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Figure 1

Figure 1: Figure 1

Abstract

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RADIOMETRIC STUDY OF THE CHROMATOGRAPHY OF DI- AND TRIVALENT IONS IN THE CONCENTRATION RANGE FROM 10^{-1} TO 10^{-9} N

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The development of theoretical studies in the field of chromatography has led to the conclusion that chromatographic processes depend both on equilibrium physicochemical factors and on transport phenomena. Attempts at a mathematical solution of chromatographic problems in general form lead to very complicated equations, the exact solution of which is not always possible ([1]).

In the present work we set ourselves the task of assessing the role of transport phenomena in the chromatography of di- and trivalent ions in the concentration range from 10^{-1} to 10^{-9} N.

Such a large range could be covered by using the carrier-free radioelements Ce^{144} and Sr^{89}. The method we used had the special feature that the motion of ions along the column was recorded radiometrically by means of a coincidence circuit. Since the β-radiation of Sr^{89} ($E \sim 1.5$ MeV) is strongly absorbed by the glass walls of the column, for this case we constructed a column with walls made of X-ray film 0.1 mm thick.

Fig. 1. Dynamics of sorption of Ce from a 0.01 N solution of $CeCl_3$. Volumetric flow rate 0.5 ml/cm^2 · min

As adsorbent we used KU-2 cation exchanger with a capacity of 1.9 mg-equiv/ml. The cation exchanger has one functional group, HSO_3^-.

We first studied the dynamics of sorption of Sr^{89} and Ce^{144} ions on a column containing 15 g of KU-2 cation exchanger in the H-form, with a particle size of 40 mesh. The general course of sorption dynamics on the adsorbent is illustrated in Fig. 1. As can be seen, after the period of establishment of the Ce^{+3} ion front, a regime of parallel transport is observed. It can be shown that both for the divalent ion Sr^{2+} and for the trivalent ion Ce^{+3}, the known Shilov equation is obeyed,

$$\theta = aL - \tau, \tag{1}$$

where θ is the time of filtration of the solution; L is the length of the adsorbent layer used; τ is the time of establishment of the front. The rate of motion of the front obeys the Shilov equation

$$W = u\frac{C_0}{q_{\mathrm{Me}} + \alpha C_0}. \tag{2}$$

Here u is the linear rate of flow of the solution; C_0 is the concentration of metal ions in the solution; q_{Me} is the adsorbed amount of cation ions per 1 ml of exchanger in the exhausted layer; α is the volume of voids in the adsorbent layer. Thus, knowing the ion-exchange constant for the ions Sr^{2+} and Ce^{3+}, we can calculate the rate of motion of the ion front. The ion-exchange constant determined by us for Ce^{3+}—H^{+} is equal to 2.94, and for Sr^{2+}—H^{+} is equal to 1.72.

Using the Nikolskii ion-exchange equation

$$q_{\mathrm{Me}} = k_j^Z \frac{f_{\mathrm{Me}} C_{\mathrm{Me}}}{f_{\mathrm{H}} C'_{\mathrm{H}}} q_{\mathrm{H}}^Z \tag{3}$$

(where f is the activity coefficient; C_{Me}, C_{H} are, respectively, the concentrations of metal and hydrogen ions; q_{H} is the adsorbed amount of hydrogen ions; Z is the charge of the ion), we can calculate the rate of motion of the ion front under equilibrium conditions.

Table 1

Motion of Ce^{3+} and Sr^{2+} fronts during adsorption

Ion	Conc. of Me ions, g-equiv/l	Conc. of H^+ ions, g-equiv/l	Filtration rate u_0, ml/cm^2 · min	Rate of front motion W, cm/hour, calc.	Rate of front motion W, cm/hour, exp.
Sr^{2+}	0.005	10^{-3}	0.5	0.080	0.072
Sr^{2+}	0.01	10^{-3}	0.5	0.16	0.149
Sr^{2+}	0.1	10^{-3}	0.5	1.58	1.46
Sr^{2+}	0.01	10^{-3}	1.22	0.38	0.35
Sr^{2+}	0.01	10^{-3}	3.0	0.95	0.86
Sr^{2+}	0.01	10^{-3}	6.0	1.90	1.72

Fig. 2

Figure 2: Fig. 2

Ion	Conc. of Me ions, g-equiv/l	Conc. of H^+ ions, g-equiv/l	Filtration rate u_0, ml/cm^2 · min	Rate of front motion W, cm/hour, calc.	Rate of front motion W, cm/hour, exp.
Sr^{2+}	0.1	0.3	0.5	2.20	1.99
Ce^{3+}	0.01	10^{-3}	0.5	0.16	0.14
Ce^{3+}	0.1	1.2	0.5	2.75	2.40

Table 1 gives the results of a comparison of the calculated and experimental data.

The data of Table 1 show that, when the concentration of metal ions is varied from 0.005 to 0.1 *n* and the concentration of hydrogen ions from 10^{-3} to 1.2 *n*, the rates of motion of the ions through the column can be calculated. The process proceeds under conditions close to equilibrium.

Fig. 2. Influence of the concentration of the filtered solution on the spreading of the sorption front of Sr and Ce ions. Volumetric flow rate 0.5 ml/cm^2 · min: *A*–$SrCl_2$ (*a*–0.005 *n*, *b*–0.01 *n*, *v*–0.1 *n*, *g*–0.3–0.4 *n*); *B*–$CeCl_3$ (*a*–0.01 *n*, *b* –0.1 *n*, *v*–0.3–0.5 *n*)

Comparison of the shapes of the fronts (Fig. 2) shows that, on passing from low concentrations to high concentrations, the front contracts. At a concentration of 0.3 *n* this contraction ceases–the front becomes stable. Consequently, by the most sensitive criterion–the spreading of the front–it may be judged that, at volumetric rates commonly used in chromatography, equal to 0.5-1.0 ml/cm^2 · min, at ion concentrations > 0.1–0.3 *n*, transfer phenomena may be disregarded. We clarified the role of ultralow ion concentrations in studying displacement chromatography.

The balance equation for the displaced ion for an infinitely small segment of the column can be written as follows:

$$u_0 \frac{\partial C_{\mathrm{Me}}}{\partial x} = -\frac{\partial q_{\mathrm{Me}}}{\partial t} - \alpha \frac{\partial C_{\mathrm{Me}}}{\partial t}. \tag{4}$$

Here t is time, x is the distance along the column.

In writing the equation it was assumed that the solution flows uniformly through the pores in the bed and that the volume of cationite during the process remains

Fig. 3. Dynamics of Ce desorption (with 1.4 N HCl solution). Volumetric flow rate 1 ml/cm² · min

Figure 3: Fig. 3. Dynamics of Ce desorption (with 1.4 N HCl solution). Volumetric flow rate 1 ml/cm² · min

unchanged. Longitudinal diffusion was not taken into account. The validity of this assumption was checked with the aid of Ce^{144}. A column with adsorbed microzone of cerium was filled with 1.4 N HCl and left for several days. The distribution of the active zone in this case changed almost not at all. Evidently, in our experiments the migration of ions along the column can be neglected.

Fig. 3. Dynamics of Ce desorption (with 1.4 N HCl solution).
Volumetric flow rate 1 ml/cm^2 · min

When a metal ion is displaced from the column by a hydrogen ion of variable concentration, $q_{\text{Me}} = f(C_{\text{Me}}, C_{\text{H}})$, the change in adsorption $\partial q_{\text{Me}}/\partial C_{\text{Me}}$ depends both on C_{Me} and on C_{H}. In the general case, C_{Me} and C_{H} depend on time and other parameters.

$$-\frac{\partial q_{\text{Me}}(C_{\text{Me}}, C_{\text{H}})}{\partial t} = -\frac{\partial q_{\text{Me}}}{\partial C_{\text{Me}}}\frac{\partial C_{\text{Me}}}{\partial t} - \frac{\partial q_{\text{Me}}}{\partial C_{\text{H}}}\frac{\partial C_{\text{H}}}{\partial t}. \tag{5}$$

Introducing the notations $\partial q_{\text{Me}}/\partial C_{\text{Me}} = q'_{\text{Me}}(C_{\text{Me}})$ and $\partial q_{\text{Me}}/\partial C_{\text{H}} = q'_{\text{Me}}(C_{\text{H}})$ and substituting into the balance equation, we have:

$$u_0\frac{\partial C_{\text{Me}}}{\partial x} = q'_{\text{Me}}(C_{\text{Me}})\frac{\partial C_{\text{Me}}}{\partial t} + q'_{\text{Me}}(C_{\text{H}})\frac{\partial C_{\text{H}}}{\partial t} + \alpha\frac{\partial C_{\text{Me}}}{\partial t}. \tag{6}$$

An analogous equation also holds for the phenomena of molecular liquid chromatography with an exchange mechanism of adsorption of molecules. In the special case when $C_{\text{Me}} + C_{\text{H}} = \text{const}$, integration of this equation leads to the formula

$$\left(\frac{x}{t}\right)_{C_{\text{Me}}} = \frac{u_0}{q'_{\text{Me}}(C_{\text{Me}}) - q'_{\text{Me}}(C_{\text{H}}) + \alpha}. \tag{7}$$

Consequently, the rate of motion of the section of the zone must be determined by the difference of the derivatives.

In the case of equivalent ion exchange and a constant capacity of the adsorbent, one may write:

$$C_0 = C_{\text{Me}} + C_{\text{H}}; \qquad S = q_{\text{Me}} + q_{\text{H}}, \tag{8}$$

Figure 4

Figure 4: Figure 4

where C_0 is the concentration of the displacing agent, and S is the capacity of the ion exchanger. Then equation (6) becomes the following:

$$\left(\frac{x}{t}\right)_{C_{\mathrm{Me}}} = \frac{u_0}{\partial q_{\mathrm{Me}}/\partial C_{\mathrm{Me}} + \alpha}. \tag{9}$$

Substituting here the value of the derivative from the isotherm (equation (3)) for divalent and trivalent ions, we obtain:

for the ion Sr^{+2}

$$\left(\frac{x}{t}\right)_{C_{\mathrm{Me}}} = \frac{u_0}{\dfrac{q_{\mathrm{Me}}^2}{C_{\mathrm{Me}}^2}\dfrac{C_0^2 - C_{\mathrm{Me}}^2}{k_1^2(S^2 - q_{\mathrm{Me}}^2)} + \alpha}; \tag{10}$$

for the ion Ce^{3+}

$$\left(\frac{x}{t}\right)_{C_{\mathrm{Me}}} = \frac{u_0}{\dfrac{q_{\mathrm{Me}}\left(C_0^3 - 3C_0C_{\mathrm{Me}}^2 + 2C_{\mathrm{Me}}^2\right)}{C_{\mathrm{Me}}\left[3k_1^3C_{\mathrm{Me}}(S - q_{\mathrm{Me}})^2 + (C_0 - C_{\mathrm{Me}})^3\right]} + \alpha}; \tag{11}$$

$$k_1 = k_0 f_{\mathrm{Me}}^{1/Z}/f_{\mathrm{H}}.$$

Thus, the velocity of motion of the front in displacement equilibrium chromatography depends on a number of parameters.

For ultralow concentrations of Ce^{144} and Sr^{89}, with constant concentration of the displacer C_0 and constant ratios of activity coefficients, the isotherm is written as follows: $q_{\mathrm{Me}} = k_2C_{\mathrm{Me}}$. Under these conditions equations (10) and (11) become $\left(\frac{x}{t}\right)_{C_{\mathrm{Me}}} = \frac{u_0}{k_2 + \alpha}$, and all points of the wave must move with a constant velocity, as was noted earlier (^{2}).

Figure 3 shows a typical picture of the dynamics of displacement of the cerium ion by hydrochloric acid. In Fig. 4 are plotted the experimental points from one of the experiments carried out by us. The points fit the calculated curve well.

Thus, for displacement chromatography under conditions of adsorption of macroquantities, at rates of liquid motion from 0.5 to 1 ml/cm^2 · min, one may use the equations of equilibrium chromatography.

Fig. 4. Agreement between experimental points and the theoretical curve in the displacement of Ce and Sr ions by HCl solutions. a–$C_0 = 1.2$ g-eq/l, $u_0 = 0.5$ ml/cm$^2 \cdot$ min; b–$C_0 = 0.3$ g-eq/l, $u_0 = 0.5$ ml/cm$^2 \cdot$ min.

In the adsorption of ultralow amounts of Ce^{144} and Sr^{89}, we obtained in the upper part of the column a narrow highly radioactive ring. The filling of the adsorbent was $\approx 10^{-6}$ of the capacity. After adsorption the column was washed with hydrochloric acid of various concentrations. In this case constancy of the rate of motion of the zone sections is not observed. Equation (9) is clearly not fulfilled. Consequently, at ultralow concentrations, under our conditions, even at low volumetric rates of motion of the liquid stream, we must take into account the phenomenon of ion diffusion. The rate of diffusion processes becomes significant for the process as a whole.

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Note: Figure translations are in progress. See original paper for figures.