} - \frac{1}{2\varepsilon^2 x_0(1 - x_0)} \ln\frac{x_j}{x_i}$$

where x_i and x_j are the molar fractions of the more retained species in plates i and j, respectively.

The total limit enrichment is obtained for $i = 0$ and $j = M + (P/2)$ by

$$E_l = \frac{M + (P/2)}{x_0\varepsilon} - \frac{1}{2\varepsilon^2 x_0(1 - x_0)} \ln\frac{x_e}{x_0} \tag{2}$$

where x_e is the molar fraction at the rich band extremity.

In a same way, we can calculate the total enrichment of the more retained substance in the poor zone ranging from $i = M - (P/2)$ to $j = 0$. Considering that the total enrichment (rich zone + poor zone) must be equal to zero, the poor zone total limit enrichment is equal to $-E_l$, and if x_a is the more retained substance, the molar fraction at the poor band extremity is

$$-E_l = -\frac{M - (P/2)}{x_0\varepsilon} + \frac{1}{2\varepsilon^2 x_0(1 - x_0)} \ln\frac{x_a}{x_0} \tag{3}$$

By eliminating E_l between Eqs. (2) and (3),

$$\ln (x_e/x_a) = 2P(1 - x_0)\varepsilon \tag{4}$$

Remark

Relation (1) can be written as

$$\ln\frac{x}{1 - x} - \ln\frac{x_0}{1 - x_0} = 2p\varepsilon$$

By using it for both values of p corresponding to the band extremities $M - (P/2)$ and $M + (P/2)$, we have

$$\ln\frac{x_e}{1 - x_e}\frac{1 - x_a}{x_a} = 2P\varepsilon \tag{4'}$$

which is not the same as Eq. (4). That is because Eq. (4′) defines the P distance between any two points in a band where molar fractions are x_e and x_a, whereas Eq. (4) implies a supplementary condition, that is, the points with x_e and x_a molar fractions are band extremities and are symmetrical with respect to the middle of the band.

ENRICHMENT VARIATION WHILE APPROACHING THE STEADY STATE

A simple equation cannot be used to graph $E = f(t)$ as obtained by computer simulation (*3*) (see Fig. 1). We only know that $dE/dt = 1$ when $t = 0$ and that $dE/dt \rightarrow 0$ when $t \rightarrow \infty$ (and of course, that $E \rightarrow E_l$). This leads us to consider the simpler shaped curve $dE/dt = f(t)$ (Fig. 2), with which the following equation can be associated:

$$\frac{dE}{dt} = \frac{\alpha}{1 + (t/\beta)^2} \tag{5}$$

α and β then must be determined.

The condition $dE/dt = 1$ when $t = 0$ gives $\alpha = 1$. By integrating Eq. (5)

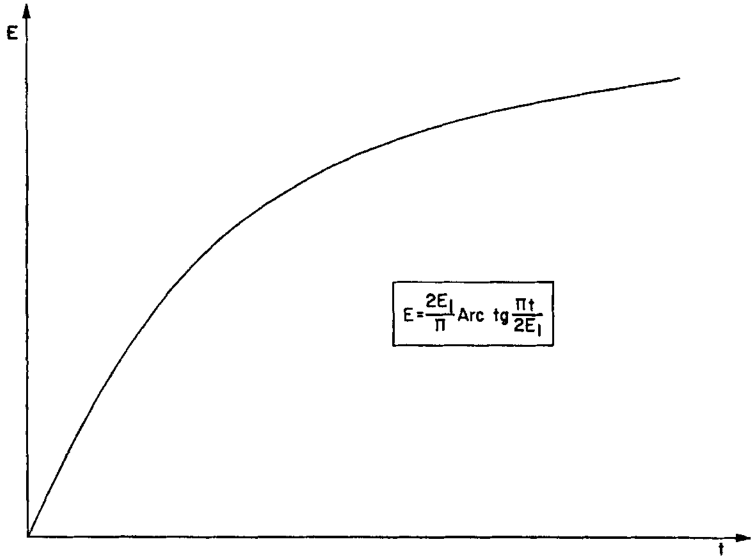

FIG. 1. Variation of enrichment E vs displacement.

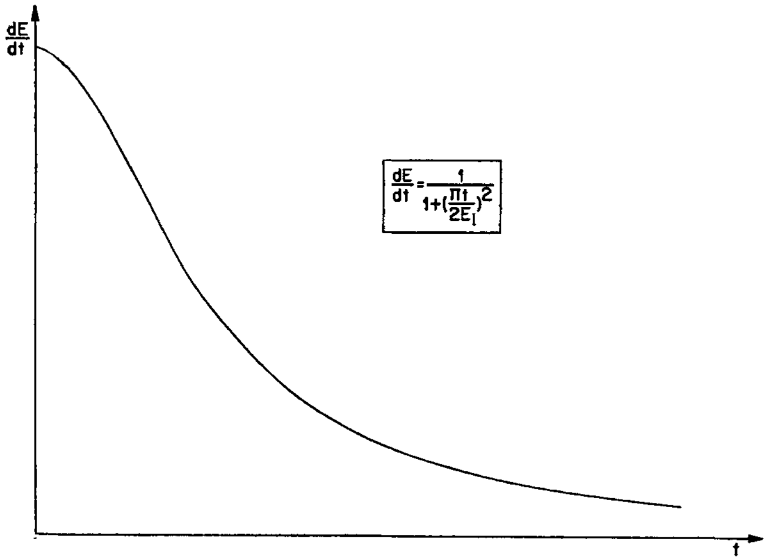

FIG. 2. Variation of marginal enrichment dE/dt vs displacement.

and considering that $E = 0$ when $t = 0$, we obtain

$$E = \beta \text{ arc tan } (t/\beta)$$

Now we know that $E \rightarrow E_l$ when $t \rightarrow \infty$, E_l being determined as a function of the band parameters (x_0, P, ε). This allows the determination of β, and we have

$$E = \frac{2E_l}{\pi} \text{arc tan} \frac{\pi t}{2E_l} \tag{6}$$

and

$$\frac{dE}{dt} = \frac{1}{1 + (\pi t/2E_l)^2} \tag{7}$$

Figures 1 and 2 represent variations of E and dE/dt vs t.

Of course, Expression (6) is only an approximation and we must check if it is suitable in practice. This can be done by comparing the results obtained by computer simulation with those given by Expression (6). This comparison has been made in numerous cases (ε varying from 0.001

TABLE 1

Comparison between True Enrichment (obtained by simulation) and that Calculated according to Eq. (6) ($P = 50$; $\varepsilon = 0.01$; $x_0 = 0.2$)

t	True E (obtained by simulation)	Calculated E	Difference $\Delta E = E_{\text{true}} - E_{\text{cal.}}$	$\frac{\Delta E}{E_{\text{true}}}\,\%$	Enrichment in the extreme plate $P = M + P/2$
100	98.52	97.90	0.62	0.6	14.08
200	187.35	184.86	2.49	1.3	20.78
300	260.31	255.86	4.45	1.7	25.96
400	319.62	311.48	8.14	2.5	30.13
500	367.14	354.61	12.53	3.4	33.51
600	405.27	388.26	17.01	4.2	36.23
700	435.73	414.88	20.85	4.8	38.42
800	460.38	436.29	24.09	5.2	40.18
900	480.05	453.78	26.27	5.4	41.58
1000	495.82	468.28	27.54	5.5	42.71

to 0.1, P varying from 20 to 320 plates, x_0 varying from 0.01 to 0.8). As an example, real enrichment values (obtained with a computer) and those calculated by Eq. (6), are reported in Table 1 for the case of a 50-plate band displacement with $\varepsilon = 0.01$ and $x_0 = 0.2$.

Maximum difference between the true value of E and that calculated according to Eq. (6) has always been found to be less than enrichment in the extreme plate [$M + (P/2)$ plate], and this is also true for all simulation cases considered.

In the example of Table 1, the difference does not exceed 6% when the band is displaced 20 times its length, which seems a quite good approximation.

APPLICATIONS

Calculation of the Necessary Displacement to Reach Steady State

Coursier and Hure (*4*) and Tremillon (*5*) proposed the following expression of the l displacement of a l_0 length band, necessary for reaching a steady state in the case of two close species:

$$l = l_0/\varepsilon$$

More recently Persoz (*6*) has shown by computer simulation that this displacement is in fact deficient, but without going as far as giving a mean of calculating it.

Strictly speaking, this displacement should be infinite, but if we know the enrichment variation as a function of the number of displaced plates, it is possible to calculate the displacement necessary to reach the steady state with a given approximation.

We shall say that steady state approaches near to δ when the total enrichment E is such that

$$\frac{E_l - E}{E_l} = \delta$$

Let us find the relation between δ and t:

$$\delta = 1 - \frac{2}{\pi} \arctan \frac{\pi t}{2E_l}$$

and

$$\arctan \frac{\pi t}{2E_l} = \frac{\pi}{2}(1 - \delta)$$

$$\frac{\pi t}{2E_l} = \tan \frac{\pi}{2}(1 - \delta) = \frac{1}{\tan (\pi/2)\delta}$$

thus

$$\frac{2E_l}{\pi t} = \tan \frac{\pi}{2} \delta$$

If δ is small, the tangent and angle can be considered as identical, so

$$\boxed{t = \frac{4E_l}{\pi^2 \delta}} \tag{8}$$

and then we get from the marginal enrichment expression dE/dt (Eq. 7):

$$\frac{dE}{dt} = \frac{1}{1 + \dfrac{4}{\pi^2 \delta^2}}$$

If δ being small, 1 is negligible with respect to $4/\pi^2\delta^2$ and

$$\frac{dE}{dt} = \frac{\pi^2 \delta^2}{4}$$

Example

Let us consider a band displacement with the following characteristics: $x_0 = 0.1$; $P = 150$; and $\varepsilon = 0.05$. Calculated $E_l = 2334$.

For $\delta = 0.1$ (steady state minus 10%), we find $t = 9460$, that it, about 63 times the band length.

For $\delta = 0.01$ (steady state minus 1%), the displacement must be 10 times greater, that is, 630 times the band length.

According to Coursier and Hure's relation $l = l_0/\varepsilon$, the steady state should be reached when the band is displaced 20 times its length.

The difference is quite important.

Discussion

Tremillon experimentally checked the relation $l = l_0/\varepsilon$, so we wonder why there is such large a difference between the various displacements necessary to reach steady state according to the relation used.

From a purely experimental viewpoint, steady state is considered to be reached if, within the accuracy limits of analysis, the front shape appears unchanged when the band is still displaced. This practical definition of steady state is quite different from the rigorous one we adopted and which is based upon the difference with limit enrichment. For example, consider the case where $\delta = 10\%$. Then we have

$$dE/dt = 0.025$$

If we again consider the previous 150 plates band with $\varepsilon = 0.05$, another one plate displacement increases the total enrichment to 0.025, which will be distributed over the entire rich zone.

In order to determine this, the computer simulation should be done with great accuracy. The study of the evolution of fronts shows that enrichment always increases more in the extreme plates than in the band middle.

In order to find an approximate order of magnitude, we assume that this supplementary enrichment is uniformly distributed over the 25 head plates, and that the others in the rich zone do not vary. Then the enrichment variation is

$$\Delta E = 0.025/25 = 10^{-3}$$

If the band is displaced by one length, each front plate will have an enrichment increase equal to $150\Delta E = 0.15$, i.e., a molar fraction increase of

$$\Delta x = P\Delta E x_0(1 - x_0)\varepsilon \sim 6 \times 10^{-4}$$

which corresponds to a relative variation with respect to the molar fraction of the original mixture of

$$\Delta x/x_0 = 6 \times 10^{-3} = 0.6\%$$

at the limit of analysis accuracy. If $\varepsilon = 0.01$, the molar fraction relative variation is five times smaller, i.e., 0.12%.

In other words, a band may appear to be rather far from the steady state because concentration variations are too slow to be shown by analysis after a one band length displacement.

We must be very careful when applying theoretical results, which are only available for a steady state, to an experimental front which does not seem to evolve but which actually does, but too slowly to have an appreciable variation of the front shape when the band is only slightly displaced. For example, applying Relation (4) to calculate the plate number may lead to wrong results if the front is not really stationary (this is generally the case in practice; a true steady state can only be provided by a very large displacement, hardly suitable for experimental realities).

Let us find the δ value corresponding to Coursier and Hure's formula $l = l_0/\varepsilon$, i.e., with our notations $t = P/\varepsilon$.

By using Eq. (8), we obtain

$$\delta = \frac{4E_l\varepsilon}{\pi^2 P} = 0.3$$

For that value the relative variation of plate composition is about 1 to 2% when the band is displaced one time its lenth (with $\varepsilon = 0.05$). Experimentally it can be considered as steady, and a fortiori if ε is smaller, when enrichment is only 70% of the limiting value.

Thus the difference between the true steady state and the experimental one is quite important even when, according to the accuracy of the analysis, the front no longer seems to be evolving.

CONCLUSIONS

We propose an approximate but very simple relation which allows the determination at any moment of a band enrichment with a known plate number. Production calculations, as developed in Ref. *1*, are then very easy.

The proposed method avoids the need for a computer for studying any separation by displacement development. It also yields a precise difference between an experimental front and the true steady state.

RFFERENCES

1. P. Conrard, *Separ. Sci.*, *8*, 1 (1973).
2. P. Conrard, M. Caude, and R. Rosset, *Separ. Sci.* *7*, 465 (1972); P. Conrard and M. Caude, *C. R. Acad. Sci., Paris, Ser. C*, *272*, 764 (1970).
3. P. Conrard and M. Caude, *Chim. Ind.*, *109*, 2431 (1971).
4. J. Coursier and J. Hure, *Anal. Chim. Acta*, *18*, 272 (1958).
5. B. Tremillon, *Bull. Soc. Chim. Fr.*, *1958*, 508.
6. J. Persoz, *Bull. Soc. Chim. Fr.* *1968*, 848.

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