

CHROMSYMP. 813

## PHYSICAL AND CHEMICAL PROCESSES IN CHROMATOGRAPHIC SEPARATION ON COMPLEXING ION EXCHANGERS

N. N. MATORINA\*, L. V. SHEPETYUK, T. I. BAKAEVA, L. V. KARLINA and O. V. KRYUCHKOVA

*Institute of Physical Chemistry, Academy of Science of USSR, Leninskii prospect 31, 117915, Moscow (U.S.S.R.)*

---

### SUMMARY

We investigated the sorption of the ions of rare earth elements and transition metals by the amphoteric vinylpyridine and iminodiacetic resins and showed the influence of the separate stages of the chromatographic process (equilibrium sorption, kinetics and dynamics sorption) on the chromatographic separation with the use of complex-forming resins.

A method for describing the selectivity of sorption on weakly dissociating resins is proposed.

The influence of the non-uniformity of functional groups on the equilibrium and kinetic characteristics of the complex-forming ion exchangers has been established. The possibility of applying ultrasound to intensify the diffusion processes in these systems has also been demonstrated.

---

The high selectivities of complexing ion exchangers have enabled a great expansion in the range of application of this type of exchangers to the separation of complicated mixtures. These sorbents become of special importance in the extraction of components present in low concentrations from solutions with complex salt compositions.

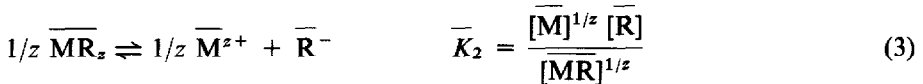
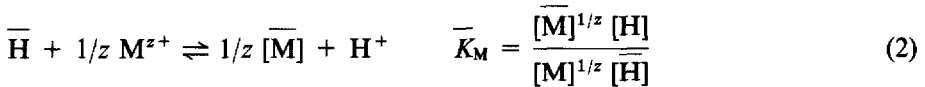
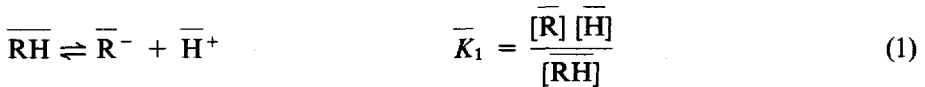
Though such exchangers have been thoroughly investigated<sup>1-5</sup>, the theory of sorption by complexing resins has been unable to predict, even qualitatively, the behaviour of systems during the chromatographic process.

The present communication is concerned with experimental studies of the dynamics and kinetics of sorption, as well as of equilibrium sorption, by complexing ion exchangers. Results are presented for the sorption of rare-earth elements (REEs) and transition metals by amphoteric vinylpyridine and iminodiacetate resins. The latter sorbents are selective in that their functional groups are capable of forming coordination compounds having different stabilities<sup>1</sup>.

However, it was not possible to use the stability constants of these complexes and the dissociation constants of the sorbent functional groups to describe the ex-

changer's adsorption isotherms over a wide range of loadings. This was because those constants (obtained, usually, by substituting the concentrations of metal and hydrogen ions in the resin phase by their concentrations in the solution phase) were dependent on the concentrations of the sorbed ions in the external solution<sup>6,7</sup>. The constants actually represented the dissociation of ions in equilibrium with solutions of a particular ion composition. The constants for dissociation of the complexes in the resin phase can be determined using the model of Rubinstein *et al.*<sup>8</sup>. However, the number of parameters needed to describe a sorption system is so large that calculations for a multicomponent system become very complicated.

We have attempted to describe the sorption isotherms using the concentration constants for ion-exchange equilibria of two-component mixtures and the equations relating these constants to the loading of the resin. This approach to the sorption by weakly dissociating resins can be justified by considering the process involved as three simultaneous stages: dissociation of different ion forms in the exchanger phase, interphase exchange of the dissociated forms and interphase redistribution of the electrolyte between the resin and solution. For example, the sorption of complexing ions by weakly dissociating resins in their hydrogen forms can be represented by the following scheme



provided that the resin can be regarded as a quasihomogeneous electrolyte solution, and that sorption of the non-exchanged electrolyte and changes in resin swelling during sorption are neglected. Here  $\overline{K}_1$  and  $\overline{K}_2$  are the dissociation constants of RH and  $\text{R}_z\text{M}$  in the exchanger phase, and  $\overline{K}_M$  is the constant for exchange of  $\text{H}^+$  of the exchanger with  $\text{M}^{z+}$  of the solution. According to eqns. 1–3 we can write

$$K_M = \frac{\overline{K}_1}{\overline{K}_2} \cdot \overline{K}_M = \frac{q_M^{1/z} a_H}{q_H a_M^{1/z}} \quad (4)$$

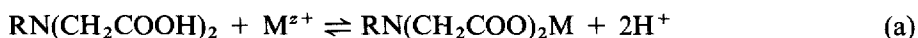
where  $K_M$  is the concentration constant of exchange,  $q_M$  and  $q_H$  are the concentrations of ions sorbed in the resin.

In Table I the two-component systems which were used in calculations of the sorption isotherms of three-component systems are given in square brackets. The resins ANKB-10 and ANKB-50 are iminodiacetate exchangers with different degrees of chemical non-uniformity of the functional groups, and the resin ANKB-2 contains picolinic acid groups. The acid–base characteristics of these resins, their structures and compositions have been reported<sup>10,11</sup>.

TABLE I  
SORBENTS AND SYSTEMS STUDIED

<i>Sorbent</i>	<i>Systems studied</i>
ANKB-10	Cu-Ni-H [RH-Cu (I)] [RH-Ni (II)] Cu-Na-H [I, RH-Na (III)] Ce-Na-H [RH-Ce, III] Yb-Na-H [RH-Yb, III]
ANKB-50	Cu-Ni-H [I, II]
ANKB-2	Y-H-Na [RH-Y (IV), III] Yb-H-Na [RH-Yb (V), III]

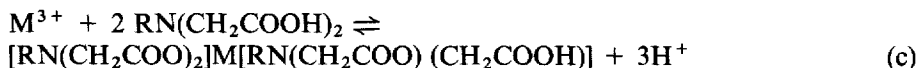
It was found that in all the systems in Table I the sorption process is actually the equivalent of ion-exchange sorption. Thus, for systems I, II in absence of protonation<sup>12,13</sup>



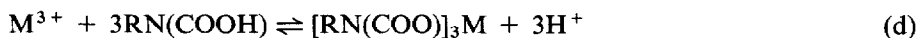
for system III<sup>10,11</sup>



while in systems IV, V in the cases of ANKB-10 and ANKB-50<sup>14,15</sup> we have:



In the case of ANKB-2 the process involved is<sup>16</sup>:



For solutions with pH ≤ 2, protonation of amino groups



was also taken into account.

In accordance with the above, the concentration constants of the equilibria a were determined from:

$$K_M = \frac{q_M C_H^2 \gamma_H^2}{q_H C_{Cu} \gamma_{Cu}} \quad (5)$$

The concentration constants of the equilibria b-d were calculated using equations similar to 4. In every case, the ion balance in the solution and resin

$$\Gamma \sim = \sum q_i \quad (6)$$

$$C_0 = \sum C_i \quad (7)$$

was taken into account.

If the value of  $K_M$  changes with the resin loading, the sorption isotherms for three-component mixtures were calculated using the experimental dependences  $K_M = f(N)$ ,  $N = q_M/\Gamma \sim$  being the exchanger loading which, in many cases, can be expressed by

$$\log K_M = \log K'_M + \alpha N \quad (8)$$

where  $K'_M$  is the concentration exchange constant at  $N \rightarrow 0$ , and the constant  $\alpha$  depends on the composition and structure of the exchanger phase complex compounds.

The details of the techniques and conditions used to determine the sorption isotherms in two-component systems have been reported<sup>12-16</sup>.

Figs. 1 and 2 show the dependences of the ion-exchange constants for equilibria a<sup>17</sup> and d<sup>18</sup> on the exchanger loading. The dependence  $K_M = f(N)$  in Fig. 1 allows one to suggest that at least two sorption centres for copper exist in the ANKB-10 resin containing iminodiacetate (IDA) and other amine groups<sup>10</sup>. These groups, at

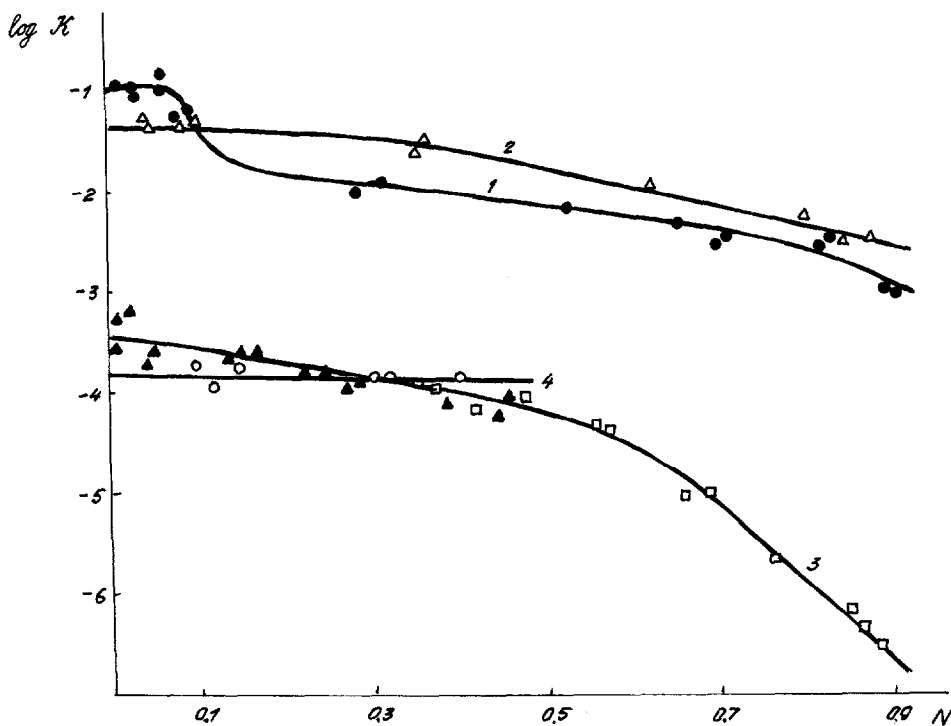


Fig. 1. Dependences of ion-exchange equilibrium constants for copper (1, 2) and nickel (3, 4) on the loading,  $N$ , of ampholytes ANKB-10 (1, 3) and ANKB-50 (2, 4).

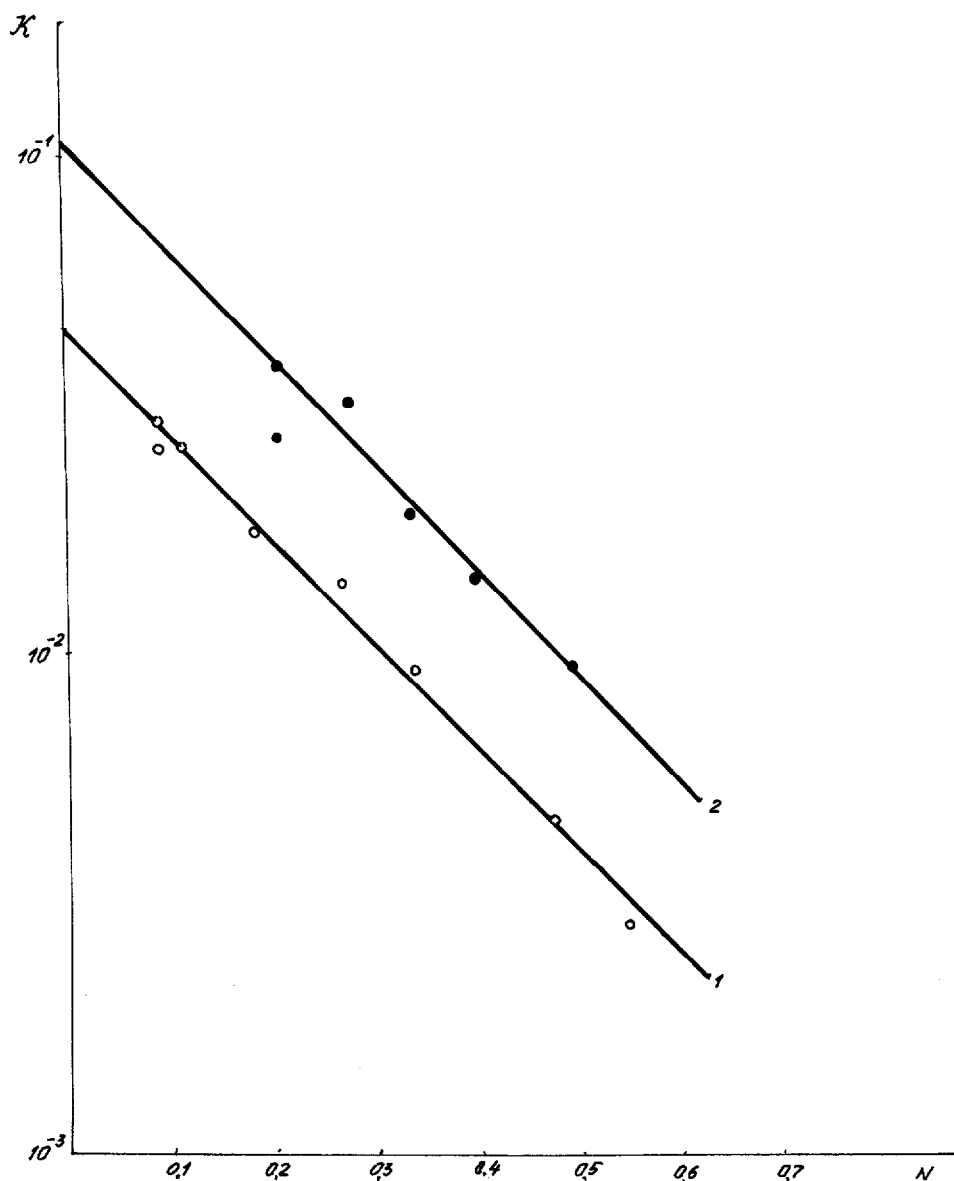


Fig. 2. Dependences of ion-exchange equilibrium constants for yttrium (1) and ytterbium (2) on the loading,  $N$ , of ampholyte ANKB-2.

certain orientation, can form additional coordination bonds  $\text{Cu} \cdots \text{N}$  because of non-complete saturation of the coordinating ability of copper by one IDA ligand. Such bonding greatly increases the stability of copper complexes in the exchanger.

In the presence of two energetically non-uniform centres, the sorption isotherm for  $\text{Cu}^{2+}$  can be described by

$$N = \frac{K_{Cu_1} \delta_1 a_{Cu}}{K_{Cu_1} a_{Cu} + a_H^2} + \frac{K_{Cu_2} \delta_2 a_{Cu}}{K_{Cu_2} a_{Cu} + a_H^2} \quad (9)$$

where  $\delta_1 = \Gamma_1/\Gamma_{\sim}$ ,  $\delta_2 = \Gamma_2/\Gamma_{\sim}$  and  $\Gamma_1, \Gamma_2, K_{Cu_1}, K_{Cu_2}$  are the concentrations of the various sorption centres in the exchanger and the corresponding exchange constants for  $Cu^{2+}$ . The values of  $q_1$  and  $\Gamma_1$  were calculated from the experimental sorption isotherm for  $Cu^{2+}$  at  $N \leq 0.1$  using the equation:

$$\frac{q_1}{a_{Cu}} = \frac{K_{Cu_1} (\Gamma_1 - q_1)}{a_H^2} \quad (10)$$

As shown previously<sup>17</sup>, the sorption isotherm calculated in this way coincides with the experimental isotherm.

When the ANKB-10 resin is heavily loaded, the value of  $K_M$  rapidly decreases (particularly for  $Ni^{2+}$ ). This is, seemingly, due to an increase in the relative content of complex forms containing monoacetate groups:



According to ref. 10, the content of carboxyl groups in the iminodiacetate groups of ANKB-10 is never greater than 64%.

The values of  $K_M$  for  $Cu^{2+}$  and  $Ni^{2+}$  on the monofunctional resin ANKB-50 and of  $K_M$  for REEs on the amphoteric resin ANKB-2 behave in a different way. The variations seem to be induced by the energetic non-uniformity of the resins because the functional groups in the sorbent phase take up different spatial positions.

In Fig. 3 the experimental sorption isotherm on ANKB-50 for copper from a nickel electrolyte (three-component mixture) is compared with that calculated using  $K_M$  for the two-component systems I and II<sup>13</sup> for the mixture  $\bar{C}_{Ni} = 2.09 M$ ,

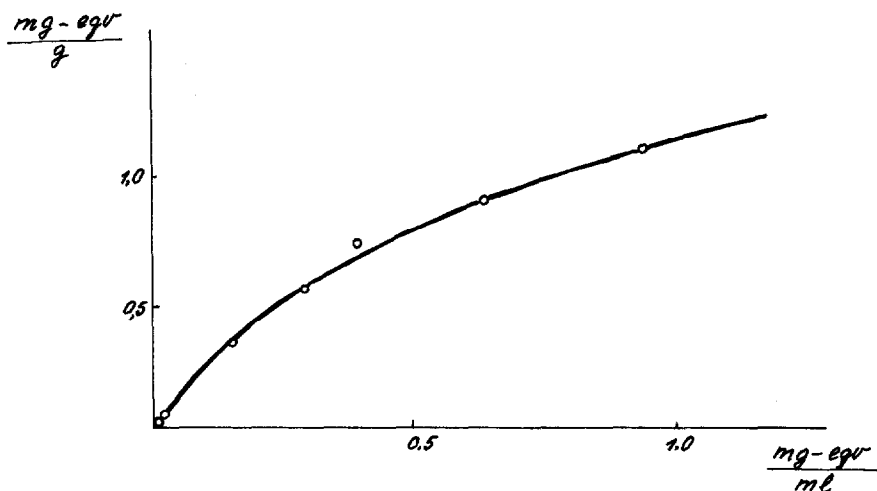


Fig. 3. Sorption isotherm for copper, from a nickel electrolyte on ampholyte ANKB-50. —, Calculated; ○, experimental data.

$\bar{C}_{Cu} = 8 \cdot 10^{-5} - 1.5 \cdot 10^{-2} M$ ,  $\bar{C}_H = 10^{-2} M$ . To calculate this isotherm we used two equations of the type 5 for  $Cu^{2+}$  and  $Ni^{2+}$  together with eqns. 6-8. The concentrations of  $Cu^{2+}$  and  $Ni^{2+}$  were determined

$$q_{Ni} = \frac{K_{Ni} (\Gamma_{\sim} - x) \bar{C}_{Ni} \gamma_{Ni}}{K_{Ni} (\Gamma_{\sim} - x) l \gamma_{Ni} + (\bar{C}_H + xl)^2 \gamma_H^2} \tag{11}$$

where  $x = q_{Cu} + q_{Ni}$ ,  $l = g/v$ ,  $g$  is the weight of the resin sample in grams and  $v$  is the volume of the external solution in ml, and:

$$\bar{C}_{Cu} = q_{Cu} \left[ l + \frac{(\bar{C}_H + xl)^2 \gamma_H^2}{K_M (\Gamma_{\sim} - x) \gamma_M} \right] \tag{12}$$

For calculations of the sorption isotherm on ANKB-10 for  $Cu^{2+}$  from the nickel electrolyte, eqn. 9 was used. If in the ion-exchanger phase complexes of the same type are formed (sorption of  $Cu^{2+}$  and  $Ni^{2+}$  on ANKB-50 and  $Ni^{2+}$  on ANKB-10), the loading is given by the expression  $N_{Cu} = x/\Gamma_{\sim}$ . If the compositions of the complexes of  $Cu^{2+}$  and  $Ni^{2+}$  are different (as in the case of sorption of  $Cu^{2+}$  on ANKB-10), it was assumed that  $N_{Cu} = q_{Cu}/\Gamma_{\sim}^{17}$ . The experimental and calculated sorption isotherms for REEs from a three-component mixture  $REE-M^+-Na^+$  on ANKB-10<sup>17</sup> and ANKB-2<sup>18</sup> are compared in Figs. 4 and 5. The sorption isotherms were obtained at constant initial concentrations of REEs and at various relative contents of hydrochloric acid and sodium chloride in the initial solutions. The results obtained indicate that the concentration exchange constants can be used to characterize the selectivities of complexing ion exchangers and to describe the sorption isotherms for three-component mixtures using the isotherms for two-component mixtures.

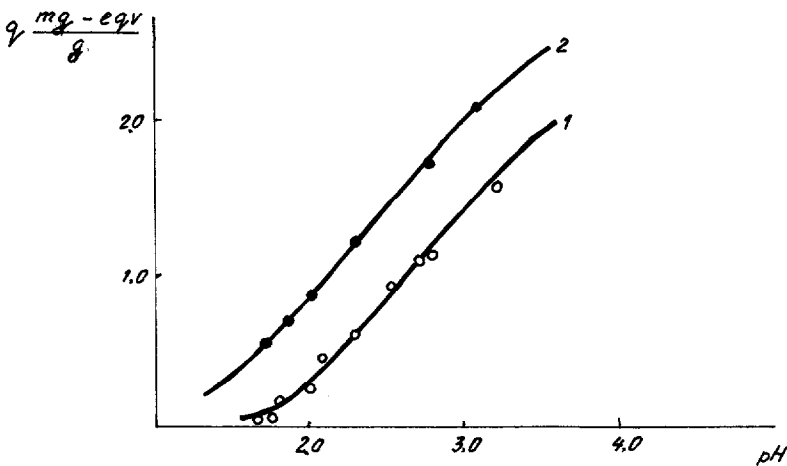


Fig. 4. Sorption isotherms for cerium (1) and ytterbium (2) on ANKB-10 resin. —, Calculated; O, ●, experimental data.

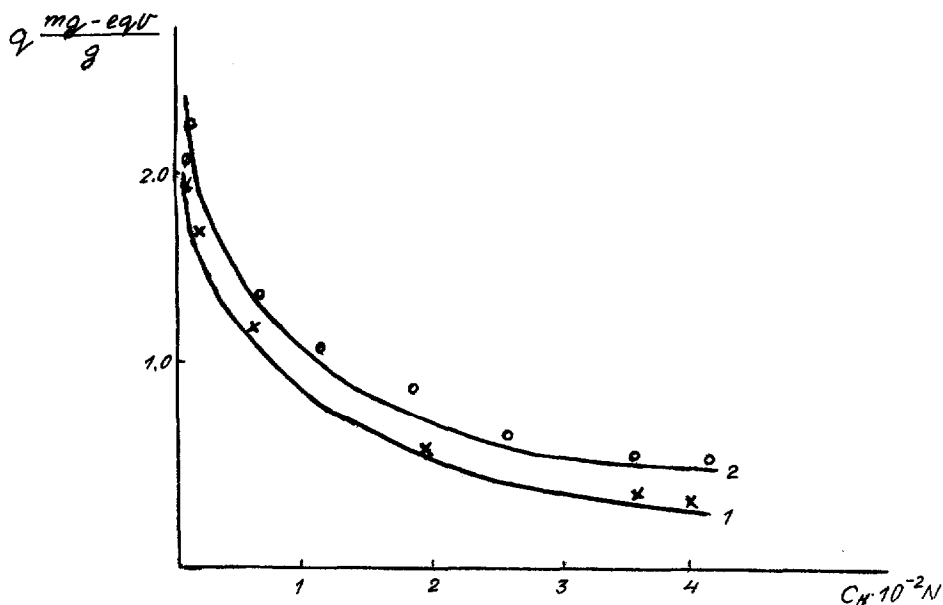


Fig. 5. Sorption isotherms for yttrium (1) and ytterbium (2) on ANKB-2 resin. —, Calculated; O, x, experimental data.

From the experimental sorption isotherms for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Y}^{3+}$  and REEs on the present resins, it can be concluded that in some cases the differences in stabilities between the ion-exchanger complexes are similar to those for the monomer analogues. Such a situation occurs, for example, in sorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by iminodiacetate resins<sup>12,13</sup> and in sorption of  $\text{Y}^{3+}$  and REEs by the amphoteric resin ANKB-2 (ref. 18, Table II).

Another example is the sorption of REEs on iminodiacetate resins<sup>14</sup>. As mentioned previously<sup>19</sup>, the stability constants,  $K_{S_1}$  for benzyliminodiacetate complexes of cerium and ytterbium in solution differ by a factor of 10, whilst the ratio of the concentration constants,  $K_{\text{Yb}}/K_{\text{Ce}}$ , for ion exchange (see Table I, system III) on ANKB-10 at  $N = 0.2$  is 2.5. It is also difficult to desorb REEs from those ion exchangers. Rare-earth elements cannot be completely removed even when concentrated (4 M) hydrochloric acid solutions are used for desorption.

TABLE II  
RATIOS OF ION-EXCHANGE CONSTANTS AND STABILITY CONSTANTS FOR COPPER AND NICKEL, AND FOR YTTERBIUM AND YTTRIUM

Sorbent	$M_1$	$M_2$	$K_{M_1}/K_{M_2}$		$K_{S_1}/K_{S_2}$ solution	Ref.
			$N \rightarrow 0$	$N = 0.5$		
ANKB-10	Cu	Ni	$2.4 \cdot 10^2$	$1.4 \cdot 10^2$	$4.9 \cdot 10^2$	19
ANKB-50	Cu	Ni	$2.9 \cdot 10^2$	$1.0 \cdot 10^2$		
ANKB-2	Yb	Y	12.7		20 25	20 21



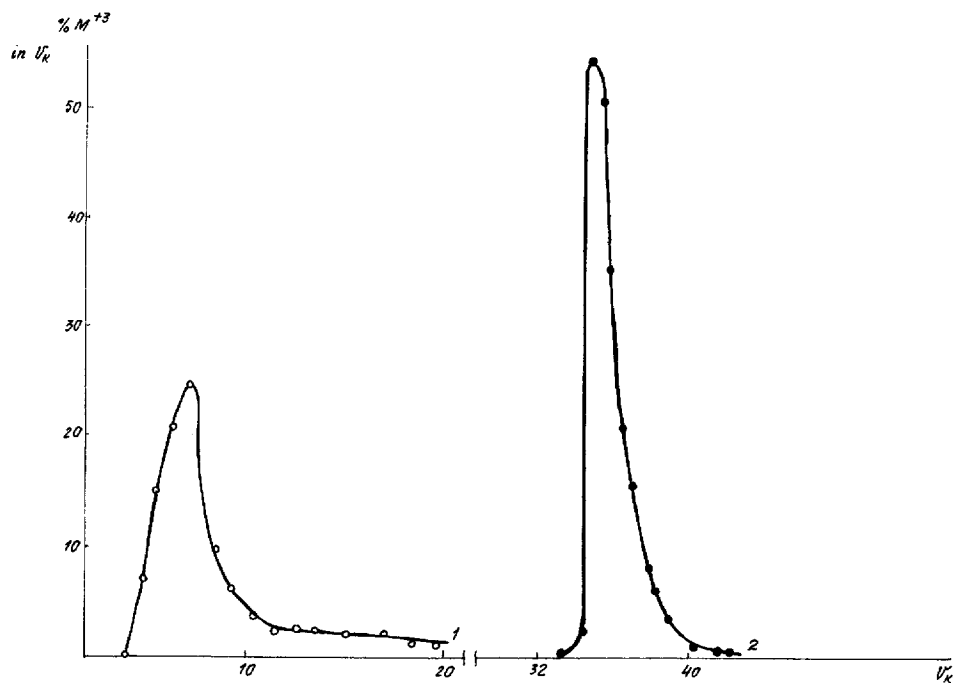
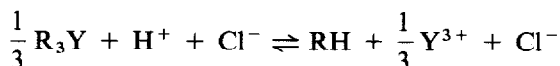


Fig. 6. Separation of yttrium (1) and ytterbium (2) by ANKB-2 ampholyte at 70°C; elution by 0.1 and 0.3 *M* hydrochloric acid respectively.

Since iminodiacetate resins are very selective with respect to copper, they can be used to isolate copper from solutions containing considerable amounts of other salts. For example, when purifying nickel electrolytes the content of copper can easily be reduced to less than 0.1 mg/l, though the initial concentrations of the solutes are very different:  $\bar{C}_{\text{Ni}} = 65$ ,  $C_{\text{Cu}} = 0.5 \text{ g/l}^{17}$ .

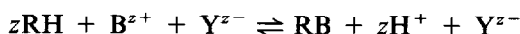
On the basis of the results obtained for sorption of REEs and  $\text{Y}^{3+}$  on ANKB-2, a new method of chromatographic separation of yttrium from solutions containing compounds of heavy rare-earth elements was developed. The method has been patented<sup>22</sup>. The selective sorbent ANKB-2 is used to separate REEs in diluted solutions of mineral acids (0.05–0.3 *M*) without applying a complexing agent, though such agents are routinely used in separating REEs on non-selective sulphocationic resins. During desorption the complexes of  $\text{Y}^{3+}$  and REEs formed with the picoline groups of the ion exchanger are destroyed. Yttrium is eluted first (Fig. 6), since its complex is the weakest. The order of elution of heavy REEs corresponds to the sequence of increasing strengths of the complexes with the resin. In this case, this sequence is in accord with that of the stability constants of the analogous picoline complexes in solution. The strong affinities of the weakly acidic cation exchangers for hydrogen ions and of the weakly basic anion exchangers for hydroxyl ions result in the appearance of convex sorption isotherms for the displacing ions, whose concentrations in solution are much less than those in the strongly dissociated exchangers. For example, according to ref. 23, when yttrium is desorbed by hydrochloric acid, a sharp front of the displacing ions is formed at  $C_{\text{HCl}} > \Gamma \sim K_{\text{M}}^{-3/2}$  (ref. 17). The

values of  $C_{\text{HCl}}$  determined<sup>17</sup> by using the concentration constants for the ion-exchange equilibrium<sup>18,24</sup>



on the sorbents ANKB-2 and sulphocationic resin KU-2 are  $6 \cdot 10^{-2}$  and 10 *M*. Hence, the desorption of cations with  $z_2 > 1$  by mineral acids from strongly acidic cationic resins usually results in a concave sorption isotherm for the displacing ions. The use of weakly dissociating cation exchangers allows desorption to be performed under conditions of a convex isotherm for the displacing ions and at much lower acid concentrations.

The sorption of transition metal and REE ions on iminodiacetate and vinylpicoline resins in their hydrogen forms is accompanied by conversion of the exchanger's fixed groups from one form onto another<sup>2,3</sup>:



Since the concentration of dissociated groups in the exhausted layer is low, the co-ions  $Y^{z-}$  penetrate into the resin particles together with the counter ions  $B^{z+}$ . If the compounds between  $B^{z+}$  and the exchanger's functional groups formed at the inner boundary of the reacted layer are less dissociated than the A ions, a sharp boundary of ion exchange A-B moves to the centre of a particle and a RB shell appears through which the ions A and B diffuse in the presence of co-ions  $Y^{z-}$ . In contrast to common ion exchange, the rate of internal diffusion in such systems depends on the solution concentration. The kinetics of ion exchange in these systems has been qualitatively analyzed<sup>25</sup> within the framework of a mathematical model suggested in ref. 26. It was shown that the ratio of the equilibrium constants for dissociation of complexes of counter ions formed with the exchanger's fixed groups and the diffusion parameters are mutually dependent on the intraparticle concentration profiles and the rate of the intradiffusion process. Also obtained in ref. 26 was an approximate analytic solution of the system of kinetic equations describing the mutual diffusion of counter- and co-ions through the external associated layer of the particles. This solution relates the effective diffusion coefficient,  $\bar{D}_{\text{eff}}$ , to the individual diffusion coefficients,  $\bar{D}_A$  and  $\bar{D}_B$

$$F = 3 \sqrt{\frac{2 \bar{D}_{\text{eff}} C_0 t}{a_0 r_0^2}}; \quad \bar{D}_{\text{eff}} = \frac{(z_B - z_Y) \bar{D}_A \bar{D}_B}{z_B \bar{D}_B - z_Y \bar{D}_A} \quad (14)$$

where  $a_0$  is the exchange capacity of the sorbent and  $C_0$  is the solution concentration. According to ref. 25, the solution 14 can be used in the case of a convex isotherm ( $\bar{K}_{RA}/\bar{K}_{RB} > 1$ ) for quantitative estimations at  $\bar{D}_A \gg \bar{D}_B$  and for qualitative considerations at  $\bar{D}_A < \bar{D}_B$ .

We have studied experimentally the kinetics of sorption of  $Y^{3+}$  from solutions of yttrium trichloride (0.025–0.1 *M*) and at constant (0.01 *M*) hydrochloric acid concentration on the amphoteric resin ANKB-2 (hydrogen form), of copper and nickel from nickel sulphate at different concentrations of  $M^{2+}$  and  $H^+$  on amphoteric

iminodiacetate resins and the kinetics of desorption of those ions by hydrochloric acid ( $Y^{3+}$ , ANKB-2) and by sulphuric acid ( $Ni^{2+}$ , ANKB-35). The studies were carried out by the thin-layer method at 20°C and at flow-rates not less than 100 cm/min.

The results for equilibrium sorption (Figs. 1 and 2) indicate that the systems studied are much more complicated than those whose kinetic properties can be adequately described by the mathematical model<sup>26</sup>. In such systems, the dissociation constants of complexes formed inside the resin particles do not stay constant, since the sorption affinities of yttrium and nickel noticeably decrease with increasing resin loading (see Figs. 1 and 2). This is, possibly, due to energetic non-uniformity of the resin which can be caused by both chemical non-uniformity of the functional groups and by their spatial locations. According to ref. 27, such non-uniformities induce a decrease in the effective coefficient of internal diffusion.

The process of mass transfer in amphoteric resins may be further complicated by protonation reactions in the resin particles at pH values depending on the dissociation constants of the amino groups. Due to the reaction *e* which occurs simultaneously to *d*, the hydrogen ions evolved during sorption of  $M^{z+}$  on ANKB-2 (*d*) are bound to amino groups (*e*), where<sup>11</sup>:

$$K_N = \frac{[RNCOO][H]}{[RNCOOH]} = 0.1$$

Thus, the concentration profile of  $M^{z+}$  sorbed inside a particle sharpens and the exchange rate increases. During desorption of  $M^{z+}$  by an acid, protonation of the amino groups causes broadening of the concentration profile of hydrogen ions in the

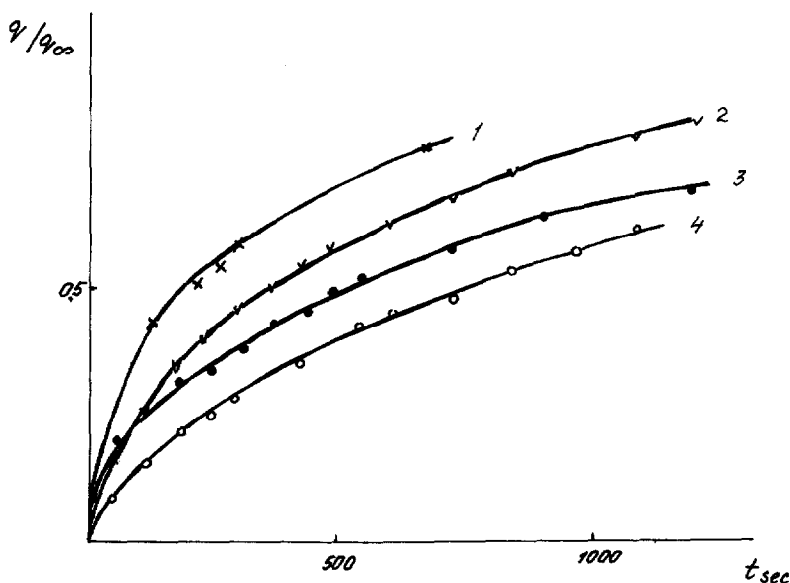


Fig. 7. Kinetic desorption curves for yttrium on ANKB-2 by 0.1 (1, 2), 0.5 (3) and 0.03 *M* hydrochloric acid (4). Curves: 1, 3, 4, preliminary treatment of resin (hydrogen form) with acid.

TABLE III  
DESORPTION OF YTTRIUM BY HYDROCHLORIC ACID

Concn. of HCl (M)	q/c	$D_{eff} \cdot 10^6$	$\frac{D_{eff} \cdot 10^8}{q/c}$	$D_Y \cdot 10^6$
0.1	30.6	$2.9 \pm 0.2$	$9.5 \pm 0.9$	$1.7 \pm 0.2$
0.05	56.5	$2.6 \pm 0.1$	$4.6 \pm 0.3$	$1.5 \pm 0.1$
0.03	89.5	$2.8 \pm 0.2$	$3.1 \pm 0.2$	$1.6 \pm 0.2$

particle and decreases exchange rate (Fig. 7). If the conditions are chosen so that the effect of reaction e vanishes, the kinetic curves are satisfactorily described by eqn. 14 (see Table III). Hence, in the case of desorption of yttrium by hydrochloric acid solutions at different concentrations, resins were used which were saturated with yttrium from solutions at hydrochloric acid concentrations equal to that of the desorbing solution.

Table IV presents the coefficients of internal diffusion of REEs obtained by sorption on the sulphocationic resin KU-2 in the presence of diethylenetriaminepentaacetic acid (DTPA), which forms stable complexes with REEs in solution which are not sorbed by the resin<sup>28</sup>, and of  $Y^{3+}$  obtained under similar conditions by sorption on ANKB-2. Also shown are the heights equivalent to a theoretical plate (HETP) obtained for similar flow-rates (1 cm/min) and resin particle dimensions ( $r = 2.6 \cdot 10^{-2}$  cm). As seen in Table IV, the kinetic properties of these systems exhibit no discrepancies. However, the absolute values of HETP, 0.2–0.4 cm, were obtained at 75–85°C and at flow-rates of about 1 cm/min, *i.e.*, under conditions not satisfying the requirements of highly efficient chromatography.

The chemical non-uniformities of the resin's functional groups have a negative effect on the rates of ion intradiffusional processes which are already complicated by complexing reactions in the resin particles. When studying the kinetics of copper sorption from nickel electrolytes on the monofunctional resin ANKB-50 and the polyfunctional resin ANKB-50, we have found out that variation of the copper concentration from  $2.5 \cdot 10^{-5}$  to  $4.2 \cdot 10^{-3}$  M (the loading,  $N_{Cu}$ , changes from  $1.7 \cdot 10^{-3}$  to 0.125) does not affect the exchange rate and the kinetic curves can be described using the Fick model with a constant coefficient of internal diffusion,  $\bar{D} = 3 \cdot 10^{-9} \pm 0.4 \cdot 10^{-9}$ .

In this concentration interval, the rate of copper sorption on ANKB-10 was

TABLE IV  
COEFFICIENTS OF INTERNAL DIFFUSION AND HETP VALUES FOR SORPTION OF YTTRIUM AND EUROPIUM ON ANKB-2 AND KU-2, RESPECTIVELY

Sorbent	Ion	$\bar{D}_{eff} \cdot 10^7$	HETP (cm)	
ANKB-2	$Y^{3+}$	$1.2 \pm 0.3$	$5.8 \pm 0.5$	0.42
		(30°C)	(70°C)	(70°C)
KU-2	$Eu^{3+}$	$2.2 \pm 0.2$	$8.2 \pm 0.8$	0.2
		(30°C)	(85°C)	(85°C)

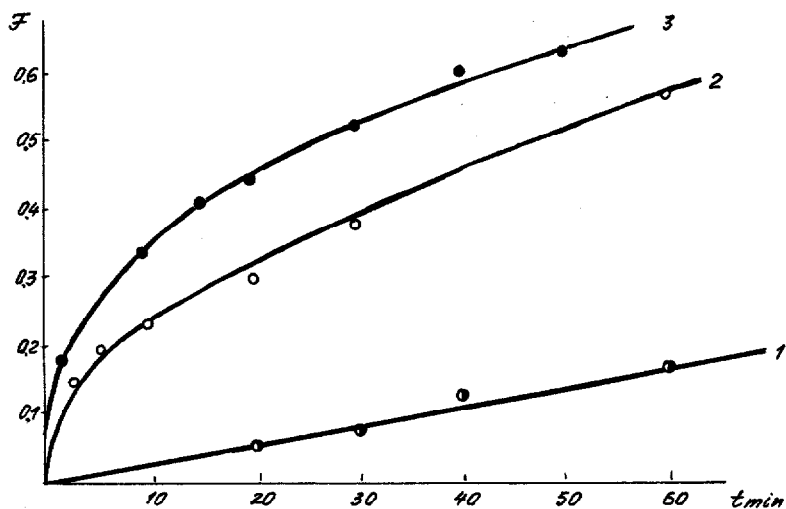


Fig. 8. Kinetic sorption curves for copper from a nickel electrolyte ( $C_{Cu} = 5 \text{ mg/l}$ ) on ANKB-10 at  $25^\circ\text{C}$ : 1, with mechanical stirring (750 rpm); 2, 3, with external cooling ( $25^\circ\text{C}$ ) under ultrasound intensities of 2 (2) and  $4 \text{ W/cm}^2$  (3).

much less than that on ANKB-50 and increased with the copper concentration. At  $N_{Cu} = 0.3$  the effective coefficient of internal diffusion is constant,  $5.6 \cdot 10^{-10} \pm 0.4 \cdot 10^{-10}$  (ref. 17). Since  $\bar{D}$  increases most strongly at low loadings at which the sorption affinity of  $\text{Cu}^{2+}$  to the resin is abruptly augmented (see Fig. 1), the decrease in  $\bar{D}$  for copper sorption on ANKB-10 seems to be due to chemical non-uniformities of the sorbent's functional groups.

Ultrasound strongly affects the kinetic properties of complexing resins<sup>17</sup>. The application of ultrasound reduced the time needed for 20% isolation of copper from a nickel electrolyte ( $\bar{C}_{Cu} = 5.0 \text{ mg/l}$ ,  $\bar{C}_{Ni} = 65 \text{ g/l}$ ) by use of the amphoteric resin

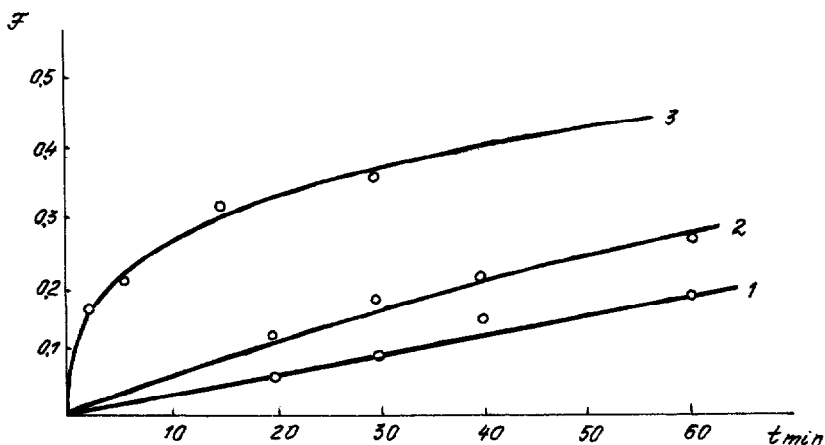


Fig. 9. Kinetic sorption curves for copper from a nickel electrolyte on ANKB-10 at  $25^\circ\text{C}$  with mechanical stirring (750 rpm): 1, 2, non-irradiated resin (1,  $C_{Cu} = 5 \text{ mg/l}$ ; 2,  $C_{Cu} = 10 \text{ mg/l}$ ); 3, preliminary irradiation by ultrasound.

ANKB-10 from 4 h to 2 min. The equilibrium copper sorption then increases from  $2.6 \cdot 10^{-2}$  up to  $3.8 \cdot 10^{-2}$  mg-equiv./g. The effect of ultrasound on the kinetics of copper sorption from a nickel electrolyte is illustrated in Fig. 8. The kinetic properties of ANKB-10 were improved also by preliminary irradiation of the resin. For example, the value of  $F$  for an irradiated resin contacted for 30 min with a nickel electrolyte containing 8 mg/l of copper was 0.35, while that for the corresponding non-irradiated resin was 0.11 (Fig. 9). These data allow us to suggest that ultrasound changes the resin's structure. This has been verified for ANKB-10 resin by electron microscope studies (see Fig. 10).

The investigations described show that the sorption efficiencies of complexing

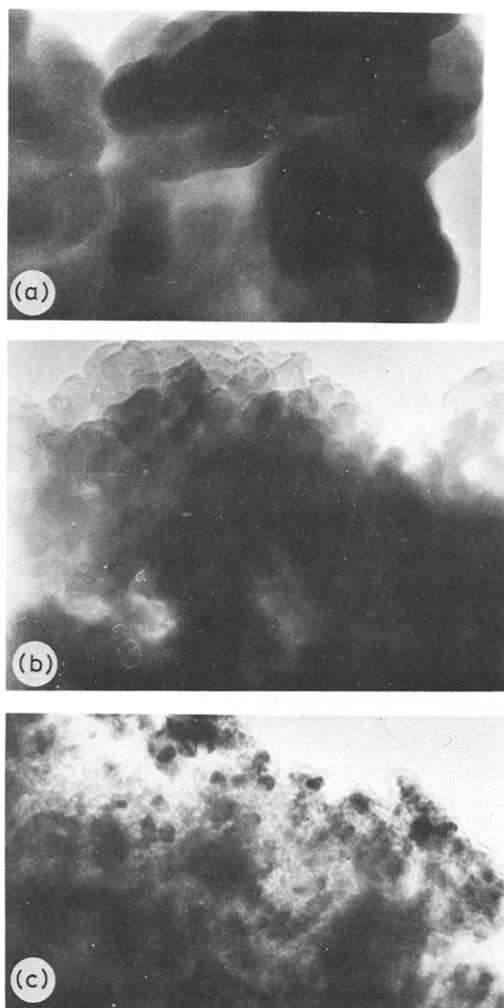


Fig. 10. Electron microscope studies of the structure of ANKB-10: a, initial sample (magnification  $\times 73\,500$ ); b, c, samples treated by ultrasound in water (b) and in a nickel electrolyte (c) (magnification  $\times 68\,250$ ).

resins with weakly dissociated compounds in the resin particles are strongly affected by kinetic properties which, in turn, depend on the resin structure and on the equilibrium and kinetic properties of the systems involved.

## REFERENCES

- 1 R. Hering, *Chelabildende Ionenaustauscher*, Akademie-Verlag, Berlin, 1967.
- 2 F. Helfferich, *J. Phys. Chem.*, 69 (1965) 1178.
- 3 F. Helfferich, *Ionenaustauscher*, Verlag Chemie, Weinheim, 1959.
- 4 H. P. Gregor, L. B. Lutinger and B. M. Loebel, *J. Phys. Chem.*, 59 (1955) 34-39, 366-372.
- 5 K. M. Saldadze and V. D. Kopylova-Valova, *Complexing Ion Exchangers* (in Russian), Khimiya, Moscow, 1980.
- 6 K. M. Saldadze, V. D. Kopylova and T. V. Mekvabishvili, *Zh. Fiz. Khim.*, 46 (1972) 2090.
- 7 N. K. Yufryakova, E. A. Chuveleva, P. P. Nazarov and K. M. Chmutov, *Zh. Fiz. Khim.*, 46 (1972) 1223.
- 8 R. N. Rubinstein, V. A. Alekseenko and E. M. Malakhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8 (1974) 1962.
- 9 N. N. Matorina, S. M. Kagiants, L. V. Shepetyuk and O. V. Kryuchkova, *5th All-Union Conference on Application of Ion Exchange in Industries and Analytical Chemistry, Voronezh, 1981* (in Russian), p. 146.
- 10 N. N. Matorina, L. V. Shepetyuk, L. V. Karlina, O. V. Chelysheva, S. M. Kagiants, K. V. Chmutov, N. B. Galitskaya, M. K. Makarov and A. A. Lobachev, *Sorption and Chromatography* (in Russian), Nauka, Moscow, 1979, p. 122.
- 11 N. N. Matorina, L. V. Shepetyuk, T. I. Formalnova and K. M. Chmutov, *Sorption and Chromatography* (in Russian), Nauka, Moscow, 1979, p. 125.
- 12 N. N. Matorina, S. M. Kagiants, O. V. Kryuchkova and K. V. Chmutov, *Zh. Fiz. Khim.*, 52 (1978) 1991.
- 13 N. N. Matorina, L. V. Shepetyuk, L. V. Karlina, K. V. Chmutov and I. B. Galitskaya, *Zh. Fiz. Khim.*, 52 (1978) 1709.
- 14 N. N. Matorina, S. M. Kagiants, O. V. Kryuchkova and K. V. Chmutov, *Zh. Fiz. Khim.*, 52 (1978) 2005.
- 15 N. N. Matorina, L. V. Shepetyuk, L. V. Karlina, K. V. Chmutov and N. B. Galitskaya, *Zh. Fiz. Khim.*, 52 (1978) 2000.
- 16 L. V. Shepetyuk, N. N. Matorina, T. I. Bakaeva and K. M. Chmutov, *Zh. Fiz. Khim.*, 52 (1978) 1739.
- 17 S. M. Kagiants, *Thesis* (in Russian), Moscow, 1983.
- 18 L. V. Shepetyuk, N. N. Matorina and T. I. Bakaeva, *Zh. Fiz. Khim.*, in press.
- 19 R. Hering, W. Krüger and G. Kuhn, *Z. Chem.*, 2 (1962) 374.
- 20 T. F. Gritmon, M. P. Goedken and G. R. Choppin, *J. Inorg. Nucl. Chem.*, 39 (1977) 2021.
- 21 L. C. Thompson, *Inorg. Chem.*, 3 (1964) 1319.
- 22 N. N. Matorina, L. V. Shepetyuk and T. I. Bakaeva, *U.S.S.R. Pat.*, 1,057,061.
- 23 G. V. Samsonov, *Dokl. Akad. Nauk SSSR*, 97 (1954) 707.
- 24 P. M. Buchatskii, N. N. Matorina and K. V. Chmutov, *Zh. Fiz. Khim.*, 50 (1976) 2621.
- 25 A. I. Kalinichev, T. D. Semenovskaya and K. V. Chmutov, *Sorption and Chromatography* (in Russian), Nauka, Moscow, 1979, p. 144.
- 26 K. V. Chmutov, A. I. Kalinichev and T. D. Semenovskaya, *Dokl. Akad. Nauk SSSR*, 239 (1978) 650.
- 27 G. I. Ushakova, *Thesis* (in Russian), Moscow, 1978.
- 28 N. N. Matorina, L. V. Shepetyuk and K. V. Chmutov, *Zh. Fiz. Khim.*, 41 (1967) 2345.