N. N. MATORINA, Corresponding Member of the USSR Academy of Sciences K. V. CHMUTOV,

N. D. SAFONOVA, L. V. SHCHETOK

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

N. N. MATORINA, Corresponding Member of the USSR Academy of Sciences
K. V. CHMUTOV,
N. D. SAFONOVA, L. V. SHCHETOK

KINETICS OF ION-EXCHANGE PROCESSES IN THE PRESENCE OF COMPLEX-FORMING REAGENTS

When complex-forming eluents are used in the chromatographic separation of ions, as a result of the penetration of the complexing agent into the ion-exchanger grain, additional factors arise that may exert a substantial influence on zone broadening. Neglect of the uptake of the complexing agent when considering the causes of band broadening has often led to incorrect explanations of the phenomenon and to incomprehensible regularities.

The present communication is devoted to a detailed study of the kinetics of ion-exchange processes in the presence of complex-forming reagents, using as an example the extraction of rare-earth elements (REE) by ethylenediaminetetraacetate (EDTA) solutions. For comparison, in certain cases citric acid (H_3Cit) and diethylenetriaminepentaacetic acid (DTPA) were used. To explain the different broadening of chromatographic bands during the separation of REE with citrate and EDTA solutions, some investigators ([1,2]) have put forward the assumption that, in extraction of REE with EDTA solutions, diffusion is not the controlling stage, and that the slowest processes are the complex-formation reactions occurring in solution. Although similar opinions have been expressed repeatedly in our and in foreign literature, as far as we know there are still no direct experimental data confirming this assumption.

Fig. 1. Dependence of the uptake of DTPA (*I*), EDTA (*II*), and H_3Cit (*III*) by KU-2 cation exchanger on the pH of the solution (C_a and C_0 are the concentrations of the complexing agent in the ion exchanger, in mmoles/ml of adsorbent, and in solution, in mmoles/ml of solution).
$C_0 = 0.01\ M$ (DTPA and EDTA) and $0.0139\ M$ (H_3Cit)

1. Sorption of the complexing agents studied

Because of the lack of quantitative data on the uptake of H_3Cit, EDTA, and DTPA by a cation exchanger, the sorption of these acids was studied at various pH values at a temperature of 30°C. The results obtained for KU-2 cation exchanger (8–10% DVB) are shown in Fig. 1. As follows from the curves, the

Fig. 2. Kinetic curves of Eu sorption at pH 3.0 and $t = 30°C$ from a $NaCl$ solution $0.02\,N$ (I) and an EDTA solution $0.01\,M$, $C_{Na} = 0.02\,N$ (II)

Figure 1: Fig. 2. Kinetic curves of Eu sorption at pH 3.0 and $t = 30°C$ from a $NaCl$ solution $0.02\,N$ (I) and an EDTA solution $0.01\,M$, $C_{Na} = 0.02\,N$ (II)

Fig. 3. Effect of KU-2 grain size on the kinetics of Eu desorption by an EDTA solution, pH 3.00, $C_{Na} = 0.02\,N$, $t = 30°C$. $I{-}r = 1.14 \cdot 10^{-2}$ cm, $II{-}r = 2.24 \cdot 10^{-2}$ cm, $III{-}r = 3.78 \cdot 10^{-2}$ cm

Figure 2: Fig. 3. Effect of KU-2 grain size on the kinetics of Eu desorption by an EDTA solution, pH 3.00, $C_{Na} = 0.02\,N$, $t = 30°C$. $I{-}r = 1.14 \cdot 10^{-2}$ cm, $II{-}r = 2.24 \cdot 10^{-2}$ cm, $III{-}r = 3.78 \cdot 10^{-2}$ cm

sorption values decrease sharply with increasing pH, and also on going from DTPA to EDTA and H_3Cit. The sorption of DTPA at pH 2.54 amounted to 0.098 mmole/ml of adsorbent, which is almost 10 times greater than the concentration of DTPA in the initial solution and 20 times greater than in the equilibrium solution.

Since EDTA, DTPA, and H_3Cit are weak polybasic acids, the pH of the solution determines the ratio between dissociated–

ated forms of the acid. When considering the sorbability of these acids as a function of the concentration of the undissociated form of the acid in solution, it was established that the amount of absorbed H_3Cit changes linearly with an increase in the concentration of $[H_3Cit]^\circ$ in solution; for EDTA and DTPA a more complex dependence is observed, and the sorbed amounts of these acids are many times greater than the equilibrium concentration $[H_{nA}]^\circ$. This permits the assumption that, in the cases under consideration, molecular sorption of the undissociated forms of these acids takes place. Thus, H_3Cit, EDTA, and DTPA penetrate into the ionite grain, and therefore it is necessary to take into account the presence of complex ions in the grain even in the case where they are not sorbed by the ionite.

2. Kinetics of ion exchange

Kinetic studies were carried out under conditions excluding external-diffusion retardation. The experimental procedure was analogous

Fig. 2. Kinetic curves of Eu sorption at pH 3.0 and $t = 30°C$ from a $NaCl$ solution $0.02\,N$ (I) and an EDTA solution $0.01\,M$, $C_{Na} = 0.02\,N$ (II)

Fig. 3. Effect of KU-2 grain size on the kinetics of Eu desorption by an EDTA solution, pH 3.00, $C_{Na} = 0.02\,N$, $t = 30°C$. $I{-}r = 1.14 \cdot 10^{-2}$ cm, $II{-}r = 2.24 \cdot 10^{-2}$ cm, $III{-}r = 3.78 \cdot 10^{-2}$ cm

to the procedure described by Kressman and Kitchener ([3]). The component un-

der investigation was present in microconcentration. In the work Ce^{144}–Pr^{144} and $Eu^{152-154}$ were used. In all cases the adsorbent KU-2 with 8-10% DVB was used, preliminarily swollen in the solution under study and brought into equilibrium with this solution with respect to the exchanging and nonexchanging macroions. In this way constancy of the concentrations of all macrocomponent ions in the solution and in the grain was achieved throughout the entire experiment. Determinations were carried out at $t = 30^{\circ}$. The diffusion coefficients were calculated from Boyd' s equation ([4])

$$D = Br^2/\pi^2. \tag{1}$$

The coefficient of internal diffusion determined in this way does not depend on the degree of exchange and is the coefficient of internal diffusion of the microcomponent in the ionite of the given cationic form.

Table 1

$D \cdot 10^8$, cm^2/sec	$r \cdot 10^2$, cm
2.0 ∓ 0.2	1.14 ∓ 0.01
2.1 ∓ 0.2	2.24 ∓ 0.03
1.8 ∓ 0.3	3.78 ∓ 0.07
2.0 ∓ 0.2	

Table 2

$D \cdot 10^7$, cm^2/sec	t, $^{\circ}C$
0.21 ∓ 0.02	30
1.1 ∓ 0.1	54
2.4 ∓ 0.1	83

Figure 2 shows the results of a study of the kinetics of absorption of Eu^{3+} from a $NaCl$ solution $0.02\,N$, pH 3.0, by a cationite in the Na form, and of Eu desorption under the same conditions but in the presence of EDTA $10^{-2}M$. In the latter case, Eu in solution is practically completely bound in a complex (concentration of $M^{3+} \sim 0.01\%$). Since at pH 3.0 the concentration of EDTA in the ionite is close to its concentration in the solution, it may be assumed that, in the case of Eu desorption by an EDTA solution, Eu is present in the grain in the form of the complex $[MA^-]$, and in the case of NaCl–in the form of the hydrated ion M^{3+}. As follows from Fig. 2,

process of ion desorption in the presence of EDTA is substantially slowed. When these data were treated by Boyd' s method (4), a linear dependence of Bt on t was obtained both for the free ion and for the complex ion. Similar data were also obtained for Ce. The internal-diffusion coefficients for the free ions

were $4.0(\pm 0.6) \cdot 10^{-7}$ (Eu^{3+}) and $4.3(\pm 0.8) \cdot 10^{-7}$ (Ce^{3+}); for the corresponding complex ions they were $2.0 \cdot 10^{-8}$ and $1.5 \cdot 10^{-8}$. These data make it possible to suppose that, under the conditions considered, the kinetics of REE EDTA desorption is diffusional, while the processes of formation and dissociation of the complexes exert no noticeable influence.

To confirm this assumption, the effect of particle size was investigated. Figure 3 presents the desorption of Eu EDTA, $10^{-2} M$, pH 3.0, $C_{\mathrm{Na}} = 0.02\,N$, for three particle sizes. The diffusion coefficients calculated from these data are shown in Table 1.

The differences among the individual values of D amount to $\pm 10\%$, which corresponds to the accuracy of measurement of these quantities (10–20%).

Table 3

Conditions of determination	$[CeA^-]/[Ce^{3+}]$	$[Ce^{3+}]$, %	$D \cdot 10^8$, cm^2/sec
$C_{\mathrm{EDTA}} = 0$		100	43 ∓ 8
pH 3.00, $C_{\mathrm{Na}} = 0.02\,N C_{\mathrm{EDTA}} = 0.01\,m$	200	0.5	5.4 ∓ 0.7
pH 3.00, $C_{\mathrm{Na}} = 0.078\,N C_{\mathrm{EDTA}} = 0.01\,m$pH 3.70, $C_{\mathrm{Na}} = 0.02\,N$	10500	0.01	1.5 ∓ 0.1

In Table 2 are given the internal-diffusion coefficients obtained for Eu under these same conditions, but at three temperatures. The activation energy determined from these data is 9000 ± 1000 cal. This value is close to the activation energy published by Boyd and Soldano (5) for the free ions La^{3+} (7530 cal) and Y^{3+} (7310 cal), and is characteristic of a diffusion process in ion exchangers.

Table 3 gives the internal-diffusion coefficients obtained as a result of studying the desorption kinetics of Ce EDTA at different ratios $[CeA^-] : [Ce^{3+}]$. The ratios $[MA^-] : [M^{3+}]$ given in Table 3 correspond to the solution, not to the ion exchanger. However, since these data were obtained under conditions in which the EDTA concentration in the solution and in the ion exchanger is almost the same, they can be used for a qualitative illustration of the influence of the ratio $[MA^-] : [M^{3+}]$. It follows from the data of Table 3 that the rate of ion exchange increases with an increase in the relative concentration of the more rapidly diffusing ion Ce^{3+}.

Table 4

pH	$D \cdot 10^7$, cm^2/sec – H_3Cit, Eu	$D \cdot 10^7$, cm^2/sec – EDTA, Eu	$D \cdot 10^7$, cm^2/sec – EDTA, Ce	$D \cdot 10^7$, cm^2/sec – M^{3+}, Eu^{3+}	$D \cdot 10^7$, cm^2/sec – M^{3+}, Ce^{3+}	C_a/C_p, % – H_3Cit	C_a/C_p, % – EDTA	C_n/Γ_∞, %
3.00	3.0 ∓ 0.2	0.2 ∓ 0.02		4.0 ∓ 0.6	4.3 ∓ 0.8	52 ∓ 5	74 ∓ 7	7
4.40	1.8 ∓ 0.2	1.4 ∓ 0.2				0	0	0.3
3.70			0.15 ∓ 0.01					1.5

Figure 4 compares the results of studying the kinetics of Eu desorption by citrate and ethylenediaminetetraacetate solutions. Curves I and IV were obtained under conditions in which Eu is practically completely bound in the complex (the concentration of $M^{3+} \sim 0.15\%$ for H_3Cit and 0.01% for EDTA), and the concentration of the complexing agent in the grain is almost equal to its concentration in the solution. Curves II and III are for conditions in which H_3Cit and EDTA are practically not absorbed by the ion exchanger (pH 4.40). From these data it follows that the rate of internal diffusion of the Eu citrate complex considerably exceeds the rate of its EDTA complex. The closeness of the internal-diffusion coefficients in the case of EDTA and H_3Cit at pH 4.40 is due to the absence of complexing agent in the grain. In this case, internal diffusion of the free metal ion takes place. The values of the internal-diffusion coefficients obtained under these conditions are given in Table 4. The decrease in D_s in the presence of H_3Cit and EDTA at pH 4.40, compared with D_s of M^{3+}, is apparently due to hydrolysis of M^{3+} in the grain.

For comparison, Table 4 gives the values of the diffusion coefficients of free ions Eu^{3+} and Ce^{3+}, as well as quantities characterizing the relative uptake of H_3Cit and EDTA under various conditions (C_a and C_p are the concentrations of the complexing agent in the adsorbent and in the solution, in millimoles per milliliter of adsorbent and milliliter of solution, respectively) and the relative content of H^+ in the ion exchanger. A comparison of these data shows that the coefficients of internal diffusion of hydrated metal ions decrease with increasing radius of the hydrated ion, i.e., with decreasing atomic number of the rare-earth element, whereas the coefficients of internal diffusion of complex ions increase with increasing atomic number of the rare-earth element, since with increasing atomic number the dimensions of the complex ions decrease. The mobilities of hydrated metal ions and of their complex ions obtained by Shvedov and Stepanov ([6,7]) in an electromigration study of EDTA and citrate complexes of the rare-earth elements change in an analogous way. It should also be noted that the differences in the mobilities of rare-earth ions and of their citrate complexes are considerably smaller than the corresponding differences obtained for EDTA complexes.

Fig. 4. Kinetic curves of Eu desorption by EDTA and H_3Cit solutions.

Figure 3: Fig. 4. Kinetic curves of Eu desorption by EDTA and H_3Cit solutions.

Fig. 4. Kinetic curves of Eu desorption by EDTA and H_3Cit solutions.
I–H_3Cit 0.1 M, pH 3.00, $C_{Na} = 0.1\,N$;
II–H_3Cit $1.39 \cdot 10^{-2}\,M$, pH 4.40, $C_{Na} = 0.02\,N$;
III–EDTA $10^{-2}\,M$, pH 4.40, $C_{Na} = 0.02\,N$;
IV–EDTA $10^{-2}\,M$, pH 3.00, $C_{Na} = 0.02\,N$.

The considerations presented here make it possible to explain the sequence of changes in the coefficients of internal diffusion obtained by Tunitskii in the study of desorption of rare-earth elements by citrate solutions ([8]).

Thus, in considering the broadening of zones in ion-exchange complex-forming chromatography, it is necessary to take into account the possibility of penetration of the complexing agent into the ion-exchanger grain, as well as the state of the ions in the solution and in the sorbent. In the case where the complexing agent is absorbed by the ion exchanger, the presence of complex ions in the grain affects the magnitude of the effective coefficient of internal diffusion D_{eff}, if the D_s values of the free and complex ions differ greatly in magnitude. If, however, the D_s values of these ions are close to one another, then the presence of complex ions in the grain, without being reflected in the magnitude of D_{eff}, determines the regularity of the change of D_{eff} with change in the ionic radius. The presence of the complexing agent in the solution does not affect intradiffusion processes if, under the conditions of chromatographic separation, the complexing agent is not absorbed by the ion exchanger.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
3 VII 1963

CITED LITERATURE

1. F. W. Cornich, G. Phillips, A. Thomas, *Canad. J. Chem.*, **34**, 1471 (1956).

2. M. M. Senyavin, *Collected Volume: Ion Exchange and Its Application*, Publishing House of the Academy of Sciences of the USSR, 1959, p. 84.

3. T. R. E. Kressman, J. A. Kitchener, *Disc. Farad. Soc.*, **7**, 90 (1949).

4. Boyd, Adamson, Myers, in *Collected Volume: Chromatographic Method for the Separation of Ions*, IL, 1949.

5. G. E. Boyd, B. A. Soldano, *J. Am. Chem. Soc.*, **75**, 6091 (1953).

6. V. P. Shvedov, A. V. Stepanov, *Radiochemistry*, **1**, 162 (1959).

7. A. V. Stepanov, V. P. Shvedov, *Radiochemistry*, **1**, 668 (1959).

8. V. V. Nekrasov, E. P. Cherneva et al., in *Collected Volume: Chromatography, Its Theory and Application. Proceedings of the All-Union Conference on Chromatography*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 47.

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