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SPECIFIC FACTORS INVOLVED IN THE SPREADING OF CHROMATOGRAPHIC ZONES IN ION-EXCHANGE COMPLEXING CHROMATOGRAPHY

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SUMMARY

Studies were made of the effect on the broadening of a chromatographic zone of changes in the slope of the sorption isotherm, caused by the changes in the process of separation, ion-exchange constants, pH of the solution and the composition and instability constants of complexes formed.

It is demonstrated that complexing in a solution produces a pH gradient at the displacing ion–separated mixture interface, which results in a considerable broadening of the bandwidth of the displacing ion and in its penetration into the zone of separated elements. The last two characteristics depend on the pH gradient, the absolute value of the equilibrium pH in the zone of separated elements and the slope of the sorption isotherm of the displacing ion. The changes in the sorption isotherm of the displacing ion, observed in the process of transfer of this ion from the separated zone into the layer of free ion exchanger, depend on the cationic form of the layer of free ion exchanger and affect both the shape and the width of the zone of separated elements.

INTRODUCTION

The processes of complexing in ion-exchange chromatography affect the selectivity of absorption and both the shape and the width of the chromatographic zones. This influence may be caused both by the change of state of the absorbed ions in the external solution and by the formation of complex compounds of unequal stability inside the ion exchanger phase.

The role of complexing processes in the external solution has been described in detail[1–10]. Our publications, in particular, analyzed the effects of additional factors related to complexing in the solution, namely the concentration and pH of the complexing reagent, its dissociation constant and that of the complexes formed, on the shape of the sorption isotherm[9,10] and on the ion-exchange kinetics[11]. These investigations established quantitative relationships, which enable the conditions for forming a steady state or a spreading sorption front to be determined.

This paper discusses the possible effects of varying the ion-exchange constants

and the pH of the solution in the process of separation, and also the effects of changing the ionic form of the sorbent and the complex composition on the shape of the chromatographic zones and the build-up time of a steady-state front. The effects of these factors are not taken into account in the analysis of zone spreading and are often attributed to the influence of kinetic parameters[12].

EXPERIMENTAL AND RESULTS

The concentration constants of ion-exchange equilibria ($K_{M/H}$) are known to depend on the loading of the ion exchanger and are frequently a complicated function of the cation composition of the ion-exchange resin. However, the effect of varying exchange constants on the shape of chromatographic zones still remains unknown.

We have established[13] that for yttrium and cerium the concentration constants of rare-earth elements (REE) exchange on the KU-2 cation exchanger in the H^+ and Na^+ form increase as the loading of the ion exchanger increases. Fig. 1 shows the experimental curves obtained for log $K_{M/H}$ as a function of the loading of the cation exchanger with REE. These results signify that the exchange constant for cerium remains constant up to $\bar{X} = 0.25$, where $\bar{X} = q_M/\Gamma_\infty$, and $K_{M/H} = 1.7 \pm 0.04$, and for yttrium up to $\bar{X} = 0.4$ and $K_{M/H} = 1.5 \pm 0.03$ (q_M is the concentration of metal ion in the ion exchanger in milliequivalents per gram). A further increase in the loading of the ion exchanger increases the exchange constant by a factor of 2–3. Such an increase in the concentration constants of ion-exchange equilibria, brought about by the increased loading, results in enhancement of the partition coefficient by a factor of 15–30, and this effect creates conditions for additional spreading of the leading edge of a zone.

Fig. 2 shows the distribution of yttrium over the height of the sorbent (KU-2) column in the process of selective washing of yttrium out of a yttrium and cerium-containing mixture, for yttrium contents in the initial mixture of (a) 10% with a maximum yttrium concentration $\bar{X} = 0.6$, and (b) 5% with a maximum yttrium concentration $\bar{X} = 0.25$. Separation was effected by means of a diethylenetriaminepenta-

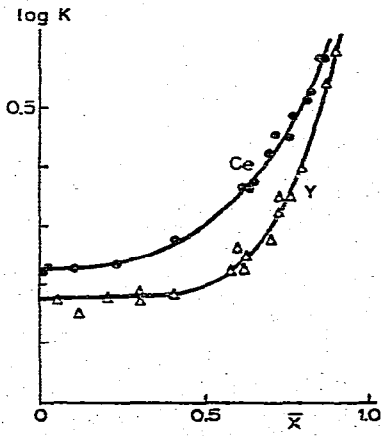

Fig. 1. Resin (H^+)–Ce(III) and resin (H^+)–Y(III) exchange constants for KU-2 cation exchanger as functions of the loading of the cation exchanger ($\bar{X}$) by REE.

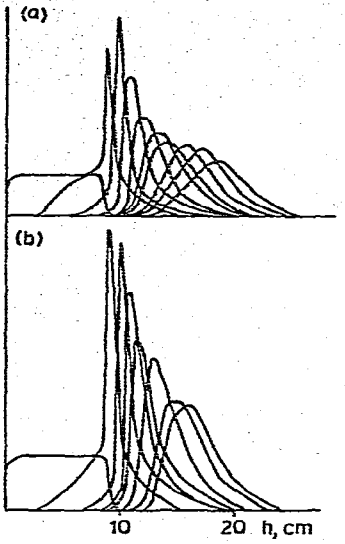

Fig. 2. Selective separation of yttrium from a cerium–yttrium mixture on KU-2 cation exchanger at (a) 10% and (b) 5% yttrium content in the initial mixture.

acetic acid (DTPA) solution (0.01 M, pH 2.50, $C_{Na} = 0.03\ N$). Concentrations of sodium and hydrogen ions in the eluent were chosen in accordance with the earlier derived equation[9,10]

$$C_{Na} < \frac{K_{M/H}^{3/2}\,\Gamma_\infty}{\left(1 + \frac{C_0\,\delta\,K_S}{\psi}\right)^{1/2}} \tag{1}$$

and in such a manner that the advancing yttrium front was steady state for a minimal value of the exchange constant ($\bar{X} < 0.4$). In eqn. 1, $K_{M/H}$ is the exchange constant for $RH\text{–}M^{z+}$, Γ_∞ is the maximum exchange capacity of the ion exchanger, $\delta = K_1 K_2 \ldots K_n$, where $K_1, K_2, \ldots, K_n$ are the step dissociation constants of the complexing reagent, $\psi = C_H^n + K_1 C_H^{n-1} + \ldots + K_1 K_2 \ldots K_n$, C_H is the concentration of hydrogen ions, n is the basicity of the acid serving as a complexing reagent, K_S is the stability constant of the $[MA]^{z-n}$ complex, z is the valency of the metal cation M and C_0 is the concentration of the complexing reagent.

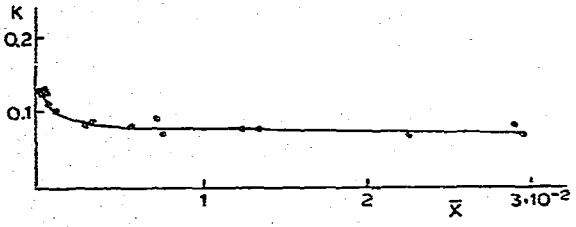

Fig. 3. Yttrium exchange constants as functions of loading ($\bar{X}$) on vinylpyridine ampholyte in the HCl form.

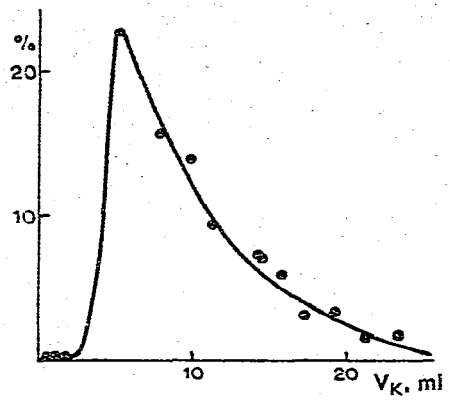

Fig. 4. Separation of Y^{91} from vinylpyridine ampholyte by 0.1 *N* HCl.

By virtue of the constants of the ion-exchange sorption of yttrium in the zone obtained with yttrium concentration $\bar{X} > 0.4$, lower concentrations will travel with lower velocity, thus producing additional spreading of the chromatographic zones. This spreading will proceed until the maximum yttrium concentration in the zone, $\bar{X} \leqslant 0.4$, is built up. The advancing yttrium front must remain stationary in the course of further motion.

These data demonstrate that, for a 5% yttrium content in the initial mixture, the steady-state front arises at a distance of 2 cm and, for a 10% yttrium content, at a distance of 8 cm. This increase in the build-up time of a steady-state front is a factor that changes the form of a chromatographic zone.

An inverse dependence of exchange constants on loading is observed when energetically non-uniform sorbents are used. An example is the absorption of yttrium by vinylpyridine ampholyte containing carboxyl groups. When yttrium is absorbed from 0.1 *N* hydrochloric acid, the exchange constant is reduced by a factor of two when the loading increases (Fig. 3). At the same time, the partition coefficient of yttrium decreases by almost an order of magnitude. A linear sorption isotherm cannot be obtained in such systems even at very low loadings. Under the conditions of sorption dynamics, this leads, at low loadings also, to the formation of highly asymmetrical peaks with a contracted leading edge and a spreading rear edge (Fig. 4). As could be expected, peak asymmetry is reduced as the loading increases, but then a long rear

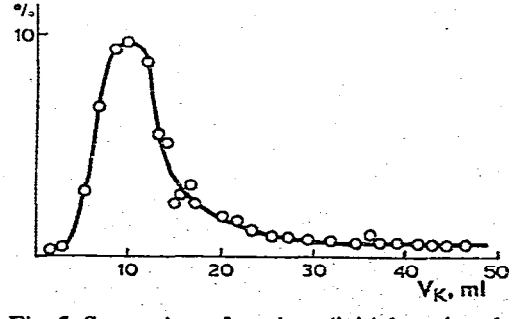

Fig. 5. Separation of yttrium (initial yttrium load 0.5 mequiv./g) from vinylpyridine ampholyte by 0.1 *N* HCl.

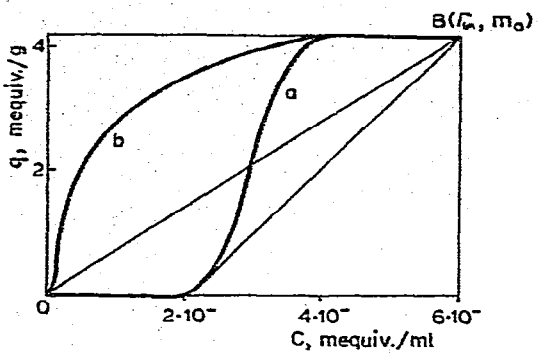

Fig. 6. Calculated sorption isotherms of (a) Na–Y and (b) Sr–Ce in the presence of complexing reagents.

tail appears (Fig. 5), which considerably impairs the separation of elements with similar properties.

A significant factor that affects the shape of a chromatographic zone is a change in the hydrogen ion concentration during separation. If displacement is effected by a complexing reagent binding the displaced ion into a non-sorbing complex, a gradient of pH is formed at the displacing ion–separated mixture interface. This gradient can radically change the slope of the sorption isotherm and lead to the formation of sigmoid isotherms. Sigmoid isotherms will be formed if, at the displacing ion–separated mixture interface, the following relationship holds:

$$m_0 = \frac{K^{(z_1 z_2)/(z_1-z_2)}\,\Gamma_\infty}{(1 + C_{A^{n-}} K_{S_2})^{z_1/(z_2-z_1)}} \tag{2}$$

where m_0 is the overall concentration of cations in the initial solution, z_1 and z_2 are the charges on the exchanged ions (subscript 1 denotes the absorbed ion and substript 2 the displaced ion), *i.e.*, the sorption isotherm of the M_1 ion will intersect the straight line OB or be a tangent to it (Fig. 6). It follows from eqn. 2 that for a given pair of exchanged ions and a given complexing reagent, the point of intersection of the sorption isotherm with the diagonal OB depends on the concentration of the A^{n-} ligand, which is a function of the concentration of hydrogen ions and the concentration of the $[MA]^{n-z_2}$ complex (Fig. 7) and is determined by the relationship

$$C_{A^{n-}} = \frac{(C_0 - C_{MA})\,\delta}{\psi} \tag{3}$$

Eqn. 2 is obtained for the case in which the displacing ion is not tied into a complex. It follows from these equations that an increased concentration of hydrogen ions must facilitate the spreading of the displacing ion front at $z_1 < z_2$ if the displacing ion remains out of the complex.

A gradient of pH forms in the solution at the displacing ion–separated mixture interface. In this instance we obtain, according to the sorption isotherm:

$$\eta_1 = \frac{q_1}{C_1} = K_{M_1/M_2}^{z_1} \left(\frac{\Gamma_\infty - q_1}{m_0 - C_1}\right)^{z_1/z_2} \left(1 + \frac{(C_0 - C_{MA})\,\delta\, K_{S_2}}{\psi}\right)^{z_1/z_2} \tag{4}$$

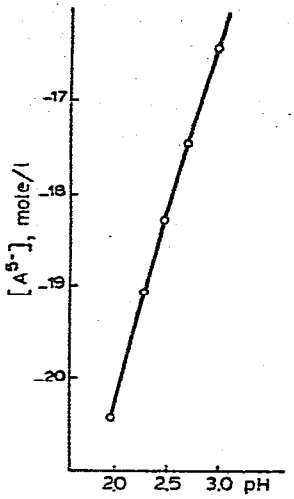

Fig. 7. Concentration of complexing anion DTPA[A^{5-}] versus pH ($C_0 = 0.02\ M$).

where q_1 and C_1 are the concentrations of the M^{z+} ion in the cation exchanger and solution, respectively.

Lower concentrations of the displacing ion will travel at higher velocity, which will lead to a considerable increase in the bandwidth of the displacing ion and to its penetration into the zone of separated elements. The bandwidth of the displacing ion and the extent of its penetration into the zone of separated elements depend on the pH gradient, the absolute value of the equilibrium pH in the separation zone and the slope of the sorption isotherm of the displacing ion.

Fig. 6 (a) shows the calculated sorption isotherm for sodium in the system Na–H–Y–DTPA. It can be seen that the isotherm has a sigmoid form with a concave initial portion. This shape of the isotherm is caused by the change in the concentration of the absorbed form of the M_2 ion, due to a non-sorbing complex being formed in the solution.

Experimental isotherms of similar shape were obtained earlier[14,15]. The sigmoid isotherm of the M_1 ion with a concave initial portion leads to the penetration of the M_1 ion into the zone of separated components, a considerable increase in the width of the zone of these components, a decrease in their concentration in the resin and the solution, and an increase in the time of steady-state build-up. According to Glueckauf[16] and Safonov[17], to determine the convex and the concave portions of the isotherm, it is necessary to draw a tangent to the isotherm from point B.

We have already shown[9] that for $z_1 < z_2$ the slope of the displacing ion isotherm increases as the ratio $m_0/\bar{m}$ increases, where

$$\bar{m} = \frac{K^{(z_1 z_2)/(z_1 - z_2)}\,\Gamma_\infty}{\left(1 + \dfrac{C_0\,\delta\,K_{S2}}{\psi}\right)^{z_1/(z_2 - z_1)}} \tag{5}$$

i.e., it increases when the exchange constant of the displacing ion ($K_{M/H}$), its charge (z_1) and the concentration of the complexing reagent (C_0) increase, the hydrogen ion

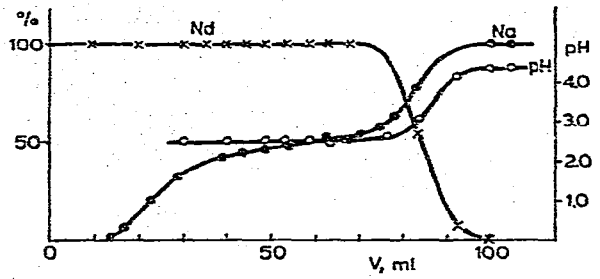

Fig. 8. Changes of Nd^{3+}, Na^{+} and H^{+} concentrations at the exit from the column (KU-2) for the separation of neodymium by 0.1 M NTA solution with acetic acid (0.2 M, $C_{Na} = 0.27$ N).

concentration decreases (ψ) or the stability of the complex of the displaced element increases.

Fig. 8 is a plot of the change in the concentration of H, Na and Nd ions at the sodium-free interface when neodymium is displaced by 0.1 M nitrilotriacetic acid (NTA) in the presence of 0.2 M acetic acid with $C_{Na} = 0.27$, initial pH 4.5 and equilibrium pH 2.9.

The slope of the sorption isotherm can be substantially increased when the displacing ion Na^{+} is replaced by a doubly charged ion. Fig. 9 shows the distribution of cerium concentration over the column height for the displacement of cerium by strontium nitrilotriacetate, with $C_0 = 0.03$ M, $C_{Sr} = 0.06$ N, pH 4.0 for the same pH gradient (equilibrium pH 2.4). For sodium, the ratio $m_0/\bar{m}$, characterizing the slope of the isotherm, is 9.1, while for strontium $m_0/\bar{m}$ is $3 \cdot 10^4$. As a result of the increased slope of the sorption isotherm [Fig. 6 (b)], the steady-state front occurs at a lower height and the extent of the penetration of displacing ion into the REE zone is considerably reduced. A similar pattern was observed when barium was used.

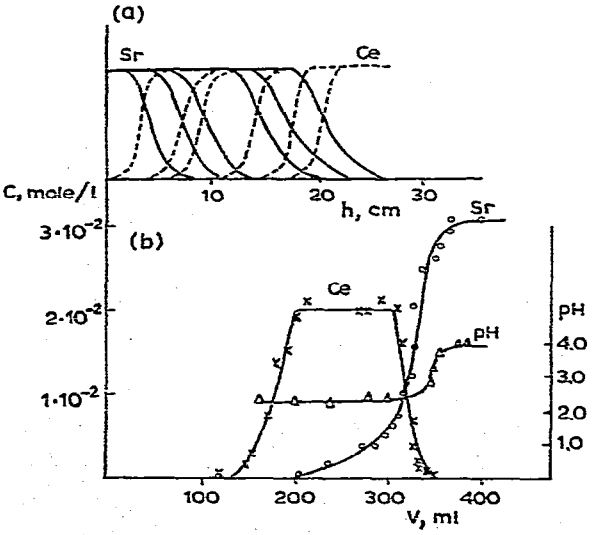

Fig. 9. Cerium distribution over the (a) column height and (b) changes in cerium, strontium and hydrogen concentrations in the process of cerium displacement by strontium nitrilotriacetate.

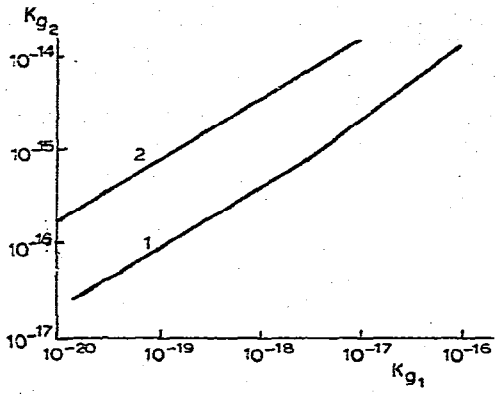

Fig. 10. $\bar{K}_{g_2}$ as function of K_{g_1} for the REE–EDTA–KU-2 system; $C_{Na} = 0.03$ *M*, pH = (1) 2.7 and (2) 4.0. $\bar{K}_{g_2}$ denotes the minimal values of the instability constants of EDTA complexes of doubly charged cations, for which a steady-state front occurs for a given REE, represented by the values of K_{g_1}. K_{g_1} denotes the instability constants of the REE–EDTA complexes.

The shape of the zone of separated elements also depends on the cationic form of the ion exchanger used for separation.

A basic equation that determines the conditions for the building up of a steady-state front in the case of binding the two exchanged ions into a complex was derived earlier[9]. It was used for the choice of a retaining ion for a given system with a view to ensuring the formation of the steady-state front of the least sorbed component on the interface with the retaining ion:

$$K_{g_2} < \bar{K}_{g_2} = \frac{C_0\,\delta}{\psi} \Big/ \left(\frac{m_0}{\Gamma_\infty}\right)^{(z_1-z_2)/z_1} \left(1 + \frac{C_0\,\delta\,K_{S_1}}{\psi}\right)^{z_2/z_1} K^{-z_2} - 1 \qquad (6)$$

As an example, Fig. 10 shows $\bar{K}_{g_2}$ as a function of K_{g_1}, calculated on the basis of published values of stability constants of EDTA complexes of REE (K_{S_1}) (ref. 18) for the separation of REE on KU-2 cationic exchanger in the M(II) form by 0.01 *M* EDTA solution with $C_{Na} = 0.03$ *M* and with equilibrium values of pH = 2.7 (1) and 4.0 (2), where $K_g = 1/K_S$. Such curves enable us to determine the value of $K_{g_2} < \bar{K}_{g_2}$ for any system shown on a plot by the values of K_{g_1}, and hence to find the doubly charged cations forming a zone with a steady-state front of the separated component.

For example, from the published values of stability constants for EDTA complexes of REE[18] and some bivalent metals[19], we can conclude that the separation of all REE, including lutetium, is possible in the steady-state regime with 0.01 *M* EDTA solution ($C_{Na} = 0.03$ *N*, pH 2.7) if Cu(II), Ni(II), Cd(II), Zn(II) and Co(II) are used as retaining ions, and impossible if Fe(II), Mn(II) and Ca(II) are used. However, Fe(II) can be used for separating light REE below samarium.

An increase in the concentration of the complexing reagent or the pH of the equilibrium solution makes it possible to increase the number of divalent metals used as retaining ions.

When reliable stability constants are available, the above method can be used to choose a suitable retaining ion and the conditions for the chromatographic separation process by displacement chromatographic analysis.

In solving problems of this type, it is nevertheless necessary to know the composition of the complexes formed and to take into account possible changes of the composition during separation. The foregoing relationships were obtained for systems in which mononuclear complexes are formed.

We know from published work that, together with mononuclear complexes (MA^{3-}) of copper, zinc, nickel and cadmium, sufficiently stable binuclear complexes (M_2A^-) are formed in solutions of DTPA, which is widely used in chromatografic analysis[20].

When displaced ions form binuclear complexes, the stationary front occurs under the conditions determined by the relationship

$$\bar{m} = \frac{K^{2z_1 z_2/(z_1-2z_2)}\, \Gamma_\infty^{[2(z_1-z_2)]/(z_1-2z_2)} \left(\frac{C_0\,\delta}{\psi}\right)^{z_1/(z_1-2z_2)} \bar{K}_{S_2}^{z_1/(z_1-2z_2)}}{\left(1+\frac{C_0\,\delta}{\psi}\,K_{S_1}\right)^{2z_2/(z_1-2z_2)}} \tag{7}$$

$z_1 > 2z_2$, $m_0 < \bar{m}$; $z_1 < 2z_2$, $m_0 > \bar{m}$ or, if $C_0 K_{S_1}\,\delta/\psi \gg 1$ then

$$\bar{m} = \frac{K^{2z_1 z_2/(z_1-2z_2)}\, \Gamma_\infty^{[2(z_1-z_2)]/(z_1-2z_2)} \left(\frac{C_0\,\delta}{\psi}\right) K_{S_2}^{z_1/(z_1-2z_2)}}{K_{S_1}^{2z_2/(z_1-2z_2)}} \tag{8}$$

The range of hydrogen ion concentrations for which the sorption front at the interface with the free layer of the ion exchanger is stationary is described by the equation

$$\psi > \frac{K^{2z_1 z_2/(z_1-2z_2)}\, \Gamma_\infty^{[2(z_1-z_2)]/(z_1-2z_2)}\, (C_0\,\delta)\, K_{S_2}^{z_1/(z_1-2z_2)}}{K_{S_1}^{2z_2/(z_1-2z_2)}} \tag{9}$$

It follows from these equations that an increase in the concentration of hydrogen ions leads, for a valence ratio of exchanged ions of $z_1 < 2z_2$, to a contraction of the displaced ion front at the interface with the layer of free ion exchanger.

We used these relationships to find the conditions of steady-state band formation in the separation of a mixture of cerium, praseodymium and yttrium on the KU-2 cation exchanger by 0.02 *M* DTPA solution, Cu^{2+} and Zn^{2+} being used as retaining ions.

Table I lists the calculated values of the equilibrium pH for which a steady-state band is formed with mononuclear and binuclear complexes of copper and zinc,

TABLE I

CALCULATED AND EXPERIMENTAL EQUILIBRIUM pH FOR FORMATION OF A STEADY-STATE BAND

Ion	*Experimental equilibrium pH*	*Calculated pH of the front contraction*	
		MA^{3-}	M_2A^-
Zn	2.20	>3.90	<2.58
Cu	1.90	>1.54	<4.0

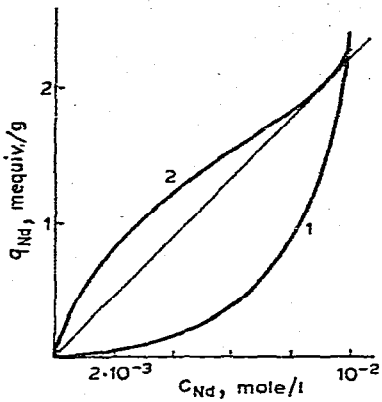

Fig. 11. Calculated sorption isotherms of yttrium in the system Y–Na–Zn–DTPA. (1) Zn^{2+} forms a mononuclear complex, ZnA^{3-}; (2) Zn^{2+} forms a mixture of complexes, $ZnA^{3-} + Zn_2A^-$.

as well as the experimental values of the equilibrium pH. The results demonstrate that when zinc is used, the steady-state band can be formed only when a binuclear complex is produced.

Additional confirmation of this conclusion was obtained by comparing the calculated isotherms for the sorption of yttrium in the system Y–Na–Zn–H–DTPA with the formation of both mononuclear and binuclear complexes (Fig. 11). Calculations were performed by solving a system of equations that included balance equations for the solution and the resin, equations of the sorption isotherms and dissociation equations for all of the complex forms. A sigmoid shape of the yttrium isotherm was established from the fact that, at small loadings of the resin with zinc ions, the concentration of the ZnA^{3-} complex is greater than or similar to that of the Zn_2A^- complex.

The formation of a zinc binuclear complex during separation reflects the distribution of zinc between various forms in a DTPA solution. According to Chaberek *et al.*[20], the concentration of the binuclear complex under these conditions is 97–98%. This conclusion was confirmed by comparing the experimental and calculated velocities of the steady-state yttrium band in the zinc layer, the latter being based on the assumption that binuclear Zn_2A^- complexes are formed in the solution in the process of Y^{3+}–Zn^{2+} exchange together with mononuclear ZnA^{3-} complexes. The calculated and experimental values are $2.2 \cdot 10^{-2}$ and $2.8 \cdot 10^{-2}$ cm/min, respectively.

The cationic form of the ion exchanger influences not only the form of the band of the displaced ion, but also that of the displacing ion if the latter has a suffi-

TABLE II

SLOPE OF ABSORPTION ISOTHERM FOR ABSORPTION OF SODIUM

Complex	$m_0/\bar{m}$			
	Cu	*Ni*	*Zn*	*Co*
MA^{3-}	6.7	0.8	10^{-2}	$1.3 \cdot 10^{-2}$
M_2A^-	41	7.1	0.8	0.5

ciently spread band and penetrates into the zone of the elements being separated. In this instance the decisive part is played by the change in the slope of the sorption isotherm of the displacing ion in the process of its transfer from the zone of separated elements into the free layer of ion exchanger.

Table II lists the values of $m_0/\bar{m}$, characterizing the slope of the sodium sorption isotherm in the process of absorption of sodium from 0.02 M DTPA solution (C_{Na} = 0.06 N, pH = 2.3) by a cation exchanger saturated with various doubly charged cations, capable of forming mono- and binuclear complexes.

The conditions for contraction of a sodium band are determined by the inequality $m_0/\bar{m} > 1$. It follows from Table II that a steady-state sodium band will be formed if the ion exchanger is used in the Cu and Ni forms, and only in the Cu form if the possibility of binuclear complexing is excluded. This signifies that if, for the separation of REE by DTPA, we use a free layer of a cation exchanger in the Zn, Co or some other cationic form with the condition $m_0/\bar{m} < 1$ satisfied, then sodium will penetrate not only into the separation zone, but also into the layer of free ion exchanger; the extent of penetration is determined by the value of $m_0/\bar{m}$. The pattern must be different if copper is used. In this instance, contraction of the sodium band on the REE–copper interface results in the enhancement of the sodium concentration in the separated zone, which consequently reduces the concentration of REE.

Taking into account the character of the variation of the slope of the sorption isotherm of the displacing ion, caused by changes in the cationic form of the ion exchanger, we can find the conditions that enable the concentration of the elements separated to be increased.

CONCLUSIONS

This investigation demonstrates that changes in all of the parameters that affect the slope of the sorption isotherm must be taken into account in the analysis of the factors that determine the spreading of chromatographic zones in ion-exchange complexing chromatography. This is the only approach that permits a correct description of the effects of kinetic factors and the sorption isotherm on the spreading of chromatographic zones to be made, and makes it possible to find effective methods for the enhancement of the chromatographic separation process.

The quantitative dependences obtained allow one to choose a suitable displacing ion, a cationic form of the free ion exchanger layer and separation conditions for displacement chromatography without the need to conduct an experiment.

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