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DISPLACEMENT ION-EXCHANGE DYNAMICS OF SORPTION AND CHROMATOGRAPHY

ВЫТЕСНИТЕЛЬНАЯ ИОНООБМЕННАЯ ДИНАМИКА СОРБЦИИ И ХРОМАТОГРАФИИ

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Abstract. *The theory of ideal displacement ion-exchange sorption dynamics, taking into account the effect of the perturbation factors of the fronts, makes it possible to reveal the dominant regularities in the formation of displacement chromatograms, including the most important technological parameters-the lengths of the ion exchange bed and the time needed to separate the ion mixture. The conducted experiments confirm the results of theoretical studies.*

Keywords: *ion exchange, displacement dynamics of sorption, chromatography.*

Introduction.

Earlier [1-3, 7], the main provisions of the theory of frontal and elution ion-exchange dynamics of sorption and chromatography were presented. Elution ion exchange chromatography makes it possible to separate substances in very small amounts [3], but only by means of displacement ion-exchange chromatography, complete preparative separation of the ion components is possible.

The method of chromatographic separation of preparative quantities of mixtures of substances, proposed by A. Tiselius, has been known for a long time, but the theory of this method has not been developed sufficiently [4, 5, 9].

Questions of the general theory of the formation of displacement chromatograms were generalized in [4, 7-9]. The conditions under which the regime of the displacement dynamics of sorption is realized are clarified.

In [8, 9], the patterns of the rearrangement of the front chromatograms were established for the displacement dynamics of sorption.

The obtained results of theoretical studies were tested experimentally. These experiments have made it possible to understand the possible application of an ideal sorption model and the need to introduce appropriate corrections for describing real chromatographic processes [11].

The main text. The diverse use of ion-exchange processes is due to the heterogeneity of the system, i.e. the possibility of a simple phase separation (for example, by simple filtration of a solution through an ion exchange bed) and the ability of sorbents to exchange ions, which causes the separation of ions differing in sign, charge size or degree of hydration.

Most often in the calculations of ion-exchange processes, the law of acting masses is recorded in analytical concentrations, since data on the coefficients of ion activity in mixed solutions are practically absent:

$$\frac{S_1^{1/Z_1}}{S_i^{1/Z_i}} = k_{1,i} \frac{C_1^{1/Z_1}}{C_i^{1/Z_i}}, \quad (1)$$

where S_1 and S_i are the equilibrium ion concentrations in the sorbent, C_1 and C_i are the equilibrium concentrations in the solution, Z_1 and Z_i are the valences of the ions, $k_{1,i}$ is the concentration constant of ion-exchange equilibrium.

When studying the sorption dynamics in the columns of the sorbent, it is expedient to use linear concentrations of N_1 and Ni - ion concentrations in the sorbent in mg-eq/cm length of the ion exchanger column, n_1 and n_i are the concentrations of these ions in the solution in the same units.

At these concentrations, equation (1) takes the following form:

$$\frac{N_1^{1/Z_1}}{N_i^{1/Z_i}} = k_{1,i} \frac{n_1^{1/Z_1}}{n_i^{1/Z_i}}, \quad (2)$$

where the constant $k_{1,i}$ is a dimensionless quantity.

The sorbability of ions is determined by the ion exchange constants. The study of the processes of ion-exchange sorption dynamics greatly simplifies the law of equivalence of ion exchange (charge conservation law)

$$\sum_{i=1}^{j} n_1 = n_0 = const, \sum_{i=1}^{j} N_i = N_0 = const, \quad (3)$$

where n_0 is the total concentration of ions in the solution, N_0 is the total ion concentration in the sorbent (ion exchange capacity).

Let us consider the simplest case of formation of an ideal displacement ion-exchange chromatogram.

Let ion 2 be introduced into a column of ion exchanger saturated with ion 1 and a primary rectangular zone of ion 2 is formed.

Exchange capacity of ion exchanger N_0, concentration of ion 2 in solution n_0 (Fig. 1, *a*).

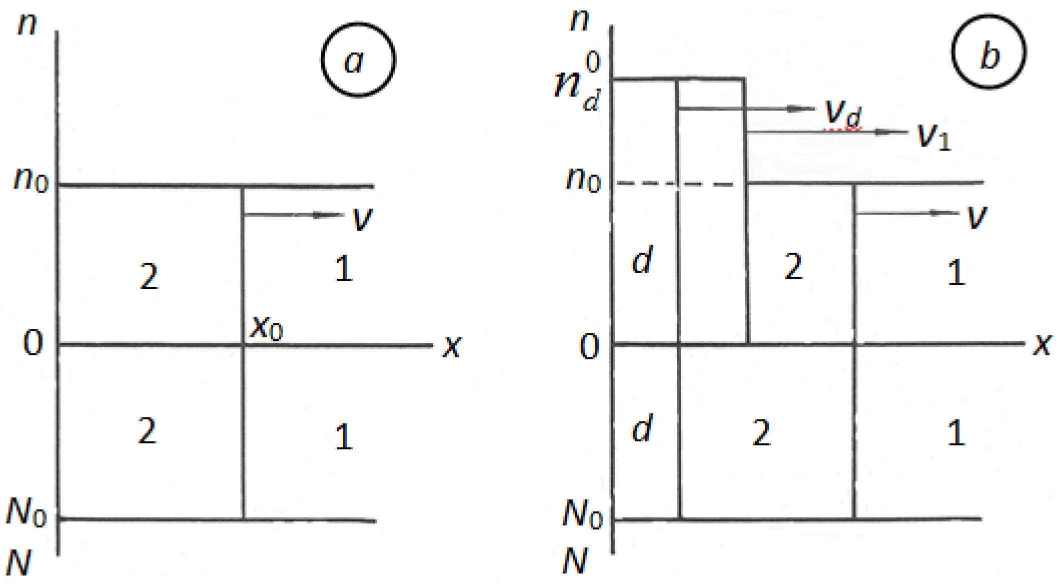

Fig. 1. Formation of the displacement ion-exchange chromatogram of one substance, $h_d > h_0$

We introduce into the column an ion-displacer *d*. The process of displacement is possible if the velocity of the ion-displacer v_d is greater than the velocity v of the ion 2.

Based on the balance of matter, the velocity of the leading front of ion 2

$$v = u\,\frac{h_0}{1+h_0}, \tag{4}$$

Similarly, the velocity of the displacement ion d

$$v_d = u\,\frac{h_d}{1+h_d}, \tag{5}$$

where $h = \frac{n}{N}$ is the ionic (distributive) ratio.

The formation of a displacement chromatogram for $h_d > h_0$ ($n_d^0 > n_0$) is shown in Fig. 1, *b*.

The speed of the leading edge of the new zone is determined by the balance of the ion 2:

$$(v_1 - v_d)\left(\frac{v_d}{n_d} + N_0\right) = (v_1 - v)(n_0 + N_0), \tag{6}$$

from the equality (4), (5), (6) we have:

$$v_1 = u\ . \tag{7}$$

The calculation shows that, as expected, the leading edge of the new zone moves with the flow velocity.

The width of the original zone decreases with the speed $v_1 - v = u - v$.

Time of formation of a new zone of ion 2

$$t = \frac{x_0}{u-v} = \frac{v \cdot t_0}{u-v} = t_0\left(\frac{u}{v} - 1\right)^{-1} = t\left(\frac{u}{un/(n_0+N_0)} - 1\right)^{-1} = t_0\,\frac{n_0}{N_0} = t_0 \cdot h_0, \tag{8}$$

where t_0 is the time of formation of the primary (frontal) chromatogram (zones of ion 2).

If $h_d < h_0$, then the displacement occurs as shown in Fig. 2.

And in this case, the leading edge of the new zone moves with the flow velocity, and the time of formation of the displacement chromatogram is determined by the formula (8).

Let us consider the equilibrium displacing dynamics of the sorption of two ions in the absence of perturbation factors for ion exchange fronts [8]. The frontal chromatogram of two ions has the form shown schematically in Fig. 3, *a*.

A necessary and sufficient condition for obtaining a front chromatogram is that the difference in sorbability of ions ($k_{2,3} < 1$) is a necessary and sufficient condition for the formation of an ion-exchange chromatogram.

To simplify the description of processes in the column, we introduce the ion-displacer *d*, preserving the same ionic (distributive) ratio as in front-end

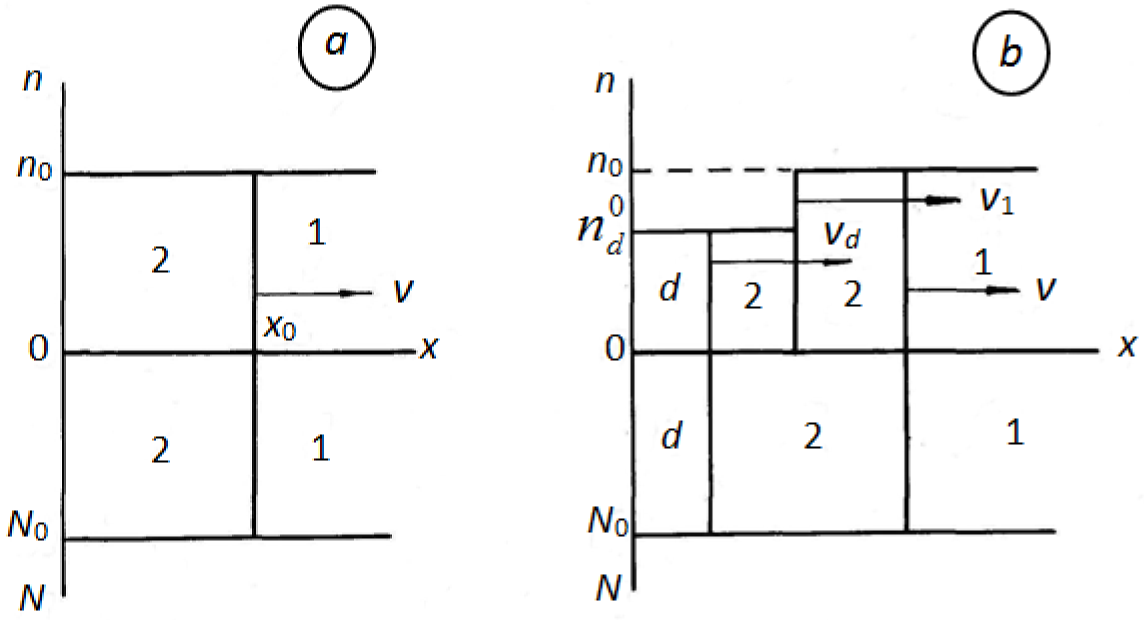

Fig. 2. Formation of the displacement ion-exchange chromatogram of one substance, $h_d < h_0$

chromatography:

$$h = \frac{n_0}{N_0} = h_d = \frac{n_d^0}{N_d^0} = \frac{\sum_{i=1}^{j} n_i^0}{\sum_{i=1}^{j} N_i^0}, \qquad (9)$$

From the introduction of the ion-displacer in the column, a pure zone of ion 3 appears immediately behind the mixed zone of ions 2 and 3.

The velocities of the boundaries of the zones are determined by the corresponding distributive ratios of the ions.

$$v = u\frac{h}{1+h},\ v_2 = u\frac{h_{2,2}}{1+h_{2,2}},\ v_3 = u\frac{h_{3,2}}{1+h_{3,2}},\ v_d = v = u\frac{h_d}{1+h_d} = u\frac{h}{1+h}, \qquad (10)$$

where $h_{2,2} = \frac{n_2^0}{N_2^0}$, $h_{3,2} = \frac{n_3^0}{N_3^0}$. (11)

It is not difficult to show that $h_{2,2} > h > h_{3,2}$ and, respectively, $v_2 > v > v_3$.

The difference in the velocities of ions 2 and 3 ensures a complete separation of the ions.

At some instant of time *t* the mixed zone disappears, the ion distribution shown in Fig. 3, *c*. From this point on comes the stationary stage of the displacement process - all fronts begin to move at a constant speed $v_d = v$.

The time of formation of the displacement chromatogram of ions 2 and 3:

$$t = \frac{x_3^0}{v_2 - v_3} = t_0\left(\frac{v_2}{v_3} - 1\right)^{-1} \qquad (12)$$

or, taking into account equalities (10) and (11)

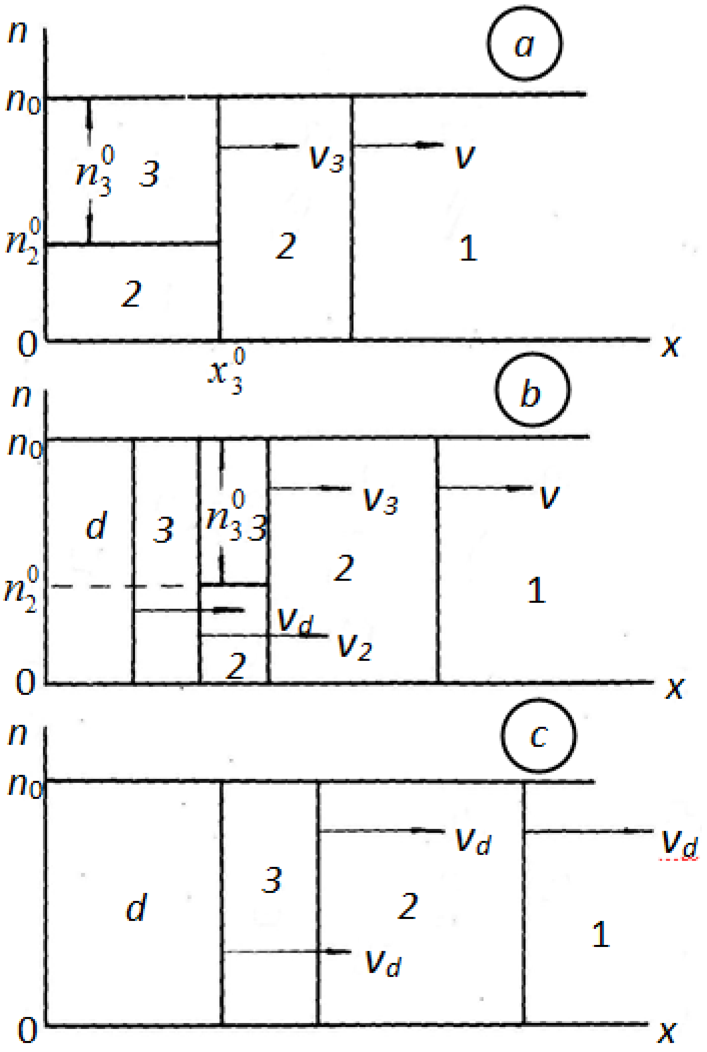

Fig.3. Formation of a displacement chromatogram of two incoming ions

$$t = t_0 \left[\frac{h_2^0 / \left(1 + h_2^0\right)}{h_3^0 / \left(1 + h_3^0\right)} \right]^{-1} . \qquad (13)$$

The total separation time of ions 2 and 3 is equal to the sum of the time spent on obtaining the front and displacement chromatograms

$$T = t_0 + t = t_0 \left(1 - \frac{v_3}{v_2}\right)^{-1} . \qquad (14)$$

Since the velocity of the leading front v is constant both in the formation of the frontal and the formation of the displacement chromatogram, the length of the ion exchange column necessary for the separation of ions 2 and 3 (without removal from the column)

$$L = v \cdot T = L_0 \left(1 - \frac{v_3}{v_2}\right)^{-1} , \qquad (15)$$

where $l_0 = v \cdot t_0$ is the length of the front chromatogram of ions 2 and 3.

The minimum column length required to remove the separated ions from the column is numerically equal to the coordinate *x* in which the mixed zone of ions 2 and 3 disappears:

$$L_1 = x_3^0 + v_3 \cdot t = v_3 \cdot t_0 + v_3 \cdot t = v_3 \cdot t_0 \left(1 - \frac{v_3}{v_2}\right)^{-1} = \tilde{o}_3^0 \left(1 - \frac{v_3}{v_2}\right)^{-1}. \qquad (16)$$

Let us find out how well the theory of ideal ion-exchange excitation dynamics of sorption agrees with the results of the ion-separation experiment.

As an example, consider the formation of a displacement chromatogram of Rb^+ and Ca^{2+} ions. To obtain a front chromatogram, a mixture of these ions is introduced into the column, one of which (the least sorbed Rb^+) is labeled with a radioactive isotope having a hard radiation penetrating through the wall of the glass tube. The concentration of the displacement ion was taken equal to the concentration of the initial mixture of ions, $h_d = h_0$ (Fig. 4).

Then, at different amounts of the ion-displacer, we successively shoot a series of radiochromatograms that clearly illustrate the evolution of the process of displacement sorption dynamics. The volume of the displacer introduced into the column is indicated on each radiochromatogram.

The length of the ion exchange layer necessary to separate ions from the mixture did indeed correspond to formulas (15) and (16).

The heights of chromatographic zones of frontal and displacement radiochromatograms are unchanged, which corresponds to the law of equivalence of ion exchange.

With convex isotherms, fronts of ion-exchange chromatograms are stabilized at the asymptotic stage.

At the front boundary, an exchange occurs weaker the sorbed ion Rb^{*+} of the mixture and the H^+ ion that saturates the ion exchanger. To form a stationary front, it is necessary that $k_{H,\ Rb} < 1$.

At the rear boundary of the mixed zone, there is an exchange of a stronger than the sorbed ion of the Ca^{2+} mixture and the ion-displacer Sr^{2+}. The stationary front is realized for $k_{Ca,\ Sr} < 1$.

The stationary nature of the H^+ - Rb^{*+} ion exchange fronts at the front boundary of the pure Rb^{*+}, Rb^+ and Ca^{2+} zones at the front boundary of the mixed zone is performed with high accuracy (these fronts can be combined in Figure 4.).

However, at the rear boundary of the mixed zone, the ion exchange front Rb^{*+}-Ca^{2+}, visible on radiochromatograms, progressively expands, in spite of the fact that $k_{Rb,\ Ca} < 1$.

This is explained by the fact that in this front the exchange of Rb^+-Ca^{2+} is determined by the sorption of the stronger sorbed Ca^{2+} ion and the exchange of Ca^{2+}-Ca^{2+} at the same boundary.

Because of the equivalence of the exchange, the exchange front of Ca^{2+}-Ca^{2+} ions is "imposed" on the Rb^{*+} - Ca^{2+} front of exchange.

This ion exchange corresponds to a linear sorption isotherm. In this case, the width of the mixed zone increases in proportion to the displacement time (the volume of the introduced displacer) [4, 8, 9].

The velocity of the point of half the concentration of the ion exchange front at the back boundary of the mixed zone is constant, which also indicates the linearity isotherm of the ion exchange at the boundary of the mixed zone and of the zone of

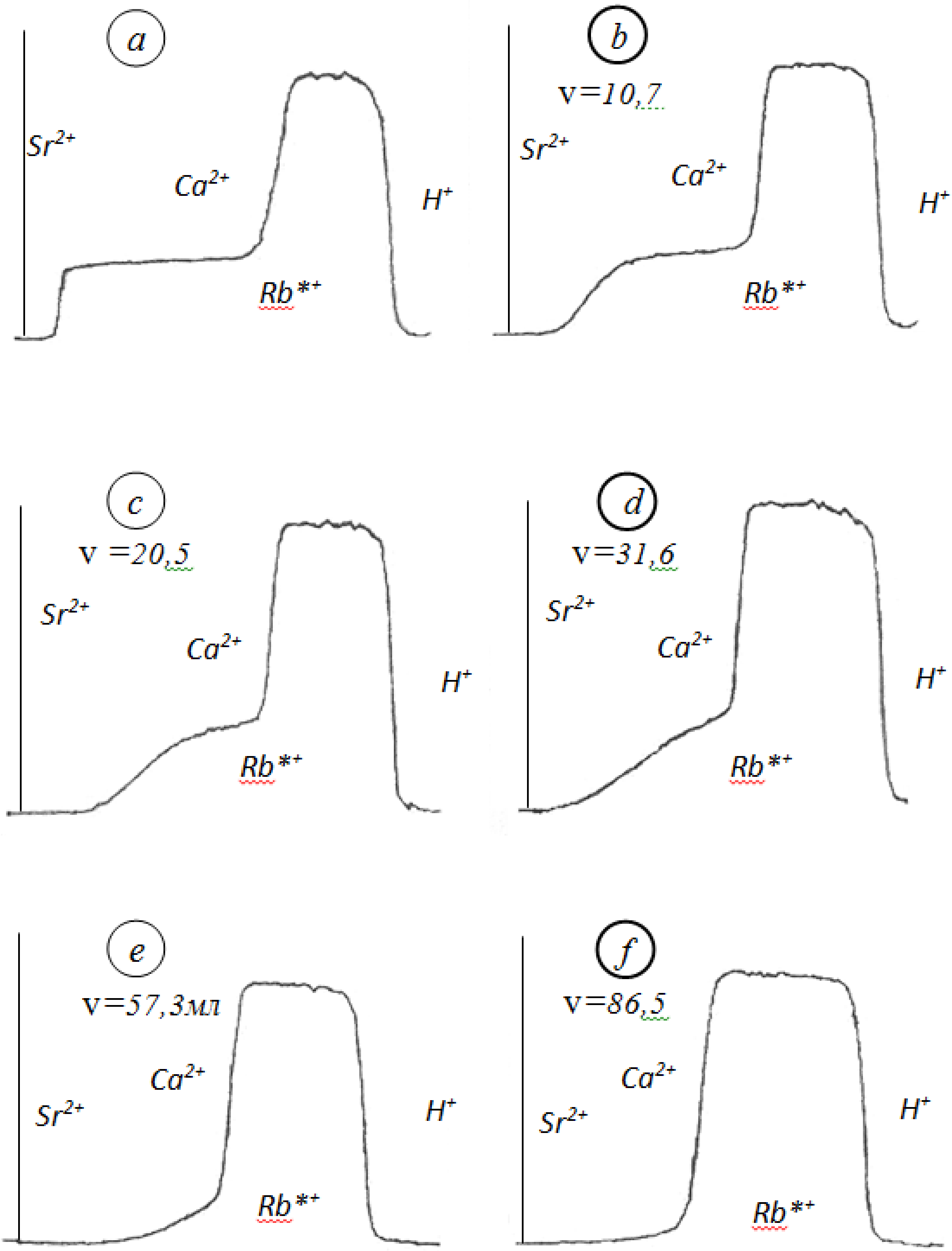

Fig. 4. Formation of a displacement chromatogram of Rb^{*+} and Ca^{2+} ions. The radioactive label is the ^{86}Rb isotope. Solutions of $Rb^{*}Cl$ and $CaCl_2$ were used ($C_{Rb} = C_{Ca} = 0.05n$). The displacer is 0.1n $SrCl_2$.

the stronger sorbed of the ion.

Characteristics of the ion exchange fronts obtained in the study of radiochromatograms in which the more strongly sorbed ion carries radioactive label were the same also in the case of a "labeled" weaker sorbed ion.

After the disappearance of the plateau of the mixed zone, the velocity of movement is weaker of the sorbed ion decreases, and therefore, in practical separations, it makes no sense to achieve complete stationarity of the ion exchange fronts.

Note that in the front chromatogram all fronts are stationary.

The correctness of the schemes of chromatograms considered in [6-9, 11], including multicomponent ones, was verified upon separation of three ions (Fig. 5.).

When expelling, the zone with the largest number of components shrinks. The Rb^{*+} and Mg^{2+} ions pass into the front zones, while the more sorbed Mg^{2+} and Sr^{2+} enter the rear ions formed. After the disappearance of the zone containing all three ions, the separation of K^{*+}-Mg^{2+} ions occurs and Mg^{2+}- Sr^{2+}. On the radiochromatogramms in Fig. 5 shows a picture of the motion of the ion K*.

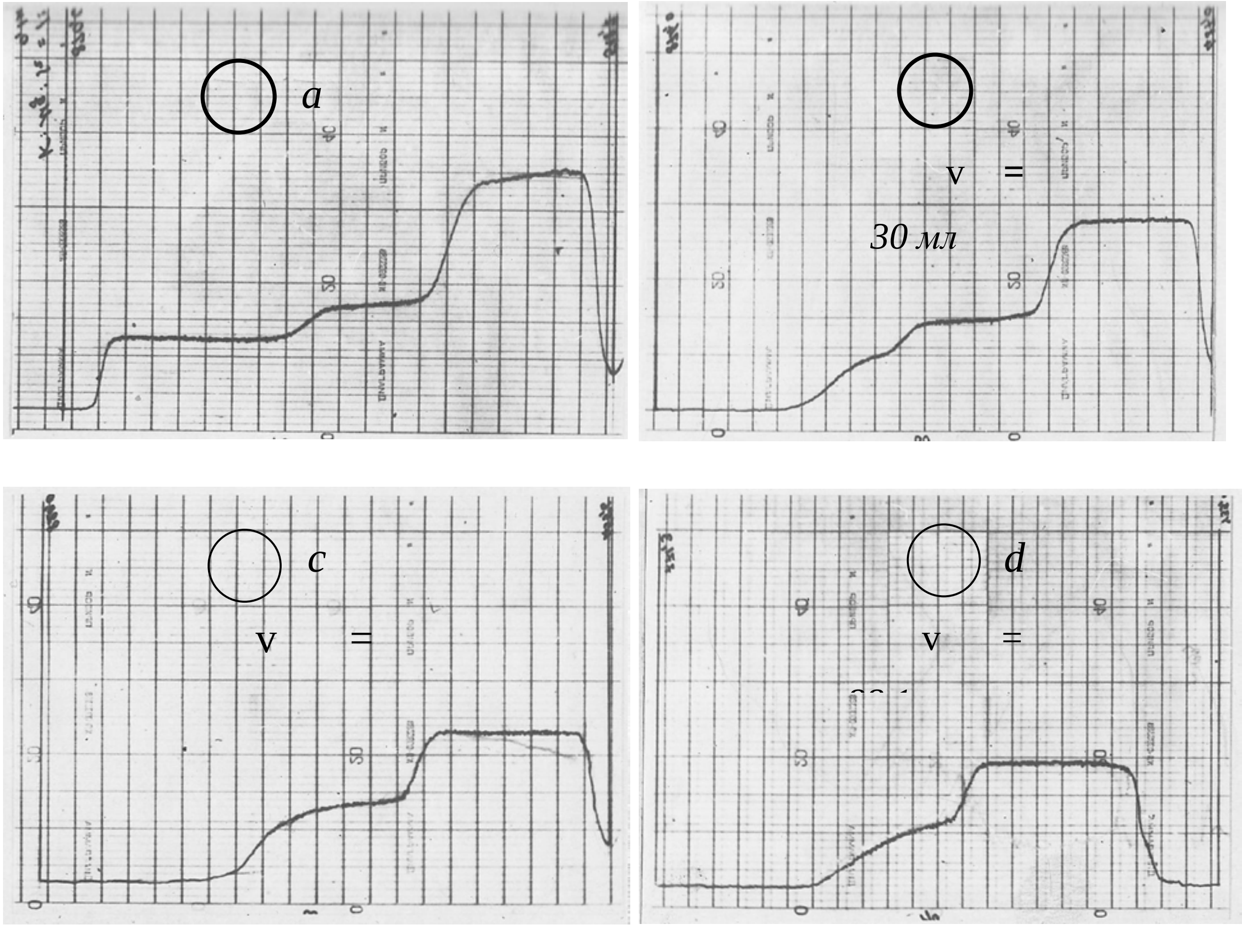

Fig. 5. Displacement chromatograms of K^{*+} - Mg^{2+} - Sr^{2+}. ($C_k = C_{Mg} = C_{Sr} =$ 0,033n). The displacer is 0.1n $SrCl_2$. The decrease in the height of the hromatograms is explained by the fact that the half-life of the radioisotope ^{42}K is brief.

Summary and Conclusions.

The theory of ideal displacement ion-exchange sorption dynamics can be successfully used to describe the processes of formation of displacement chromatograms and to determine the most important technological parameters-the length of the ion exchange bed and the time required to separate the ion mixture.

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Аннотация. *Теория идеальной вытеснительной ионообменной динамики сорбции с учетом действия факторов возмущения фронтов позволяет выявить доминирующие закономерности в формировании вытеснительных хроматограмм, в том числе и важнейшие технологические параметры – длину слоя ионита и время, необходимые для разделения смеси ионов. Проведенные эксперименты подтверждают результаты теоретических исследований.*

Ключевые слова: *ионный обмен, вытеснительная динамика сорбции, хроматография.*

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