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FORMATION OF ION-EXCHANGE CHROMATOGRAMS

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Introduction

Ion exchange chromatography is widely used in various branches of science and technology for the analysis and separation of both inorganic and organic substances with similar properties.

The exceptional importance of the methods of ion exchange and ion exchange chromatography is evidenced by the hard-to-see number of publications on the use of ion exchangers in scientific research, biology, medicine, agriculture, and various industries.

It is enough just to get acquainted with the lists of literary sources, given at least only in some well-known monographs and collections of scientific works [1-4, 12-14].

In ion-exchange chromatography, the separation of mixture components occurs due to the reversible interaction of ionized substances with the ionic groups of the sorbent.

Ion exchange chromatography can be used to separate any compounds that can be ionized in any way.

The degree of ionization of the components of the distributed mixture can be changed, in particular, with the help of complexation, by changing the pH of the solution, which can significantly increase the efficiency of chromatographic processes and expand the area of their application.

For example, chromatographic analysis of even neutral sugar molecules in the form of their complexes with a borate ion is possible [3].

The expediency of using one or another ion exchanger in each individual case is determined by its selectivity, exchange capacity, chemical and mechanical properties [1, 12, 13].

In the study of chromatographic processes in the overwhelming number of works, the output curves were studied, and only in some of them the distribution of substances in the columns of the ion exchanger — ion-exchange chromatograms — was considered [11, 14, 15].

The theory of the dynamics of sorption allows, knowing the nature of the interaction of components with the ion exchanger, the concentration of substances in the mixture and other conditions affecting the movement of the mixture, to obtain the regularities of the spatial distribution of substances in the ion exchanger.

1. Frontal and elution ion exchange chromatograms

There are several theories that explain the mechanism of ion exchange reactions. It is justified and productive to consider ion exchange as a heterogeneous chemical reaction, for which the law of mass action is valid. Secondary interactions of nonionic nature are possible, for example, due to adsorption or hydrogen bonds with the nonionic part of the matrix, insolubility of substances in the mobile phase, etc. [12].

However, ion exchange is regarded as the determining, basic one.

It is expedient to write the law of mass action characterizing the reaction of ion exchange using analytical concentrations of ions. The use of ion activity instead of concentration is difficult due to the limited literature data on the activity coefficients in mixed solutions [12].

The condition for the electroneutrality of the chromatographic system makes it expedient to express the concentrations in mass equivalents per unit length of the sorbent column:

$$\sum_{i=1}^{j} N_i = N_0 = const , \tag{1}$$

$$\sum_{i=1}^{j} n_i = n_0 = const , \tag{2}$$

where N_0 - exchange capacity of the ion exchanger; N_i - the concentration of the i-*th* ion in the ion exchanger; n_i - concentration of the i-th ion in the solution. The quantity $n_0 = \sum_{i=1}^{\infty} n_i$ is the same at all points of the stationary ion exchange front.

At the selected concentrations, the law of mass action, which under these conditions is also the sorption isotherm, is written in the following form:

$$\frac{N_1^{1/Z_1}}{N_i^{1/Z_i}} = K_{1,i} \frac{n_1^{1/Z_1}}{n_i^{1/Z_i}} , \qquad (3)$$

where $K_{1,i}$ - dimensionless concentration constant of ion exchange.

The differences in the sorption capacity of ions are determined by the differences in the ion exchange constants.

The criterion for the sorption of ions can also be the distribution ratio

$$h_i = \frac{n_i}{N_i} . \qquad (4)$$

The distribution of substances along the ion exchanger column in ion-exchange frontal, elutive and displacement chromatographic processes is considered from the standpoint of the general theory of the dynamics of sorption and the law of equivalence of ion exchange (the law of conservation of charge). To implement elution and displacement modes of sorption dynamics, it is necessary to create a primary frontal chromatogram. The values of the constants of ion-exchange equilibrium and the concentration of ions in solutions determine the course of the formation of chromatograms, determine the velocities of the boundaries of the formed chromatographic zones - the fronts of ion exchange. The constancy of the velocities of the boundaries of the zones determines the monotony of the frontal and elutive dynamics of sorption, the invariability of the structure of the chromatograms. So, in frontal chromatography, an increase in the volume of the initial solution introduced into the ion exchanger column only leads to an increase in the width of the chromatographic zones. In the mode of displacement dynamics of sorption, the zones of the primary frontal chromatogram are rearranged, leading to the complete separation of the components of the initial solution.

There are three main methods of carrying out chromatographic processes.

In frontal chromatography, constant initial concentrations of sorbent substances are maintained at the entrance to the ion exchanger column.

For elution chromatography (washing), a pure solvent is introduced into the column.

With displacement chromatography, a solution containing the substances to be separated is introduced into the sorbent column, and a frontal chromatogram is formed. Then a solution of the propellant component is introduced into the column.

The distribution of components in the zone of the primary frontal chromatogram predetermines the process of displacement dynamics of sorption. With displacement, the number of components in the chromatographic zones decreases, because of this, the number of zones initially increases, but further decreases to a minimum with complete separation of the substances of the initial solution [4, 10, 11, 15].

To identify the dominant regularities of the ion-exchange dynamics of sorption and chromatography, let us consider an ideal model of processes that provides for the instant establishment of sorption equilibrium in the absence of any disturbing factors. These simplifications are close to real conditions in many cases; in others, taking into account physical factors affecting the course of sorption processes allows one to introduce the necessary corrections [4, 10].
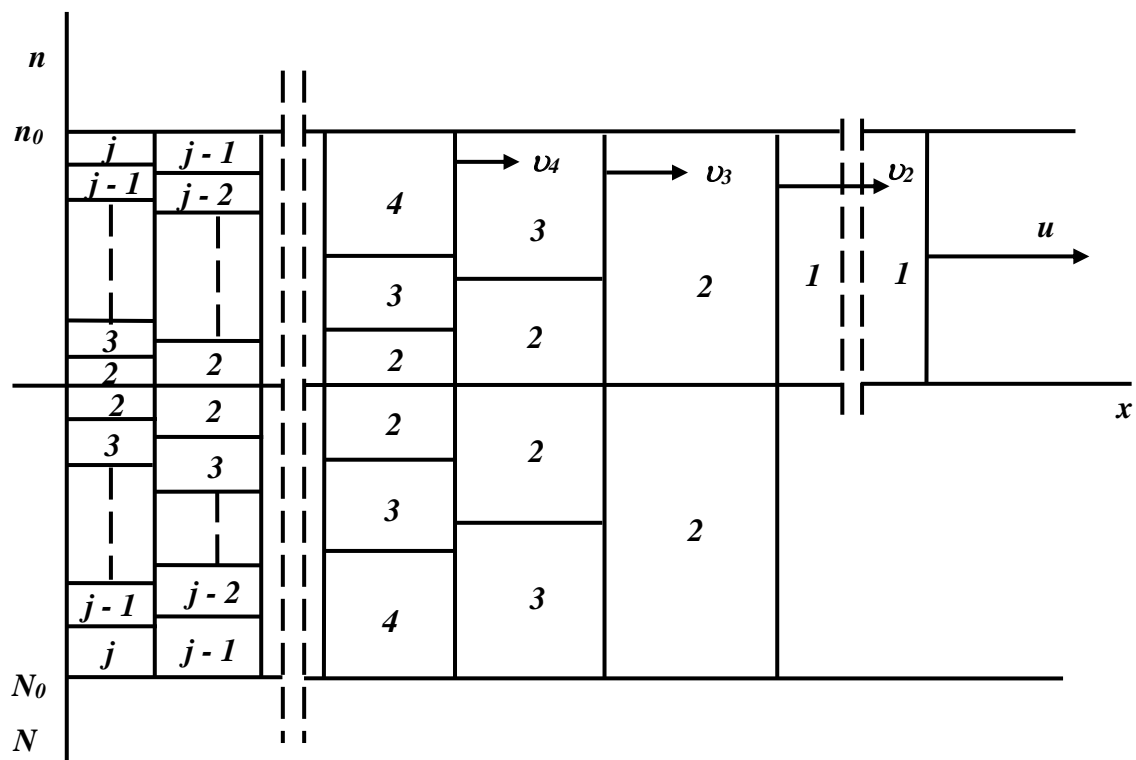

Fig. 1. Column frontal chromatograms with ideal sorption dynamics

Frontal dynamics of sorption and chromatography. Let the ion exchanger contain only ion 1, the pores of the column are filled with water. We introduce a solution of a mixture of j ions of constant concentration at a constant rate u.

Due to the differences in the ion exchange constants during multiple repetitions of sorption and desorption reactions, weaker sorbed ions are pushed forward, a certain distribution of ions over the ion exchanger column occurs, chromatographic zones are formed - a frontal chromatogram is formed [4, 10]. Figure 1 schematically shows the distribution of ions in solution and ion exchanger for an ideal sorption model.

The speed of the boundaries of the zones is found, in accordance with the general theory of the dynamics of sorption [1, 4], according to the equations of the balance of matter and the laws of ion-exchange sorption (1-3).

The front of the solution of the displacing ion 1 moves with the velocity of the introduced mixture u.

The velocity of the last front of the "clean" zone 2 is determined by the total concentration of ions n0 in the incoming solution, since the concentration of ion 2 in the solution and ion exchanger $n_2 = n_0$, $N_2 = N_0$, then

$$\upsilon_2 = u\frac{n_2}{n_2 + N_2} = u\frac{n_0}{n_0 + N_0}.$$ (5)

If we use distribution relation (4), then for zone 2 $h_2 = \dfrac{n_2}{N_2} = \dfrac{n_0}{N_0}$ and

$$\upsilon_2 = u\frac{h_0}{1 + h_0}.$$ (6)

The velocity of the leading edge of the i-th zone is determined by the distribution ratio of the ion having the highest sorption capacity among all ions in this zone, i.e. in the i-th zone:

$$\upsilon_i = u\frac{h_{i,i}}{1 + h_{i,i}},$$ (7)

where $h_{i,i} = \dfrac{n_{i,i}}{N_{i,i}}$, hereinafter, the first index is the substance number, the second is the zone number.

The speed of movement of the boundaries of the zones (hence, the width of the mixed zones), the concentration of ions in the mixed zones (the height of the "steps" in Fig. 1) depend on the constants of ion exchange and the concentration of ions in the initial solution.

The concentration of the i-th ion in the last, j-th zone is equal to the concentration of this ion in the solution introduced into the ion exchanger column, $n_{i,j} = n_i^0$.

The structure of the frontal chromatogram depends on the affinity of ions for the sorbent, the ratio of ion concentrations in the initial solution.

Figure 2 compares two frontal chromatographic processes. In Fig. 2, a) shows a frontal radiochromatogram of a solution of Rb^*Cl and $CaCl_2$, in Fig. 2, b) - radiochromatogram of $RbCl$ and $MgCl_2$ [10, 15].

The height of the "steps" in radiochromatograms is proportional to the sum of the concentrations of the labeled Rb^* ion in the solution and the ion exchanger. Since in both variants the concentration of the Rb^* ion in the solution is the same and is equal to the concentration in the initial solution in the mixed zone, the Ca^{2+} ion sorbs more strongly than the Mg^{2+} ion, $N_{Ca} > N_{Mg}$.
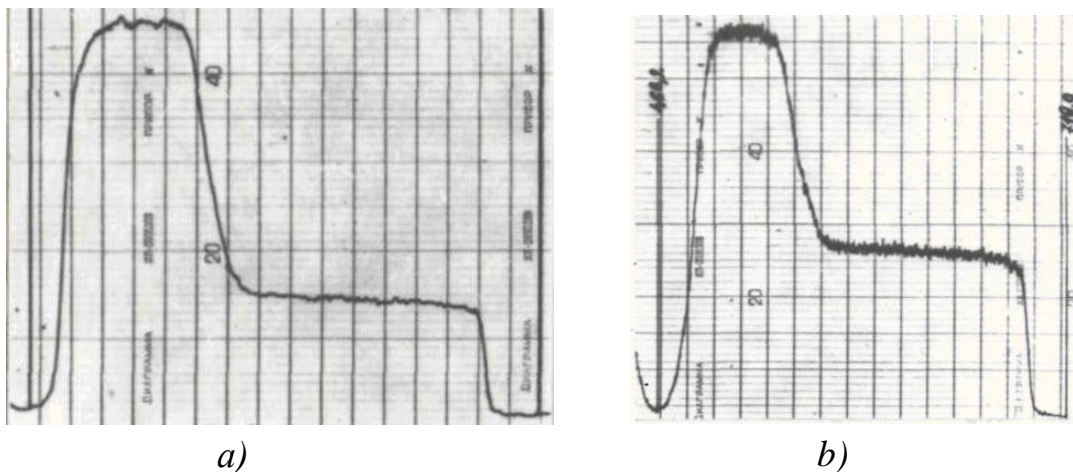

a)   b)

Fig. 2. Frontal radiochromatograms

a) **solutions of** *Rb*Cl* **and CaCl₂;** *b)* **solutions of** *Rb*Cl* **and MgCl₂. Ion exchanger Dowex50Wx12 in H⁺ -form.** *a)* $C_{Rb}^0 = 0{,}05H$; $C_{Ca}^0 = 0{,}05H$; *b)* $C_{Rb}^0 = 0{,}05H$; $C_{Mg}^0 = 0{,}05H$.

In Fig. 3 shows radiochromatograms of $Rb*Cl$ and $MgCl_2$ solutions at different ratios of ion concentrations ($C_0=0,1H$). The length of the mixed zone and the pure $Rb*$ zone depends on the ratio of the ion concentrations in the solution.
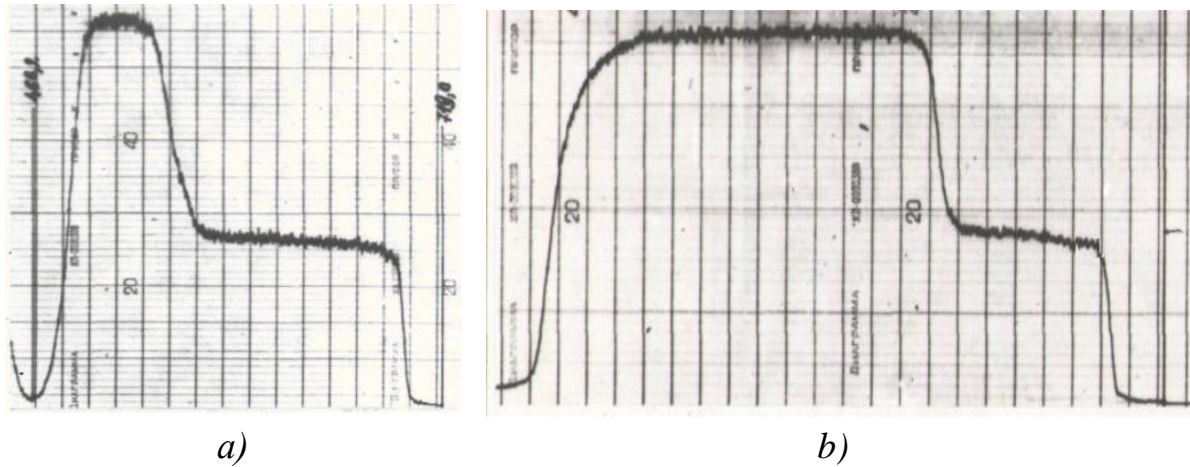

a)   b)

Fig. 3. Frontal radiochromatograms of $Rb*Cl$ and $MgCl_2$ solutions of various concentrations in a column of Dowex50Wx12 ion exchanger in H^+ -form.

a) $C_{Rb}^0 = 0,05H$; $C_{Mg}^0 = 0,05H$; **б)** $C_{Rb}^0 = 0,08H$; $C_{Mg}^0 = 0,02H$.

A copy of the frontal radiochromatography of 3 incoming ions K^{++} - Mg^{2+} -S_2^{2+} is shown in Fig. 4 [11].

The distribution of the Rb ion in the ion exchanger column also in this case corresponds to the theory of the dynamics of sorption and chromatography.
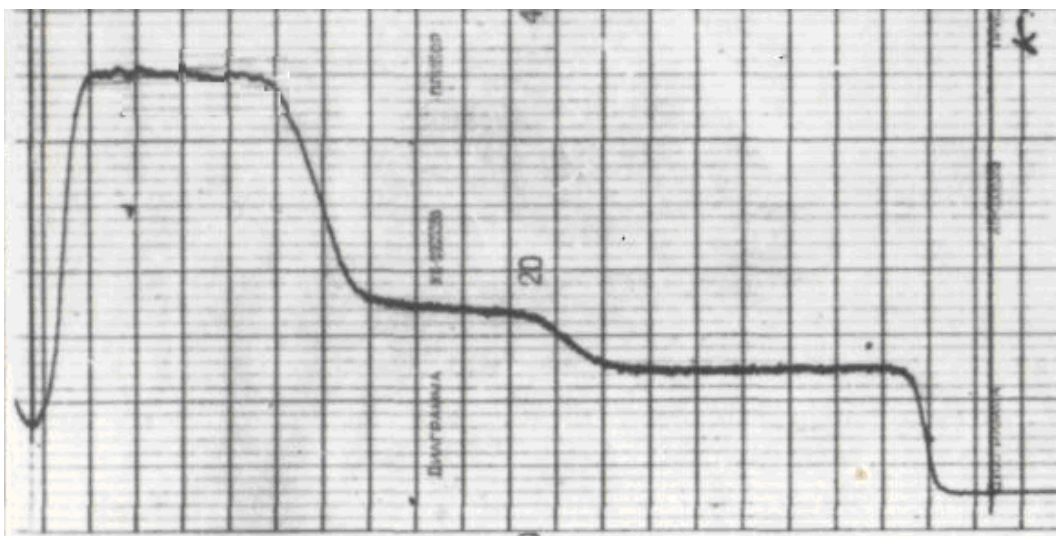

Fig. 4. Frontal chromatogram of a solution of $K*Cl$, $MgCl_2$ and S_2Cl_2 in a column of Dowex50Wx12 ion exchanger; $n_K^0 = n_{Mg}^0 = n_{S_2}^0 = 0,033H$.

In Figures 2-4, the radioactive label is carried by the ion with the lowest affinity for the ion exchanger. In this case, you can clearly imagine the distribution of substances in the chromatographic zones in the ion exchanger column.

Measurements of the speed of movement of the boundaries of the zones confirm the validity of formulas (5-7).

The ion velocities in the mixed zone were also determined by the "tagged wave" method [10].

Since the velocities of the boundaries of the zones of the frontal chromatogram are unchanged, with an increase in the volume of the initial solution introduced into the ion exchanger column, the width of the chromatographic zones only increases with the structure of the chromatogram unchanged.

Elution dynamics of ion-exchange sorption. After the introduction of microquantities of the separated mixture of ions into the column of the ion exchanger, the column is washed with a solution of the ion-macrocomponent.

If ion 1 is a macrocomponent, then its concentration can be considered equal to the total concentration of ions:

$$n_1 = \sum_{i=1}^{j} n_i = n_0,\tag{8}$$

$$N_1 = \sum_{i=1}^{j} N_i = N_0.\tag{9}$$

Substituting (8) and (9) into (3), we obtain the equation of the linear sorption isotherm

$$Ni = \left(1/K_{1,i}{}^{Z_i} \cdot h_0{}^{Z_i/Z_1}\right) n_i,\tag{10}$$

where $h_0 = \dfrac{n_0}{N_0} = \dfrac{n_1}{N_1}$.

This means that the ions-microcomponents during the elutive dynamics of sorption propagate along the ion exchanger column independently of each other.

Narrow zones of each substance are blurred [14], but the speed of movement of the maximum of the sorption wave is unchanged [4, 10], distributed by the distribution ratio $h_i = \dfrac{n_i}{N_i}$:

$$v_i = u\frac{h_i}{1+h_i}. \tag{11}$$

Elution chromatography has become especially popular for the analysis of complex mixtures of substances due to the advances in high performance liquid chromatography.
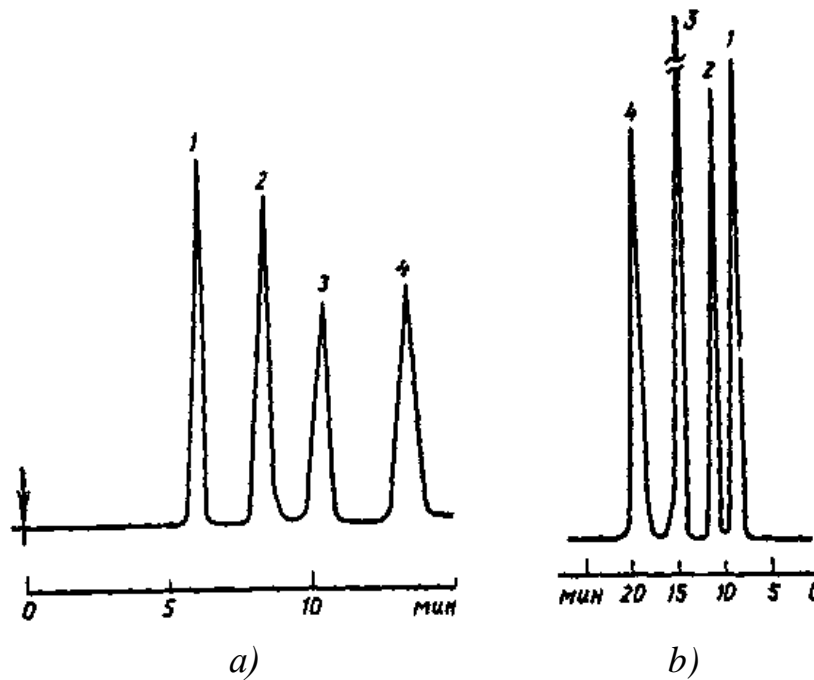

a)   *b)*

Fig. 5. Elution ion-exchange chromatograms obtained using HPLC [3].

5, *a)* **- chromatogram of catecholamines (1 - norepinephrine, 2 - adrenaline, 3 - dopamine, 4 - methyldopamine); 5,** *b)* **- chromatogamma of inorganic anions (1-phosphate, 2 - chloride, 3 - nitrate, 4 - sulfate)**

Modern technology allows for the separation and determination of substances in very small quantities. In the experiments shown in Fig. 5, the sample volume is only 20 µL [3].

In Fig. 5 also shows the time required to separate the mixture.

2. Displacement dynamics of sorption

To establish the main regularities of the displacement mode of the dynamics of sorption, let us consider the simplest case - the ideal displacement dynamics of sorption of one substance.

With ideal dynamics of sorption, sorption equilibrium is instantly established and there are no factors causing blurring of sorption fronts [2, 4, 10].

Let an ideal frontal chromatogram be formed in the sorbent column - the primary zone of one substance (Fig. 6, *a*).

The initial and boundary conditions are as follows:

$$t=0,\ 0 \leq x \leq x_0,\ n = n_0,\ N=N_0;$$
$$x > x_0,\ n=0,\ N=0, \tag{12}$$

where t - is the time, x - is the distance coordinate (along the length of the sorbent column), n_0 and N_0 - are the linear concentrations of the substance in the mobile phase and sorbent, respectively.

Let us introduce a displacer substance into the sorbent column. For instant sorption of the propellant, the initial and boundary conditions are as follows:

$$t > 0,\ x = 0,\ n = n_d^0,\ N = N_d^0;$$
$$x = \infty,\ n = 0,\ N = 0, \tag{13}$$

where n and N are linear concentrations of the propellant.

The velocities of the edge boundaries of the zones can be found as the velocities of the concentration points based on the balance of matter [4, 10]:

$$\upsilon = u\frac{n}{n+N}, \tag{14}$$

where u is the average linear flow rate of the mobile phase.

The average velocity u can be found experimentally using the obvious formula

$$u = \frac{V}{Qt}, \tag{15}$$

where V - is the volume of the mobile phase introduced into the porous medium during time t; is the cross-sectional area of the transfer of the sorbed substance in this medium.

If we introduce the distribution relation $h = \dfrac{n}{N}$, then

$$\upsilon = u\frac{h}{1+h}. \tag{16}$$

To implement the displacement process, the displacer speed υ_d must be above speed υ displaced substance $\upsilon_d > \upsilon$.

If $\upsilon_d \leq \upsilon$ (or $h_d \leq h$), then the elutive dynamics of sorption is observed [7].

With displacement sorption, the trailing edge of the primary zone moves at the speed of the leading edge of the displacement zone υ_d, and the speed of the leading edge of the primary zone remains equal υ.

This means that a new zone of the displaced primary substance with a concentration n' and the zone of the primary component is compressed (Fig. 6, b). The displacement chromatogram formation process is shown for the case $n' > n$.

As the width of the newly formed zone increases, this means that the speed of the leading edge of this zone $\upsilon' > \upsilon_d$, so that $\upsilon' > \upsilon_d > \upsilon$. Thus, the forming zone with concentration n' expands, and the primary with concentration n_0 shrinks, and at some point in time the primary zone will disappear. From this moment on, a stationary stage of the displacement process begins, the leading edge of the newly formed zone, which means that the displacer and the displaced substance move at the speed of the displacer υ_d (Fig. 6, c).
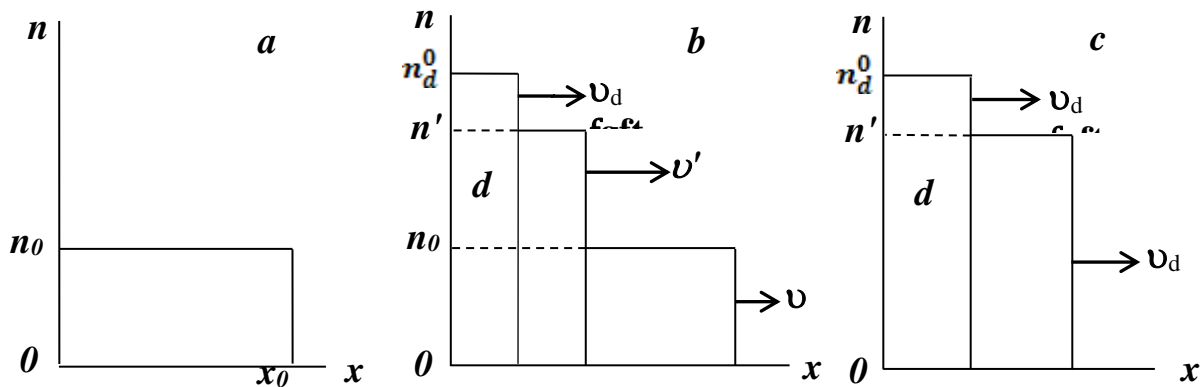

Fig. 6. Formation of a displacement chromatogram with a convex isotherm of sorption of the displaced substance

The width of the primary zone decreases with the speed $\upsilon' - \upsilon$, therefore this zone disappears in time

$$t = \frac{x_0}{\upsilon' - \upsilon},\qquad(17)$$

where $x_0 = vt_0$ is the width of the primary zone, t_0 is the formation time of this zone.

Thus, the formation time of the displacement chromatogram

$$t=\frac{x_0}{\upsilon'-\upsilon}=t_0\,(\frac{\upsilon'}{\upsilon}-1)^{-1}. \tag{18}$$

The process of displacement chromatogram formation is determined by the type of isotherms of the displaced substance and the displacer. Figure 7 shows possible combinations of isotherms of the displaced substance and displacer d, at which the condition of displacement dynamics of sorption $\upsilon_d > \upsilon$ (or $h_d > h$) can be satisfied.
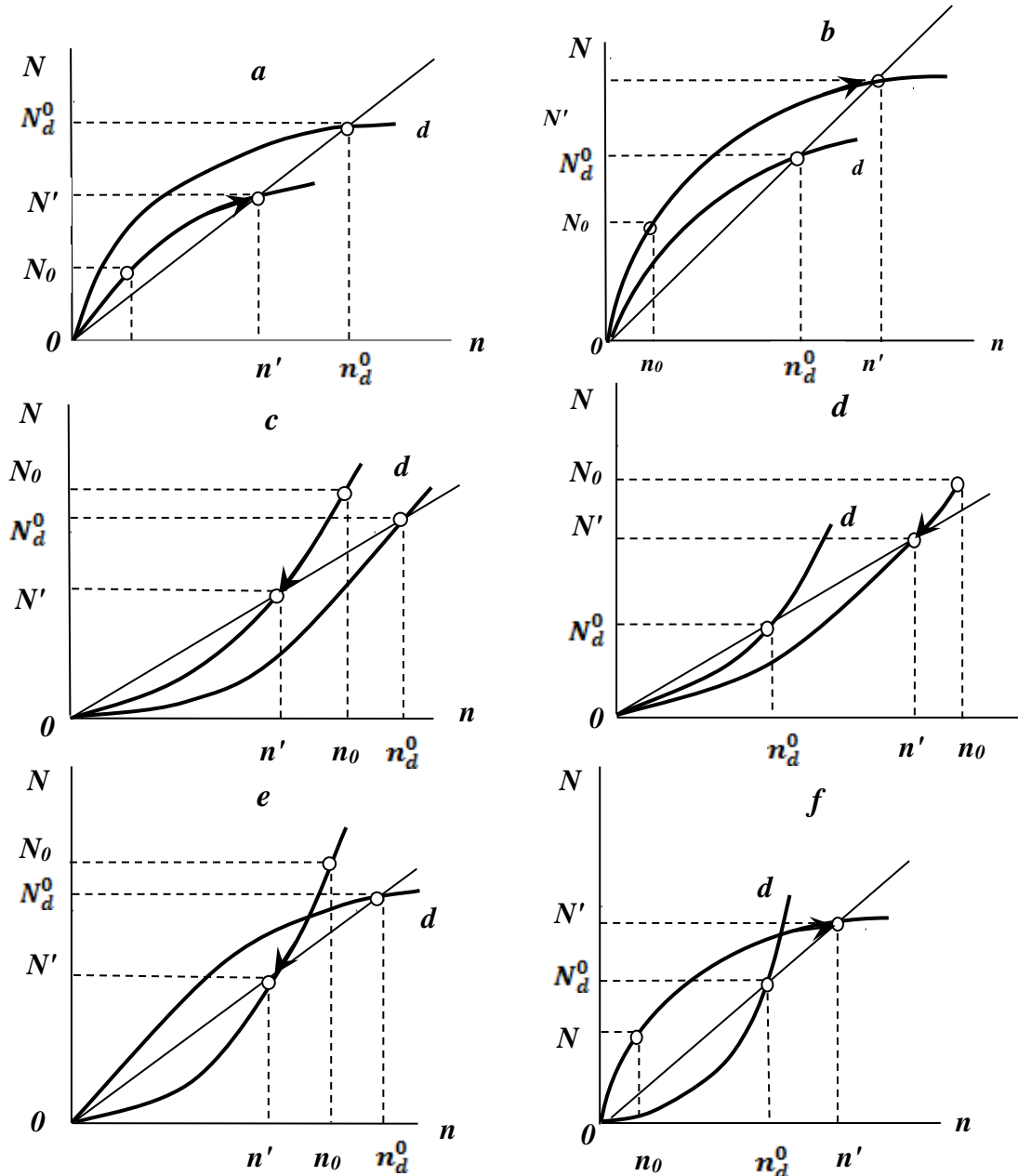

Fig. 7. Determination of the concentration n′ in the zone of the stationary displacement chromatogram with various combinations of sorption isotherms of the displaced substance and the displacer d

If the isotherm of the displaced substance is known, then the concentration of this primary component in the solution and such a displacer and such a concentration can be chosen so that the condition $h_d > h$ is satisfied.

Let both isotherms be convex, the concentration of the primary substance n_0 and the corresponding linear concentration N_0 of this component in the sorbent are given (Fig. 7, *a*).

The isotherm of the displacer d is located above the isotherm of the primary substance, which indicates a better sorption of the displacer.

To implement the displacement mode, it is necessary to select such a concentration of the displacer n_d^0, so that $h_d = \dfrac{n_d^0}{N_d^0}$ there was more $h = \dfrac{n_0}{N_0}$. To do this, draw a straight line $N = \dfrac{I}{h_d} n$, below the point (n_0, N_0). In this case, the displacement mode is implemented.

If point (n_0, N_0) is below the specified straight line, then elutive sorption occurs [4, 7].

At the end of the displacement chromatogram formation $\upsilon' = \upsilon_d$ and $\dfrac{n'}{N'} = \dfrac{n_d^0}{N_d^0}$. This means that the point (n', N') lies on this straight line, so that $n' > n_0$, concentration n' more component concentration n_0 in the primary zone. The direction of change in concentration is shown by an arrow on the isotherm of the displaced substance.

If the displacer is sorbed weaker than the displaced substance, then the isotherm of the displacer is located below the isotherm of the primary component (Fig. 7, *b*). And in this case, you can find such a concentration of the displacer n_d^0, to point (n_0, N_0) was located above the straight line $N = \dfrac{1}{n_d} n$, passing through the point (n_d^0, N_d^0). Then $h_d > h$, displacement mode is carried out.

Concentration n' in the stationary zone is located at the point of intersection of the straight line $N = \dfrac{1}{n_d} n$ with the isotherm of the displaced substance.

With convex isotherms of the displacer and the displaced substance, regardless of whether the displacer is sorbed weaker or stronger than the primary component, the concentration n' substances in the stationary zone are more concentrated n_0 in the primary zone (Fig. 7 *a, b*). The formation of a displacement chromatogram with convex isotherms is shown in Fig. 6.

In the case of concave isotherms (Fig. 7, *c, d*), the displacement mode is also possible, but the concentration n' displacing substance is less than the primary n_0.

In this case, according to the law of conservation of mass, the width of the stationary zone is greater than the width of the initial one.
Displacement chromatogram formation time

$$t = t_0 \, (\frac{\upsilon_d}{\upsilon} - 1)^{-1}. \tag{19}$$

Similarly, the displacement process can be analyzed with combinations of convex and concave isotherms of the displacer and the displaced substance (Fig. 7 *e, f*).

In the case of a convex isotherm of the displaced substance, regardless of whether it is convex or concave sorption isotherm of the displacer, the concentration of this substance in the stationary zone is n' more concentration n_0 in the primary zone (Fig. 6).

On the contrary, with a concave isotherm of the displaced substance, the concentration n' its concentration in the stationary zone is less than the concentration n_0 in the primary zone, regardless of the shape of the isotherm of the displacer (Fig. 8).
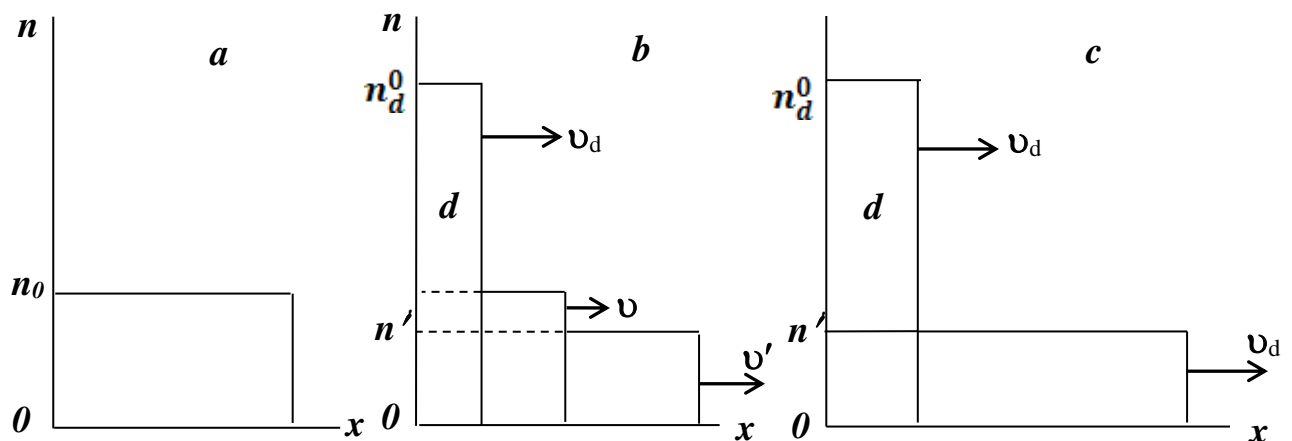

Fig. 8. Formation of a displacement chromatogram at a concave sorption isotherm of the displaced substance

The equivalence of ion exchange due to the electroneutrality of the chromatographic system simplifies the study of the formation of an equilibrium ion-exchange displacement chromatogram of one substance.

Let a rectangular zone of ion 2 be introduced in the column of an ion exchanger saturated with ions 1. The exchange capacity of the ion exchanger is N_0, the concentration of ion 2 in the mobile zone is n_0 (Fig. 9, *a*).
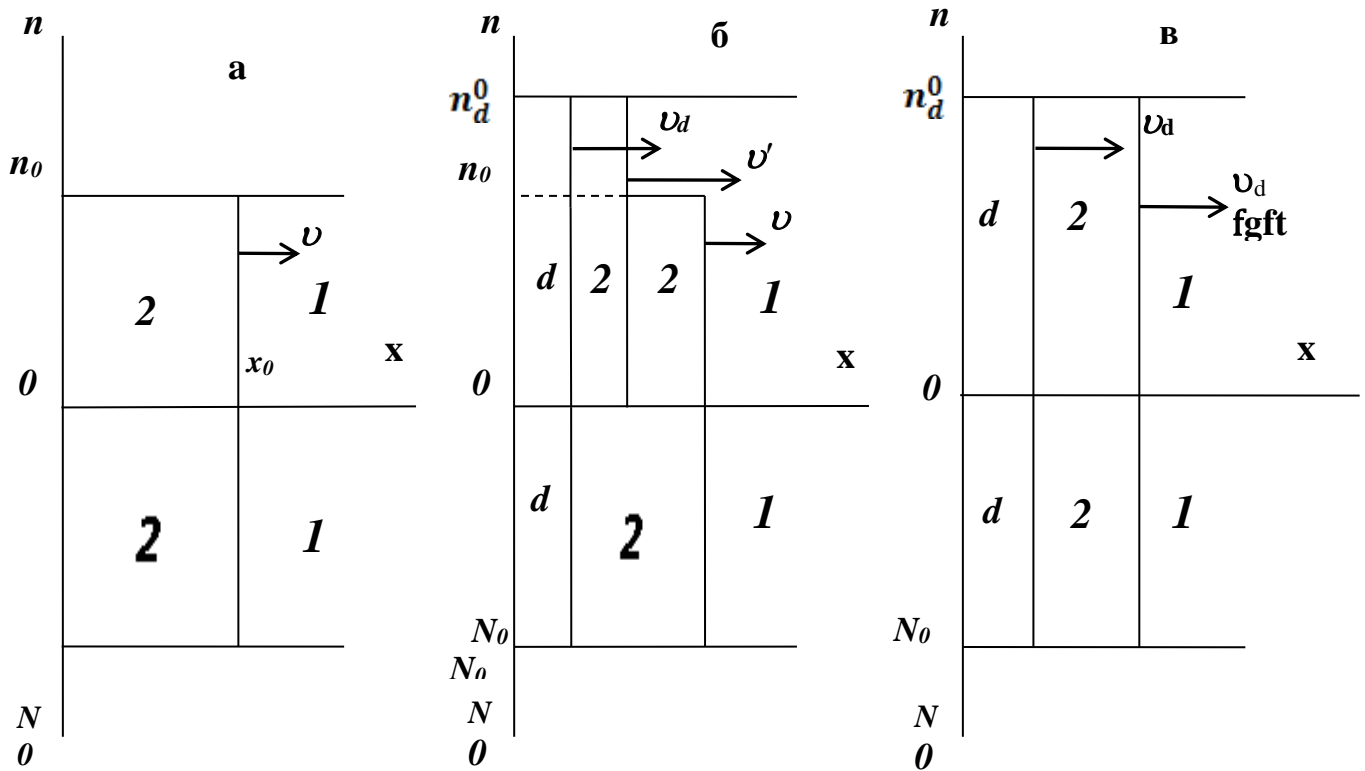

Fig. 9. Formation of displacement ion-exchange chromatogram

We now introduce into the column a propellant ion d, the concentration of which is n_d^0.

Displacement chromatogram formation at $n_d^0 > n_0$ (or $h_d > h_0$) shown in fig. 9.

Leading edge speed υ' the new zone is determined by the balance of ion 2:

$$(\upsilon' - \upsilon_d)\,(n_d + N_0) = (\upsilon' - \upsilon)\,(n_0 + N_0). \qquad (20)$$

On the other hand

$$\upsilon_d = u\,\frac{n_d^0}{n_d^0 + N_0}\;;\; \upsilon = u\,\frac{n_0}{n_0 + N_0}. \qquad (21)$$

From equalities (20) and (21) we have:

$$\upsilon' = u.$$

Then the width of the initial zone decreases with a rate $\upsilon' - \upsilon = u - \upsilon$, and the time of formation of a new, stationary zone

$$t = \frac{x_0}{u-\upsilon} = \frac{\upsilon t_0}{u-\upsilon} = t_0 \left(\frac{u}{\upsilon} - 1\right)^{-1} = t_0 \left(\frac{u}{u\,n_0 / (n_0 + N_0)} - 1\right)^{-1} = t_0 \frac{n_0}{N_0} = t_0 \, h_0 \, . \qquad (22)$$

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

Questions of the general theory of displacement chromatogram formation were summarized in [4, 6-9].

The ideal model of sorption processes (instantaneous establishment of sorption equilibrium and the absence of any other disturbing effects) makes it possible to reveal the basic laws of the dynamics of sorption and chromatography.

The general patterns of displacement chromatogram formation formulated in [6, 8, 9] are concretized by the example of the formation of ion-exchange chromatograms.

The conditions under which the mode of the displacement dynamics of sorption will be realized have been clarified. The displacement mode can be realized with both higher and lower sorption capacity of the displacer in comparison with the sorption capacity of the primary component [6].

In [8, 9], the regularities of the reformation of frontal chromatograms under the displacement dynamics of sorption were established.

The obtained results of theoretical research were verified experimentally. These experiments made it possible to elucidate the possible application of the ideal model of sorption dynamics and the necessity of introducing appropriate corrections to describe real chromatographic processes [11].

Elutive ion exchange chromatography allows the separation of substances in very small quantities [3], but only with the help of displacement ion exchange chromatography is it possible to complete preparative separation of ions - components.

Various applications of ion exchange processes are due to the heterogeneity of the system, i.e. the possibility of simple phase separation (for example, by simple filtration of the solution through a layer of ion exchanger) and the ability of sorbents to exchange ions, which determines the separation of ions that differ in sign, charge, or degree of hydration.

Most often, in calculating ion-exchange processes, the law of mass action is written in analytical concentrations, since there are practically no data on the activity coefficients of ions in mixed solutions:

$$\frac{S_1^{1/Z_1}}{S_i^{1/Z_i}} = k_{1,i} \, \frac{C_1^{1/Z_1}}{C_i^{1/Z_i}} \; , \qquad (23)$$

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

When studying the dynamics of sorption in sorbent columns, it is advisable to use linear concentrations of N_1 and N_i - the concentration of ions in the sorbent in meq/cm of the length of the ion exchanger column, n_1 and n_i - the concentration of these ions in solution in the same units.

At these concentrations, equation (23) takes the following form:

$$\frac{N_1^{1/Z_1}}{N_i^{1/Z_i}} = k_{1,i} \, \frac{n_1^{1/Z_1}}{n_i^{1/Z_i}} \; , \qquad (24)$$

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

The sorbability of ions is determined by the constants of ion exchange.

The study of the processes of ion-exchange dynamics of sorption greatly simplifies the law of equivalence of ion exchange (the law of conservation of charge)

$$\sum_{i=1}^{j} n_1 = n_0 = const \; , \quad \sum_{i=1}^{j} N_i = N_0 = const \; , \qquad (25)$$

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

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

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

The exchange constant is $k_{1,2} < 1$, ion 2 is sorbed better than ion 1. The displacement dynamics of sorption is possible if the concentration of the displacing ion d is equal to or different from the concentration of ion 2 ($n_d^0 = n_0, n_d^0 > n_0, n_d^0 < n_0$).

The exchange capacity of the ion exchanger is N_0, the concentration of ion 2 in the solution is n_0 (Fig. 10, a).
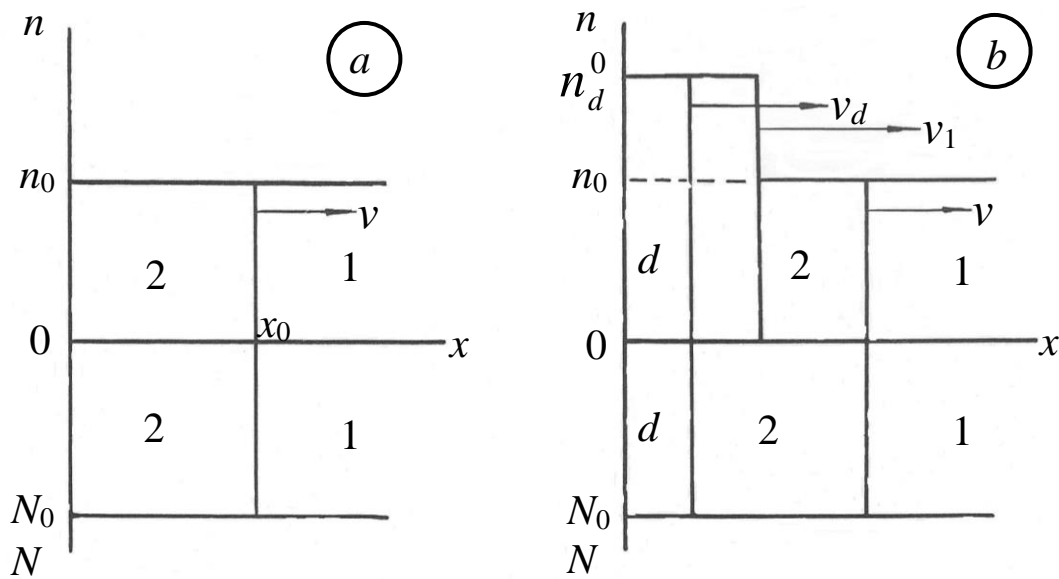

Fig. 10. Formation of displacement ion-exchange chromatogram of one substance, $h_d > h_0$

Introduce the displacer ion d into the column. The displacement process is possible if the speed of movement of the propellant ion v_d is greater than the speed v of ion 2.

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

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

(26)

similarly, the velocity of the propellant ion d

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

(27)

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

Displacement chromatogram formation at $h_d > h_0$ ($n_d^0 > n_0$) shown in Fig. 10, b.

The velocity of the leading edge of the new zone v_1 is determined from the balance of ion 2:

$$\left(v_1 - v_d\right)\left(\frac{v_d}{n_d} + N_0\right) = \left(v_1 - v\right)\left(n_0 + N_0\right),\qquad (28)$$

from equality (26), (27), (28) we have:

$$v_1 = u.\qquad (29)$$

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

$$t = \frac{x_0}{u - v} = \frac{v \cdot t_0}{u - v} = t_0 \left(\frac{u}{v} - 1\right)^{-1} = t\left(\frac{u}{un / (n_0 + N_0)} - 1\right)^{-1} = t_0 \frac{n_0}{N_0} = t_0 \cdot h_0,\qquad (30)$$

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

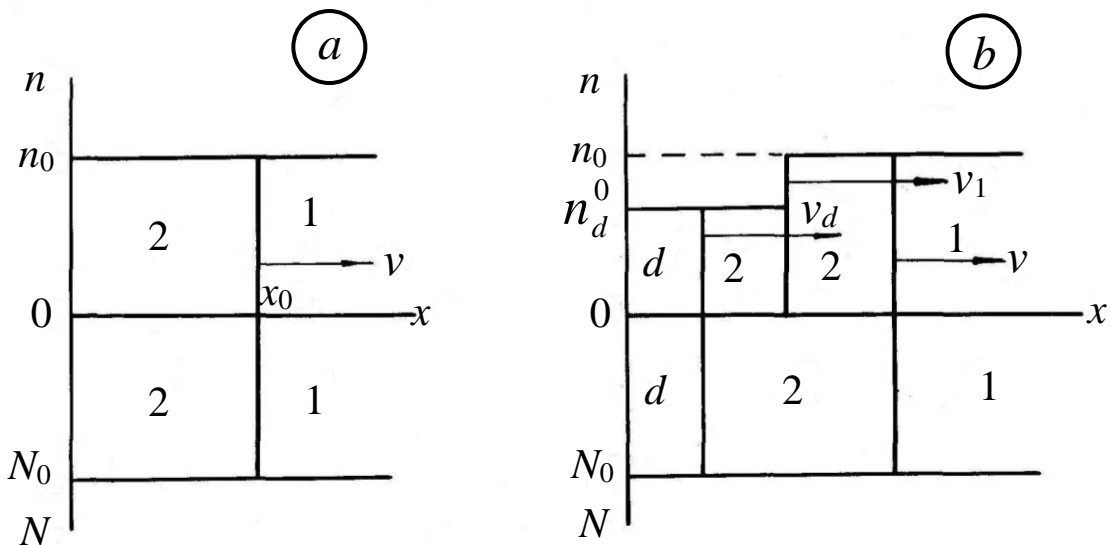If $h_d < h_0$, then the displacement occurs as shown in Figure 11.

Fig. 11. Formation of displacement ion-exchange chromatogram of one substance $h_d < h_0$

And in this case, the leading edge of the new zone moves with the flow rate, and the formation time of the displacement chromatogram is determined by formula (30).

Let us consider the equilibrium displacement dynamics of sorption of two ions in the absence of disturbance factors of the ion exchange fronts [8]. The frontal chromatogram of two ions has the form shown schematically in Fig. 12, *a.*

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

To simplify the description of the processes in the column, we introduce the displacer ion *d*, keeping the same ion (distribution) ratio as in frontal chromatography:

$$h = \frac{n_0}{N_0} = h_d = \frac{n_d^0}{N_d^0} = \frac{\sum\limits_{i=1}^{j} n_i^0}{\sum\limits_{i=1}^{j} N_i^0} . \tag{31}$$

From the moment the propellant ion is introduced, a clean zone of ion 3 immediately appears in the column behind the mixed zone of ions 2 and 3.

The velocities of the boundaries of the zones are determined by the corresponding distribution ratios of the ions:

$$v = u \frac{h}{1+h}, \quad v_2 = u \frac{h_{2,2}}{1+h_{2,2}}, \quad v_3 = u \frac{h_{3,2}}{1+h_{3,2}}, \quad v_d = v = u \frac{h_d}{1+h_d} = u \frac{h}{1+h}, \tag{32}$$

$$\text{where} \quad h_{2,2} = \frac{n_2^0}{N_2^0}, \quad h_{3,2} = \frac{n_3^0}{N_3^0}. \tag{33}$$

It is easy 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 complete separation of ions.

At some point in time *t*, the mixed zone disappears, and the ion distribution shown in Fig. 12, *c* is created. From this moment, a stationary stage of the displacement process begins - all fronts begin to move at a constant speed $v_{d=v}$.

Time of displacement chromatogram formation for ions 2 and 3:

$$t = \frac{x_3^0}{v_2 - v_3} = t_0 \left(\frac{v_2}{v_3} - 1 \right)^{-1} \tag{34}$$

or, taking into account equalities (32) and (33)

$$t = t_0 \left[\frac{h_2^0 / \left(1 + h_2^0\right)}{h_3^0 / \left(1 + h_3^0\right)} \right]^{-1} . \tag{35}$$
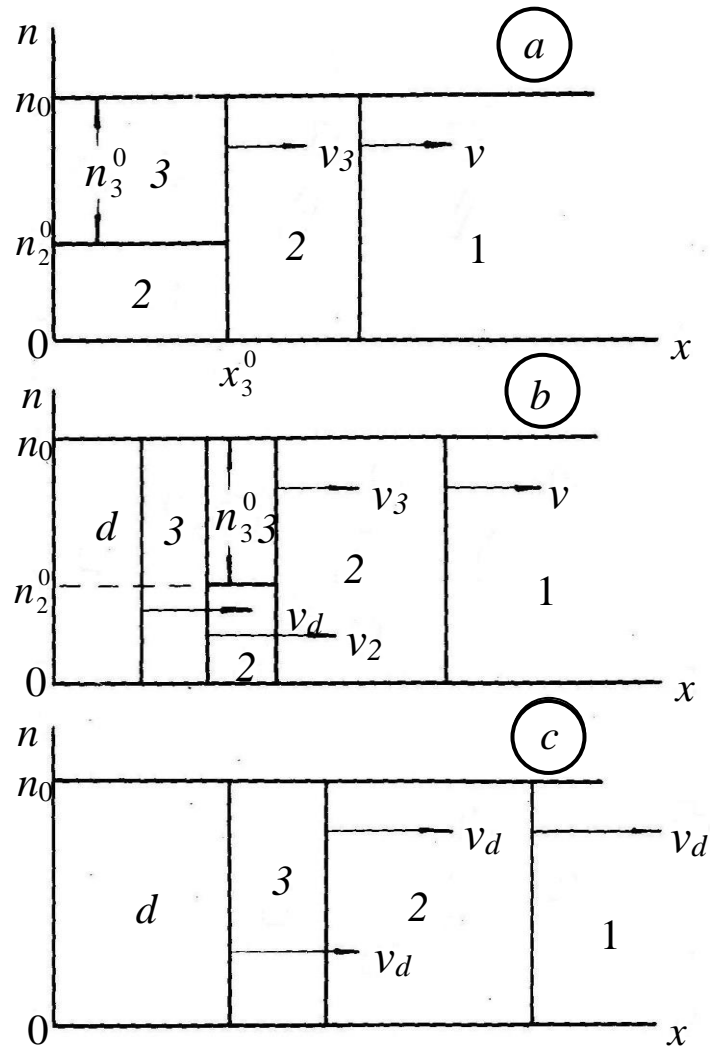

Fig. 12. Formation of a displacement chromatogram of two incoming ions

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

$$T = t_0 + t = t_0 \left(1 - \frac{v_3}{v_2} \right)^{-1} \tag{36}$$

Since the leading edge velocity v is constant during both the frontal and displacement chromatogram formation, the length of the ion exchanger column required to separate ions 2 and 3 (without removing them from the column)

$$L = v \cdot T = L_0 \left(1 - \frac{v_3}{v_2} \right)^{-1}, \qquad (37)$$

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

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

$$L_1 = x_3^0 + v_3 \cdot t = v_3 \cdot t_0 + v_3 \cdot t = v_3 \cdot t_0 \left(1 - \frac{v_3}{v_2} \right)^{-1} = x_3^0 \left(1 - \frac{v_3}{v_2} \right)^{-1} \qquad (38)$$

As an example, Fig. 13 shows the formation of a displacement chromatogram of Rb^+ and Ca^{2+} ions. The concentration of the propellant ion was taken equal to the concentration of the initial mixture of ions.

The blurring of the Rb^+ and Ca^{2+} exchange fronts is explained by the fact that the Rb^+ - Ca^{2+} exchange is predetermined by the sorption of the strongly sorbed Ca^{2+} ion and the Ca^{2+} - Ca^{2+} exchange at the same boundary. Because of the exchange equivalence, the shape of the Ca^{2+} - Ca^{2+} front is "imposed" on the exchange front of the Rb^+ - Ca^{2+} ions.

The formation of a displacement ion-exchange chromatogram of a multicomponent system can be considered on the basis of the general theory of the formation of displacement chromatograms [9].

The equivalence of ion exchange (n_0 = const, N_0 = const) greatly simplifies the calculation of the displacement multicomponent dynamics of sorption and chromatography [11].

In particular, the heights of the chromatographic zones of the frontal and displacement chromatograms are unchanged.

When studying the formation processes of displacement ion-exchange chromatograms, the ideal model of sorption was taken as a basis. This consideration allows one to estimate the most important parameters of the system for ion separation.

Under real conditions, different kinds of front blurring factors act in chromatographic columns. The nature of the deformation of the fronts is mainly determined by the type of sorption isotherm [4, 6].
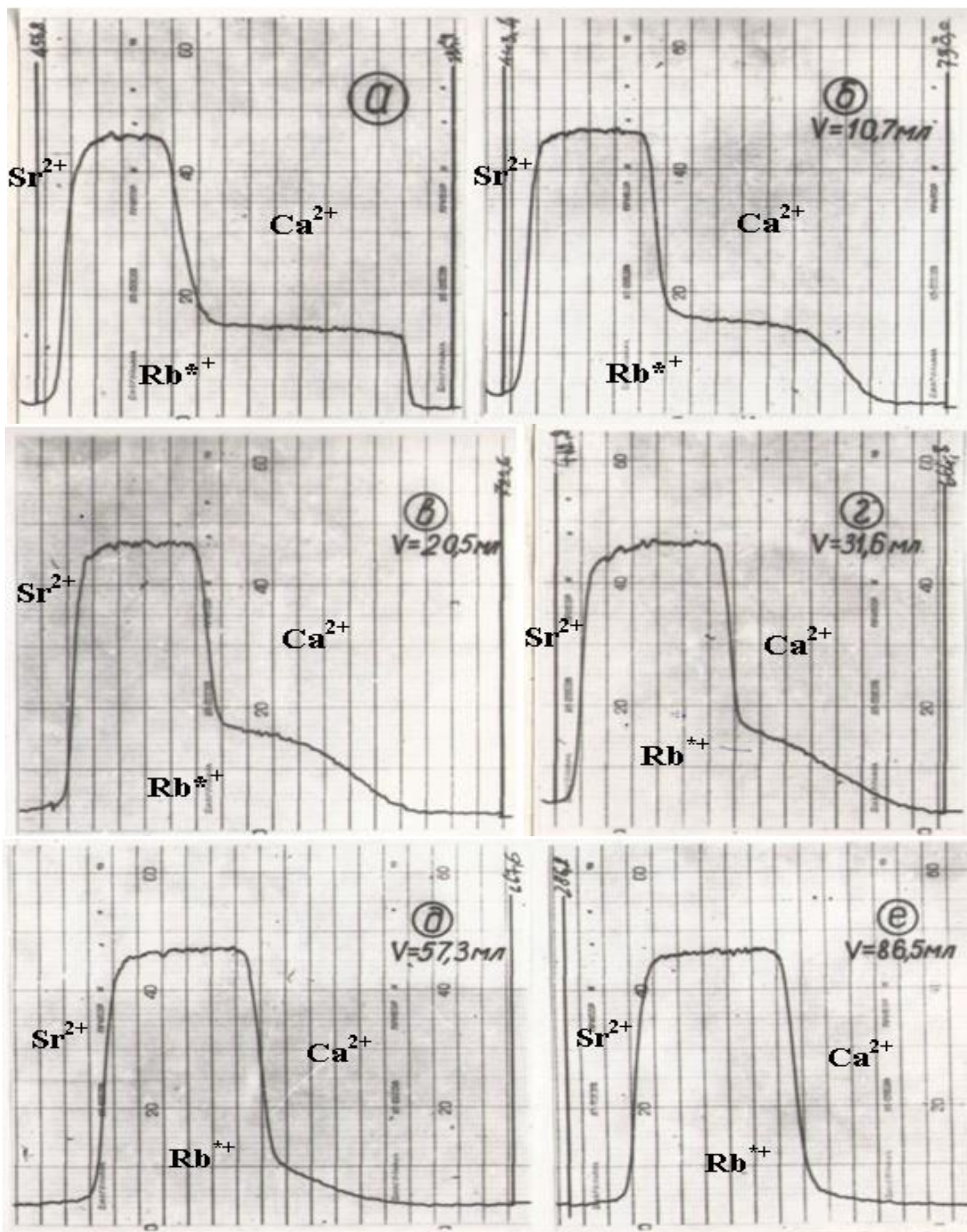

Fig. 13. Formation of the displacement chromatogram of Rb^{*+} and Ca^{2+} ions. The radioactive label is an isotope ^{86}Rb. The solutions used were Rb*Cl and CaCl$_2$ (C$_{Rb}$ = C$_{Ca}$ = 0.05n). Displacer - 0.1n SrCl$_2$.

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

Comparison of the theoretical description with experimental data makes it possible to find out what adjustments should be made to the theory of ideal displacement dynamics of sorption when considering real chromatographic processes.

The length of the ion exchanger layer required to separate ions from the mixture was determined by formulas (37) and (38).

To obtain a frontal chromatogram, an initial mixture of ions was introduced into the column, one of which (in most cases the least sorbed) was labeled with a radioactive isotope with hard radiation penetrating through the wall of the glass tube.

Then, at different amounts of the introduced propellant ion, a number of radiochromatograms are sequentially recorded, which clearly reflect the evolution of the process of displacement dynamics of sorption.

Each radiochromatogram indicates the volume of the displacer added to the column.

Note that, in accordance with the general theory of sorption dynamics, the rate of the half-concentration point of the mixed zone front is constant.

In addition, the width of the exchange front for Rb^{*+}- Ca^{2+} ions at the rear boundary of the mixed zone, as shown by measurements, increases in direct proportion to the displacement time. Note that all fronts are stationary in frontal chromatograms.

It was found that after the disappearance of the mixed zone plateau (Fig. 13), the rate of movement is weaker than the sorbed ion from the "tails" of the mixed zone, so that in practical separations it makes no sense to achieve complete stationarity of the exchange fronts of the separated ions.

The correctness of the scheme for the formation of a multicomponent system considered in the previous messages [7-9, 11] was also checked when separating three ions (Fig. 14).
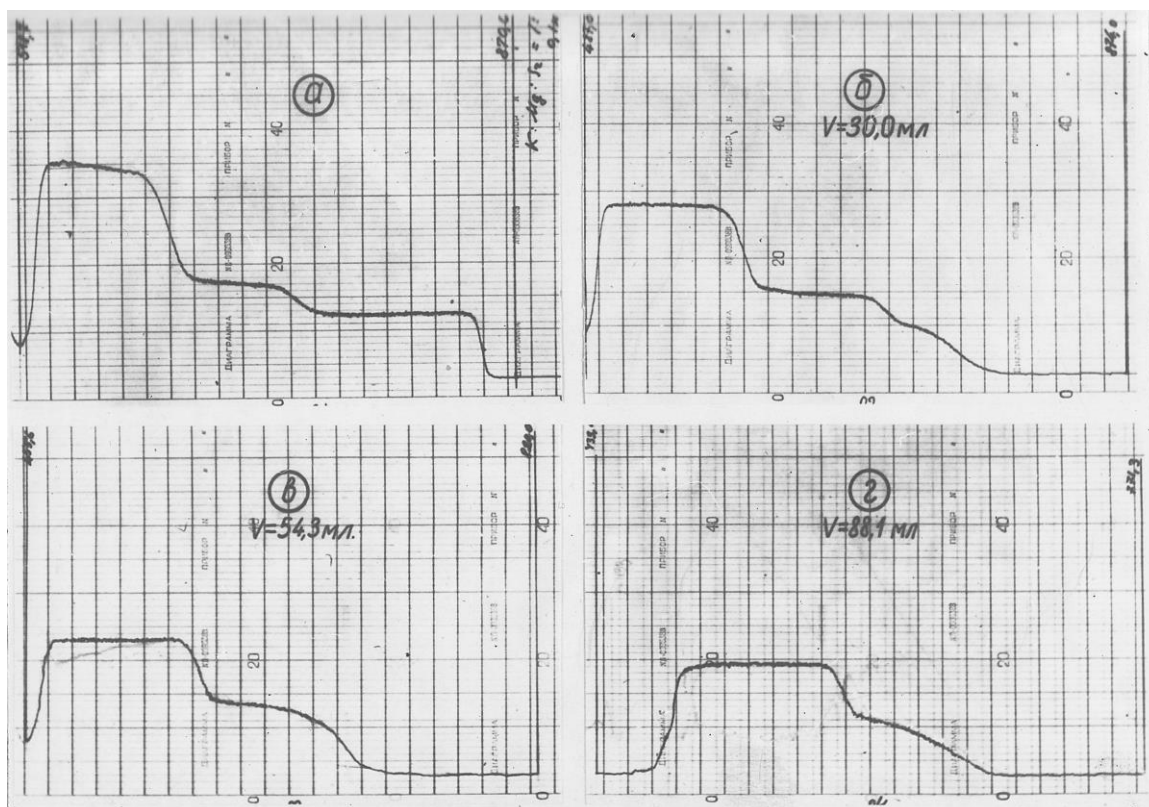
Fig. 14. Displacement chromatogram of K^{*+} - Mg^{2+} - Sr^{2+} ions

($C_K = C_{Mg} = C_{Sr} = 0.033n$). Displacer - 0.1n $SrCl_2$

The decrease in the height of the radiochromatograms is caused by the decay of the used short-lived ^{42}K radioisotope.

Conclusions

To reveal the main regularities in the formation of ion-exchange frontal, elution, and displacement chromatograms, an ideal sorption model was used, in which the equilibrium dynamics of sorption is considered in the absence of the action of kinetic and quasi-diffusion factors of blurring the ion exchange fronts - the boundaries of chromatographic zones.

The obtained results of theoretical research were verified experimentally.

Experiments convincingly indicate the advisability of using such a model of sorption dynamics for studying real chromatographic processes.

The most important technological parameters - the length of the ion exchanger layer and the time required to separate the mixture of ions - can be calculated based

on the ideas of the ideal sorption model with the introduction of appropriate corrections that take into account the front deformation factors.

References:

1. Гельферих Ф. Иониты / Ф. Гельферих. М.: ИЛ, 1962.

2. Жидкостная колоночная хроматография. Под ред.: З. Дейла, К. Маценка, Я.Янака. – М.: Мир, 1978. - Т.1-3.

3. Стыскин Е.А. Практическая высокоэффективная жидкостная хроматография. / Е.А. Стыскин, Л.Б. Ициксон, Е.В. Брауде. – М.: Химия, 1986.

4. Рачинский В.В. Введение в общую теорию динамики сорбции и хроматографии / В.В. Рачинский. – М.: Наука, 1964.

5. Тизелиус А. В сб. Химия белков. Изд-во иностр. лит., М., 1969.

6. Рачинский В.В. К теории идеальной вытеснительной динамики сорбции одного вещества / В.В. Рачинский, А.М. Кияновский. // Доклады Академии наук СССР. – 1973. – Т.208. - № 6.

7. Кияновский А.М. Формирование ионообменных хроматограмм. 1.Фронтальная и элютивная динамика сорбции. // Научные труды SWorld: международное периодическое научное издание. – Иваново: Научный мир, 2015. – Вып.№3(40) - Т.12. – С.41-49.

8. Рачинский В.В. Теория формирования вытеснительных хроматограмм. 1. Идеальная модель формирования хроматограмм двух веществ./ В.В. Рачинский, А.М. Кияновский. // Журнал физической химии. – 1974. - Т.48, №2.

9. Рачинский В.В. Теория формирования вытеснительных хроматограмм II. Многокомпонентная система. / В.В. Рачинский, А.М. Кияновский // Журнал физической химии. – 1974. – Т.48, № 4.

10. Кияновский А.М. Движение смеси веществ в пористой сорбирующей среде / А.М. Кияновский // Научные труды SWorld: международное периодическое научное издание. – Иваново: Научный мир, 2015. – Вып.№2(39). - Т.18. – С.69-76.

11. Кияновский А.М. Теория динамики ионного обмена. XX. Экспериментальное изучение формирования вытеснительных хроматограмм. / А.М. Кияновский, В.В. Рачинский// Журнал физической химии. – 1976. – Т.50. - № 11.

12. Сенявин М. М. Ионный обмен в технологии и анализе неорганических веществ / М. М. Сенявин. – М.: Химия, 1986

13. Ионный обмен. – М.: Наука, 1981.

14. Рачинский В. В. Радиохроматографические методы определения констант ионообменного равновесия / В. В. Рачинский, В. Л. Гарнецкий // Теория ионного обмена и хроматографии. – М.: Химия, 1968.

15. Рачинский В. В. Теория динамики ионного обмена. XIV. Формирование вытеснительных ионообменных хроматограмм. / В. В. Рачинский, А. М. Кияновский // Журнал физической химии. – 1973. – Т.47, №11.

Formation of ion-exchange chromatograms

Формирование ионообменных хроматограмм

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