The HETP in Exchange Electromigration and Chromatography for Isotope Separation

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The Height of an Equivalent Theoretical Plate (HETP) is a characteristic process constant for any separation column in which a small elementary effect is to be multiplied. The smaller the HETP, the steeper is the enrichment along the column. In order to determine the HETP experimentally, it is not necessary to bring the column into the final, stationary state. One can more readily evaluate it from the initial slope of the enrichment at a closed end of the column. This is demonstrated for isotope separations on lithium, copper, rubidium and uranium obtained recently by means of exchange electromigration and chromatography.

In this paper, the Heights of an Equivalent Theoretical Plate (HETP) are determined from recent experimental results on lithium, copper, and rubidium isotope separation by means of exchange electromigration, and uranium isotope separation by means of chromatography. A review of the phenomenology precedes the discussion of the experimental data.

Phenomenology

The notion of the HETP is derived from destillation columns with equidistant plates for the separation of binary mixtures (mole fractions x_1 and x_2, $x_1 + x_2 = 1$, mixing ratio $r_{12} = x_1/x_2$), where use is made of the deviation from unity of the equilibrium constant

$$K_{12} = r_{12}^{(V)}/r_{12}^{(L)} \tag{1}$$

between vapour (V) and liquid (L). The elementary effect

$$\varepsilon_{12} = (r_{12}^{(V)} - r_{12}^{(L)})/r_{12} \tag{2}$$

is supposed to be so small that it suffices to define r_{12} in (2) by $r_{12}^{(V)} \geqq r_{12} \geqq r_{12}^{(L)}$.

The performance of a plate can be visualized as consisting of three steps, which are repeated again and again:

First step: Liquid from plate $p+1$ and vapour from plate $p-1$ are mixed and collected on plate p. Both contain the same number of moles.

Second step: One half of the liquid mixture on plate p is vapourized and equilibrated with the remaining half of the liquid mixture.

Third step: The equilibrated vapour is transferred to plate $p+1$ and the equilibrated liquid is transferred to plate $p-1$.

If the column is in a stationary state without withdrawal, the liquid leaving plate $p+1$ has the same composition as the vapour leaving plate p. This is with (2) expressed by

$$r_{12}^{(V,\,p+1)} - r_{12}^{(V,\,p)} = \varepsilon_{12}\, r_{12}$$

or

$$\Delta r_{12}/\Delta p = \varepsilon_{12}\, r_{12}, \tag{3}$$

where Δr_{12} and Δp are differences between neighbouring plates. For a column without plates, the difference equation (3) becomes the differential equation

$$\mathrm{d} r_{12}/\mathrm{d}(z/H) = \varepsilon_{12}\, r_{12}, \tag{4}$$

where z is the coordinate along the column and H is called the Height of an Equivalent Theoretical Plate (HETP) [1]. If the temperature and the cross section of the column are uniform, ε_{12} and H are constants, and integration of (4) yields

$$r_{12} = (r_{12})_{z=0} \exp[(\varepsilon_{12}/H)\, z]. \tag{5}$$

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In case of exchange electromigration one defines

$$\varepsilon_{12} = v_{12}/v_{M3}, \tag{6a}$$

where v_{12} is the electromigration velocity of the coions 1 with respect to the coions 2 under the condition of equilibrium isotope distribution between the adsorbed and desorbed states of the coions, and where v_{M3} is the electromigration velocity of the coionic mixture with respect to the counterions 3. The coions being isotopes, v_{12}/v_{M3} can be considered to be independent of the coionic mixing ratio. In case of chromatography, ε_{12} is the equilibrium elementary effect between solvate (S) and adsorbate (A):

$$\varepsilon_{12} = (r_{12}^{(S)} - r_{12}^{(A)})/r_{12}. \tag{6b}$$

The chromatographic velocity v_{12} as a function of ε_{12} is found by subtracting the chromatographic velocities v_{1B} and v_{2B} of 1 and 2 with respect to a boundary B, which is impermeable for the isotopes. One has

$$v_{iB} = (x_i^{(S)}/x_i)\, x_S\, v_{SB} + (x_i^{(A)}/x_i)\, x_A\, v_{AB}, \quad i = 1, 2, \tag{7}$$

where the mole fractions obey the relations

$$x_1 + x_2 = 1, \quad x_S + x_A = 1, \quad x_1^{(S)} + x_2^{(S)} = 1 \text{ and}$$
$$x_1^{(A)} + x_2^{(A)} = 1.$$

The impermeability of the boundary is expressed by

$$x_S\, v_{SB} + x_A\, v_{AB} = 0. \tag{8}$$

From (7) and (8) follows

$$v_{iB} = x_A\, v_{BA} (x_i^{(S)} - x_i^{(A)})/x_i, \quad i = 1, 2, \tag{9}$$

and thus

$$v_{12} = x_A\, v_{BA} (x_1^{(S)} - x_1^{(A)})/x_1\, x_2. \tag{10}$$

In terms of mole fractions, (6b) takes the form

$$\varepsilon_{12} = (x_1^{(S)} - x_1^{(A)})/x_1\, x_2, \tag{11}$$

and insertion of (11) into (10) yields

$$v_{12} = v_{BA}\, x_A\, \varepsilon_{12}. \tag{12}$$

v_{BA} is the velocity of the boundary with respect to the adsorbate, i.e. the velocity of the band with respect to the adsorbent.

In the presence of concentration gradients, the flux J_{iB} of isotope i with respect to a boundary B is given by

$$J_{iB} = C(x_i\, v_{iB} - D_i\, \partial x_i/\partial z), \quad i = 1, 2 \tag{13}$$

with

$$J_{1B} + J_{2B} = 0. \tag{14}$$

C is the molar amount of the mixture per unit length of the column. If the velocities v_{1B} and v_{2B} are zero, one has according to (13) and (14) $D_1 = D_2$. If they are not zero, D_1 and D_2 can be larger, because in a longitudinal concentration gradient transverse equilibration is less complete, the larger v_{1B} and v_{2B}. The conservation of the isotopes, however, requires that D_1 still equals D_2. One therefore has to deal with only one effective Diffusion coefficient D_{eff}. This implies according to (13) and (14) that

$$v_{1B} = x_2\, v_{12}, \tag{15}$$

and thus (13) becomes for $i = 1$

$$J_{1B} = C(x_1\, x_2\, v_{12} - D_{\text{eff}}\, \partial x_1/\partial z). \tag{16}$$

In the stationary state, J_{1B} is zero, i.e. according to (16)

$$\mathrm{d} \ln r_{12}/\mathrm{d}z = v_{12}/D_{\text{eff}}. \tag{17}$$

On comparing (17) with (4) one finds the relation

$$\varepsilon_{12}/H = v_{12}/D_{\text{eff}}. \tag{18}$$

ε_{12} is usually determined by collecting after a relatively short run, when there still exists a region of unchanged mixing ratio in the column, the material between a cut in this plateau region and the nearby boundary. One measures the number of moles, N, and the mole fraction of isotope 1, $x_1^{(N)}$, of this material. The conservation of isotope 1 is expressed by

$$(x_1^{(0)} - x_1^{(N)})\, N = x_1^{(0)}\, C \int_0^t v_{1B}\, \mathrm{d}t', \tag{19}$$

where $x_1^{(0)}$ is the mole fraction of 1 in the plateau region, t the duration of the run, and v_{1B} is positive (negative) if directed away from (towards) the nearby boundary. Equation (19) can be written in the form

$$(x_1^{(0)} - x_1^{(N)})\, N = x_1^{(0)}\, x_2^{(0)}\, Q\, \varepsilon_{12}, \tag{20}$$

where in case of electromigration (cf. (6a) and (15))

$$Q = C \int_0^t v_{M3}\, \mathrm{d}t' \tag{21a}$$

is the current-time integral divided by the Faraday constant and the valency of the coions, and in case of chromatography (cf. (12) and (15))

$$Q = x_A\, C \int_0^t v_{BA}\, \mathrm{d}t' \tag{21b}$$

is the exchange capacity of the adsorbent which the boundary has passed during the run. In the plateau region equilibrium is established because, transport by diffusion being absent, there is sufficient time for equilibration. Thus the value of ε_{12} corresponds to equilibrium. The time integral in (21 a, b) implies that (20) is also valid if the run was not continuous.

When the column is filled with the isotopes by letting a front boundary enter it from a feed reservoir of constant mole fractions $x_1^{(\mathrm{F})}$ and $x_2^{(\mathrm{F})}$, the mole fractions $x_1^{(0)}$ and $x_2^{(0)}$ in the resulting plateau region within the column are necessarily different from $x_1^{(\mathrm{F})}$ and $x_2^{(\mathrm{F})}$ because the conservation of 1 and 2 at the entrance of the column requires that

$$x_1^{(\mathrm{F})}/x_2^{(\mathrm{F})} = v_{1\mathrm{W}}\, x_1^{(0)}/v_{2\mathrm{W}}\, x_2^{(0)}, \tag{22}$$

where $v_{1\mathrm{W}}$ and $v_{2\mathrm{W}}$ are velocities with respect to the wall (W) of the column. In case of exchange electromigration the counterions are fixed with respect to the wall, and therefore $v_{1\mathrm{W}}/v_{2\mathrm{W}}$ equals $1+\varepsilon_{12}$. With (22) one obtains in due approximation

$$x_1^{(0)} = (1 - x_2^{(\mathrm{F})}\, \varepsilon_{12})\, x_1^{(\mathrm{F})}. \tag{23a}$$

In case of chromatography (cf. (12)), $v_{1\mathrm{W}}/v_{2\mathrm{W}}$ equals $1+x_\mathrm{A}\,\varepsilon_{12}$, which with (22) yields

$$x_1^{(0)} = (1 - x_2^{(\mathrm{F})}\, x_\mathrm{A}\, \varepsilon_{12})\, x_1^{(\mathrm{F})}. \tag{23b}$$

On introducing (23 a) and (23 b), respectively, into (20) one obtains, again in due approximation,

$$x_1^{(\mathrm{F})} - x_1^{(N)} = x_1^{(\mathrm{F})} x_2^{(\mathrm{F})} [(Q/N) + 1]\, \varepsilon_{12} \tag{24a}$$

and

$$x_1^{(\mathrm{F})} - x_1^{(N)} = x_1^{(\mathrm{F})}\, x_2^{(\mathrm{F})} [(Q/N + x_\mathrm{A}]\, \varepsilon_{12}. \tag{24b}$$

Mind that at the front (near) boundary $Q<0$ ($Q>0$). Normally $|Q|/N \gg 1$, and therefore the second terms in the brackets of (24 a, b) can be neglected. The plateau of the eluate has the mole fraction $x_1^{(\mathrm{F})}$, and therefore on analysing the eluate the equation

$$(x_1^{(\mathrm{F})} - x_1^{(N)})\, N = x_1^{(\mathrm{F})}\, x_2^{(\mathrm{F})}\, Q\, \varepsilon_{12} \tag{25}$$

is valid.

The HETP can be obtained according to (4) from ε_{12} and the slope of $\ln r_{12}$ in a column which is in the final, stationary state. This slope already exists during the build up period at the closed ends (boundaries) of the column because there, like in the stationary state, the transport of isotopes is zero, and this provides the opportunity to obtain the stationary slope by means of a much shorter experiment. One fits a theoretical $\ln r_{12}$ vs. z curve to experimental $\ln r_{12}$ values at various distances z and thus finds $(\partial \ln r_{12}/\partial z)_{z=0}$. The duration of such a run is chosen such that in some distance from the boundary a plateau range of r_{12} still exists. This corresponds to a theoretical r_{12} vs. z curve for a column of infinite length, which is to be calculated by integrating the continuity equation

$$\frac{\partial}{\partial t}(x_1\, C) = -\frac{\partial}{\partial z} J_{1\mathrm{B}}, \tag{26}$$

which with (16) reads

$$\frac{\partial x_1}{\partial t} = -v_{12}(1-2x_1)\frac{\partial x_1}{\partial z} + D_\mathrm{eff}\frac{\partial^2 x_1}{\partial z^2}. \tag{27}$$

Provided v_{12} and D_eff are independent of t and z, this non-linear equation can be integrated by means of a transformation introduced by S. D. Majumdar [2]. In case of a separation tube of infinite length and uniform initial mole fraction $x_1^{(0)}$, the result of the integration of (27) has been discussed in [3]. If x_1 is and remains small, it is sufficient to integrate the linear equation

$$\frac{\partial x_1}{\partial t} = -v_{12}\frac{\partial x_1}{\partial z} + D_\mathrm{eff}\frac{\partial^2 x_1}{\partial z^2}. \tag{28}$$

This has been done by Mason and Weaver [4] for various initial and boundary conditions. For binary mixtures of coions their results are also applicable if x_1 is and remains close to unity [5]. At the boundary ($z=0$) of a tube of infinite length one obtains for the separation factor $\alpha_{12} = r_{12}/r_{12}^{(0)}$:

for $x_1 \ll 1$: (29)

$$(\alpha_{12})_\mathrm{B} = -(2/\sqrt{\pi})\, \vartheta \exp(-\vartheta^2) + (1+2\vartheta^2) + [1-\mathrm{erf}(\vartheta)],$$

for $x_1 \approx 1$: (30)

$$(\alpha_{12})_\mathrm{B} = \{(2/\sqrt{\pi})\, \vartheta \exp(-\vartheta^2) + (1+2\vartheta^2)[1-\mathrm{erf}(-\vartheta)]\}^{-1},$$

where

$$\mathrm{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-x'^2)\,\mathrm{d}x' \tag{31}$$

and

$$\vartheta = -(1/2)\, v_{12}\sqrt{t/D_\mathrm{eff}}. \tag{32}$$

As an approximation for values of the separation factor α_{12} close to unity, the following expression for any values of x_1 and z was suggested in [5]:

$$\ln \alpha_{12} = (\ln \alpha_{12})_\mathrm{B}\, \psi(z/d), \tag{33}$$

where

$$\psi(x) = \exp(-x^2) - \sqrt{\pi}\, x\, [1-\mathrm{erf}(x)], \tag{34}$$

$$(\ln \alpha_{12})_\mathrm{B} = (4/\sqrt{\pi})\, \vartheta \tag{35}$$

and

$$d = 2\sqrt{D_{\text{eff}}\, t}\,. \tag{36}$$

The validity of (33) can be judged by a comparison of (33) for $z = 0$ with (29) and (30): If e.g. $\vartheta = -0.2$, one obtains for $(\ln \alpha_{12})_B$ from (29), (33) and (30) 0.430, 0.450 and 0.474, respectively. Therefore, for $(\ln \alpha_{12})_B = 0.45$ the largest possible deviation of $\ln \alpha_{12}$ as found when using (33) from the correct value amounts to $\pm 5\%$. The smaller the value of $(\ln \alpha_{12})_B$, and the closer the value of x_1 to $1/2$, the smaller is this deviation.

The fitting of the theoretical $\ln \alpha_{12}$ vs. z curve given by (33)–(36) to the experimental histogram yields values of $(\ln \alpha_{12})_B$ and d which serve to evaluate the slope of $\ln r_{12}$ at the boundary by means of the equation

$$(\partial \ln \mathrm{r}_{12}/\partial z)_B = -\sqrt{\pi}\,(\ln \alpha_{12})_B / d\,. \tag{37}$$

From (4) and (37) follows

$$H = -[\varepsilon_{12}/(\sqrt{\pi}\,(\ln \alpha_{12})_B)]\, d\,. \tag{38}$$

In our definitions, 1 and 2 are chosen such that ε_{12} is positive, the positive z-direction is from the boundary towards the binary mixture, and the relative velocities are positive if they are in the positive z-direction. Therefore, at the rear of a band there is $(\ln \alpha_{12})_B < 0$, $\partial \ln r_{12}/\partial z > 0$ and $H > 0$, and at the front of a band there is $(\ln \alpha_{12})_B > 0$, $\partial \ln r_{12}/\partial z < 0$ and $H < 0$.

Exchange Electromigration

In the experiments reported in [6], [7], and [8] a strip of the cation exchange membrane Aciplex CK-1, which is a non-reinforced, strongly acidic stylene divenylbentene copolymer resin (exchange group RSO_3^-) of 0.25 mm thickness, was converted to the H^+ form and immersed in some carbonhalogenide as isolator and coolant. Then, on the application of a stationary field, the H^+ ions were replaced by the cations of the element whose isotopes were to be separated, and after migration of the band over a certain length $v_{M3}\, t$, the front part of the band was analysed as to its isotopic composition.

Table 1 gives the relevant data of nine such exchange electromigration runs. The values of $(\ln \alpha_{12})_B$ and d were obtained by fitting (33) to the experimental results listed in Table 2. ε_{12} was calculated from (24a), H from (38), and D_{eff} from the equation

$$H = D_{\text{eff}} / v_{M3}\,, \tag{39}$$

which follows from (6a) and (18).

The isotope enrichment along a separation column is steeper the larger the value of ε_{12}/H. In case of the four lithium-runs, which essentially differed in temperature only, ε_{12} increased with temperature but H increased even more. Therefore, in this system operation at low temperature is preferable. In the four rubidium-runs the migration velocity differed while ε_{12} remained constant. D_{eff} increased with increasing migration velocity but not as much as v_{M3}. Therefore at the large migration velocities the HETP was smallest and the largest isotope separation was obtained. The independence of ε_{12} of the migration velocity indicates that ε_{12} is the equilibrium value, as expected from the way in which ε_{12} was determined.

The obtained values of D_{eff} shall be compared with the isotopic interdiffusion coefficients in water at

Table 1. Characteristics of nine exchange electromigration runs. The values of $(\ln \alpha_{12})_B$ and d have been obtained by fitting (33) to the experimental data given in Table 2.

Isotopes 1, 2	Ref.	Run no.	$-v_{M3}\, t$ [cm]	$-10^4\, v_{M3}$ [cm/s]	°C	$10^3\, \varepsilon_{12}$	$(\ln \alpha_{12})_B$	d [cm]	$10^6\, D_{\text{eff}}$ [cm²/s]	$-10^3\, H$ [cm]
^{6}Li, ^{7}Li	[6]	1	30.6	6.1	6	2.3	0.499	0.419	0.66	1.09
	[6]	2	26.0	6.1	11	3.2	0.466	0.537	1.27	2.08
	[6]	3	24.8	5.83	20	3.8	0.431	0.533	1.54	2.65
	[6]	4	27.8	5.56	40	4.5	0.345	0.891	3.65	6.56
^{63}Cu, ^{65}Cu	[7]		93.5	4.7	25	0.32	0.0595	0.968	1.38	2.94
^{85}Rb, ^{87}Rb	[8]	201	20.5	6.83	25	0.9	0.0540	0.771	4.95	7.25
	[8]	202	19.5	12.6	25	0.9	0.0869	0.537	4.99	3.96
	[8]	203	20.3	22.4	25	0.9	0.0826	0.488	6.72	3.00
	[8]	204	20.5	33.6	25	0.9	0.0912	0.502	9.41	2.80

infinite dilution, which can be evaluated from the respective ionic conductances, λ, by means of the Nernst-Einstein relation

$$D\,[\mathrm{cm^2\,s^{-1}}] = 1.119 \cdot 10^{-9}\, T\,[\mathrm{K}]\, \lambda\,[\mathrm{cm^2\,\Omega^{-1}\,mol^{-1}}]. \tag{40}$$

Values of λ for Li^+, Cu^{++} and Rb^+ are given in [9]. With these one obtains the following isotopic inter-diffusion coefficients in water at infinite dilution:

Ion	°C	$10^6 D$ ($cm^2\,s^{-1}$)
Li^+	6	7.3
Li^+	11	8.8
Li^+	20	11.4
Li^+	40	18.9
Cu^{++}	25	18.7
Rb^+	25	25.5

The D_{eff} values of Table 1 are 2.7 to 14 times smaller than these D-values, which must be due to the tortuosity of the diffusion paths in the resin and the fact that the cations are attracted by the RSO_3^--groups of the resin. Since both the longitudinal diffusion and the transverse exchange velocity increase with temperature, the increase of D_{eff} with temperature observed in the lithium runs shows that the former effect is dominating. The increase of D_{eff} with increasing migration velocity indicates that the equilibrium between the solved and adsorbed states of the cations becomes more disturbed as the electrotransport in a given concentration gradient increases.

The increase of ε_{12} with increasing temperature in the lithium runs may be due to the reduced residence time of the hydration water of the Li^+ ions at higher temperatures. This should bring about an increased effectiveness of the lithium masses in the equilibrium isotope distribution between different states as well as in the kinetic processes.

Table 2. Experimental data of nine exchange electromigration runs and the values of $\ln \alpha_{12}$ resulting from the fitted expression (33).

Isotopes 1, 2	Ref.	Run no.	z/cm	$\ln \alpha_{12}$ (exp.)	$\ln \alpha_{12}$ (fitted)
^6Li, ^7Li	[6]	1	0.10	0.3175	0.3164
			0.30	0.0964	0.1019
			0.50	0.0320	0.0236
			0.70	0.0080	0.0038
	[6]	2	0.10	0.3287	0.3284
			0.30	0.1425	0.1430
			0.50	0.0492	0.0514
			0.70	0.0202	0.0150
	[6]	3	0.10	0.3006	0.3026
			0.30	0.1434	0.1307
			0.50	0.0661	0.0799
			0.70	0.0161	0.0133
	[6]	4	0.10	0.2836	0.2808
			0.30	0.1715	0.1776
			0.50	0.1062	0.1052
			0.70	0.0619	0.0581
^{63}Cu, ^{65}Cu	[7]	–	0.13	0.0464	0.0464
			0.63	0.0143	0.0144
			1.13	0.0047	0.0031
			1.63	−0.0050	0.0004
			2.13	0	0
^{85}Rb, ^{87}Rb	[8]	201	0.09	0.0432	0.0432
			0.32	0.0235	0.0234
			0.59	0.0098	0.0096
			0.86	0.0030	0.0033
			1.08	0.0010	0.0012
			1.30	0.0005	0.0004
	[8]	202	0.10	0.0493	0.0493
			0.33	0.0185	0.0187
			0.59	0.0050	0.0044
			0.84	0	0.0008
			1.08	0	0.0001
	[8]	203	0.08	0.0606	0.0605
			0.29	0.0235	0.0237
			0.54	0.0055	0.0051
			0.80	0.0005	0.0007
			1.05	0	0.0001
	[8]	204	0.10	0.0636	0.0635
			0.34	0.0200	0.0203
			0.60	0.0045	0.0043
			0.83	0.0015	0.0008
			1.07	0	0.0001

Chromatography

As an example, the separation of the uranium isotopes described in [10] shall be considered. In these experiments, tubes of 1 cm width were filled with a strongly basic anion exchange resin which, in the presence of hydrochloric acid, has adsorbed negative chlorine complexes of Fe(III). At the front of the band these are replaced by negative complexes of U(VI), and at the rear of the band the latter are replaced by chloride ions. The reactions at the boundaries are about as follows:

front:

$$2\,UCl_4 + UO_2Cl_2 + 4\,H_2O + 6\,(FeCl_4)^- \rightarrow 3\,(UO_2Cl_4)^{2-} + 8\,HCl + 4\,FeCl_2 + 2\,FeCl_3, \tag{41}$$

rear:

$$3\,(UO_2Cl_4)^{2-} + 4\,TiCl_3 \rightarrow 2\,UCl_4 + UO_2Cl_2 + 4\,TiOCl_2 + 6\,Cl^-. \tag{42}$$

Table 3. Characteristics of two chromatographic runs. The values of $(\ln \alpha_{12})_B$ and d have been obtained by fitting (33) to the experimental data given in Table 4.

Isotopes 1, 2	Ref.	Run no.	$v_{BA}\,t$ [cm]	$10^4\,v_{BA}$ [cm/s]	x_A	°C	$10^4\,\varepsilon_{12}$	$(\ln \alpha_{12})_B$	d [cm]	$10^5\,D_{eff}$ [cm^2/s]	$10\,H$ [cm]
^{238}U, ^{235}U	[10]	2	184.5	2.31	0.9	50	6.8	−0.0325	11.076	2.72	1.31
	[10]	5	−2201.0	−5.75	0.9	70	6.7	0.1075	24.723	4.50	−0.87
	[10]	5	2201.0	5.75	0.9	70	6.7	−0.1365	27.247	3.88	0.75

The charged reactants in these equations are adsorbed while the other reactants are in solution. Thus in the band a countercurrent of solved U(VI) and adsorbed U(VI) is established, and the great chemical difference between these states gives rise to a large effect in the equilibrium isotope distribution between the two.

For uranium in the two chemical state U(IV) and U(VI), (11) with 1 and 2 standing for ^{238}U and ^{235}U, respectively, can be written in the specific form

$$\varepsilon_{12} = [x_{(SIV)}\,x_1^{(SIV)} + x_{SVI}\,x_1^{(SVI)} - x_{AIV}\,x_1^{(AIV)} - x_{AVI}\,x_1^{(AVI)}]/x_1\,x_2\,, \quad (43)$$

where the sums $x_{SIV} + x_{SVI}$, $x_{AIV} + x_{AVI}$, $x_1^{(SIV)} + x_1^{(SVI)}$ and $x_1^{(AIV)} + x_1^{(AVI)}$ are unity. If x_{AIV} can be considered to be zero, and if the isotope effect between adsorbed and solved U(VI) is negligible, (43) becomes

$$\varepsilon_{12} = x_{SIV}\,\varepsilon_{12}^{*}\,, \quad (44)$$

where

$$\varepsilon_{12}^{*} = [x_1^{(SIV)} - x_1^{(SVI)}]/x_1\,x_2 \quad (45)$$

is the elementary isotope effect between U(IV) and U(VI). According to (41) and (42), x_{SIV} should be 2/3; experimentally it varied between 0.62 and 0.66.

Table 4. Experimental data of two chromatographic runs and the values of $\ln \alpha_{12}$ resulting from the fitted expression (33)

Isotopes 1, 2	Ref.	Run no.	z/cm	$\ln \alpha_{12}$ (exp.)	$\ln \alpha_{12}$ (fitted)
^{238}U, ^{235}U	[10]	2	0.10	−0.0346	−0.0320
			1.46	−0.0233	−0.0255
			2.50	−0.0194	−0.0212
			5.43	−0.0119	−0.0118
			9.18	−0.0062	−0.0048
			13.35	−0.0034	−0.0015
			15.65	−0.0010	−0.0007
	[10]	5	0.00	0.1072	0.1075
			1.31	0.0965	0.0977
			3.92	0.0815	0.0800
			10.44	0.0464	0.0456
			16.98	0.0250	0.0237
			22.20	0.0097	0.0131
	[10]	5	0.26	−0.1336	−0.1342
			0.52	−0.1311	−0.1319
			1.04	−0.1287	−0.1275
			1.57	−0.1220	−0.1230
			4.70	−0.0987	−0.0988
			7.57	−0.0817	−0.0797
			11.75	−0.0580	−0.0568
			16.98	−0.0344	−0.0355
			25.33	−0.0130	−0.0151

The relevant data of two runs published in [10] are given in Table 3. The values of $(\ln \alpha_{12})_B$ and d have been obtained by fitting (33) to the experimental results presented in Table 4. In one of the runs the isotopic analysis has been performed both in the front and rear regions of the band. ε_{12} was calculated from (25), H from (38), and D_{eff} from the equation

$$H = D_{eff}/x_A\,v_{BA}\,, \quad (46)$$

which follows from (12) and (18).

The values of D_{eff} in Table 3 are an order of magnitude greater than those in Table 1. One of the reasons is convective mixing in chromatography, which is absent in exchange electromigration. In run 5 the velocity of the band and the temperature were higher than in run 2, while ε_{12} was the same. The higher band velocity renders equilibration more difficult and thus increases D_{eff}, while the higher temperature increases the exchange velocity and this way decreases D_{eff}, though, as to the longitudinal diffusion, the higher temperature increases D_{eff}. As a result of these three effects, D_{eff} is higher in run 5 than in run 2. Ideally, the values of D_{eff} and $|H|$ obtained from the front and the rear of run 5 should be equal, respectively, but this did evidently not come out. The reason for this discrepancy is not known presently.

The question might arise why D_{eff} has not been evaluated, both in case of exchange electromigration and chromatography, by means of the simple equation (36). The answer is that D_{eff} should not be evaluated without using the value of ε_{12} because the determination of this value is independent of possible inhomogeneous packings of the column, lacking sharpness of the boundary, interruptions of the run, etc., and is therefore more accurate than the values of $(\ln \alpha_{12})_{\text{B}}$ and d, whose determination presupposes the absence of all these nonidealities of the experiments. Indeed, values of ε_{12} obtained with the equations

$$\varepsilon_{12} = -(\sqrt{\pi}/4)(\ln \alpha_{12})_{\text{B}}\, d/v_{\text{M3}}\, t \tag{47a}$$

and

$$\varepsilon_{12} = -(\sqrt{\pi}/4)(\ln \alpha_{12})_{\text{B}}\, d/x_{\text{A}}\, v_{\text{BA}}\, t \tag{47b}$$

differ somewhat from those obtained with (24a) and (25), respectively, while ideally they should coincide.

[1] cf. e.g. F. H. Spedding, J. E. Powell, and H. J. Svec, J. Amer. Chem. Soc. **77,** 6125 (1955) of A. Klemm, in: Molten Salt Chemistry, Vol. 6 (1987), edited by G. Mamantov and J. Braunstein.

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