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A Comparison of Theoretical Steady-State Isotopic Distribution and of an Experimental Profile in the Case of Separation of Nitrogen Isotopes on Ion-Exchange Columns

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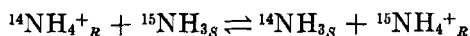
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Abstract

In displacement development of mixture of very closely related species on ion exchange columns, determination of the distance between the band middle and the point of initial composition permits an evaluation of HETP. This is applied to the work of Spedding et al. on the separation of nitrogen isotopes. It is shown that steady-state distribution was not obtained and that classical equation giving displacement length for steady-state conditions does not apply for very closely related species such as isotopes.

Spedding et al. (1, 2) have demonstrated that isotopes 14 and 15 of nitrogen can be successfully separated by displacement development on a cation exchange resin by using the exchange reaction:



where R and S indicate, respectively, the resin and solution phases with $K = 1.0257$.

Isotopic distribution in a 10-ft long ammonium band after moving 500 feet (50 times the band length) as given by Spedding is shown in

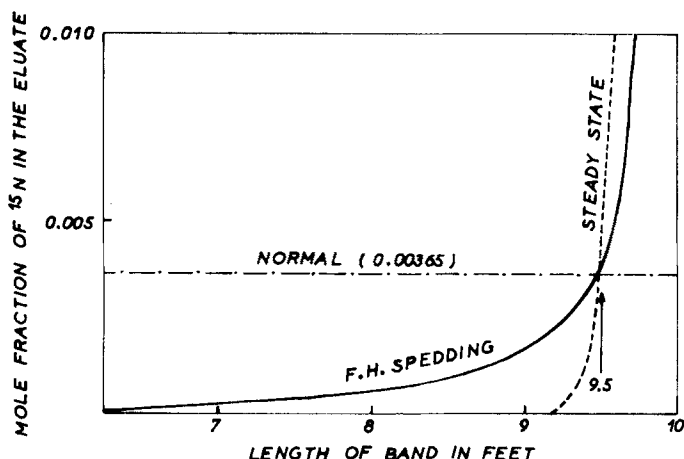


Fig. 1. Isotopic distribution in an ammonium band.

Fig. 1. The point where one finds natural isotopic composition (molar fraction of $^{15}\text{N} = 0.0365$) is at a distance of 9.5 ft from the head of the band, corresponding to an enriched zone in ^{15}N of 0.5 ft.

We shall compare these results with the theoretical steady-state isotopic distribution deduced from equations we recently published (3).

The profile given by Spedding is not, as we shall see later, a steady-state distribution. However, it corresponds to an important distance of displacement (50 times the band length) and the plateau region is reduced to a point. We can now show (and this has been demonstrated by simulation with a computer) that the position of this point of natural isotopic composition remains constant for a subsequent displacement of the band. So we know the distance from the band middle to the natural isotopic composition point taken as an origin (M) is 4.5 ft.

Expressed as the number of plates, M is given as a function of the total number of plates of the band P , $\epsilon = K - 1$, and ^{15}N molar fraction x_0 by (3):

$$M = \frac{1}{2\epsilon} \ln \left[\frac{1 - x_0}{x_0} \frac{\exp(2\epsilon P x_0) - 1}{\exp \epsilon P - \exp(\epsilon P / 2x_0 - 1)} \right] \quad (1)$$

By giving different values to HETP (and thus to P), we obtain the M values of Table 1 (with $\epsilon = 0.0257$ and $x_0 = 0.00365$).

Note: When x_0 is very small, $\exp(\epsilon P / 2x_0 - 1)$ may be neglected

before $\exp \epsilon P$. Further,

$$\frac{1 - x_0}{x_0} \sim \frac{1}{x_0} \quad \text{and} \quad \exp (2\epsilon P x_0) - 1 \sim 2\epsilon P x_0$$

so Eq. (1) becomes

$$M = \frac{1}{2\epsilon} \log \frac{2\epsilon P}{\exp \epsilon P}$$

$$M = \frac{1}{2\epsilon} [\log (2\epsilon P) - \epsilon P]$$

Because the experimental value of M is 4.5 ft, we can conclude that HETP is about 1.5 mm.

We can now give the steady-state isotopic distribution. On the curve whose equation is

$$p = \frac{1}{2\epsilon} \log \frac{x}{1 - x} \quad (2)$$

we place the plate corresponding to $x = x_0 = 0.00365$; then, from this plate, we place the median plate at -906 plates and, finally, we consider 1000 plates to the right and to the left of M . A portion of this curve corresponding to the rear of the band is shown in Fig. 1.

We can calculate the molar fraction of ^{15}N in the rear of the band at steady state. The plate corresponding to band rear has for its abscissa, from the point of natural isotopic composition,

$$p = 1000 - 906 = 94$$

TABLE 1

HETP (mm)	P	M (calculated) (in number of plates)	M (in feet)
2.5	1200	518	4.31
2	1500	663	4.42
1.5	2000	906	4.53
1	3000	1396	4.65
0.5	6000	2876	4.79

and Eq. (2) yields $x/(1 - x) = 2.1$, so $x = 0.68$. With a distance of elution of 50 times the band length, Spedding et al. obtained ^{15}N with a molar fraction of 0.22. This shows that the classical equation, giving a displacement of $[K/(K - 1)]L$ for steady-state conditions (here 40 times the band length L), does not apply for very closely related species as isotopes.

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