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Ion exchange on resins with temperature-responsive selectivity II. Thermo-induced concentration waves in ion-exchange column

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Abstract

The kinetics of $H^+ - Cu^{2+}$, $H^+ - Zn^{2+}$, $Zn^{2+} - Cu^{2+}$, and $Cu^{2+} - Zn^{2+}$ exchanges on iminodiacetic resin Lewatit TP-207 at 293 K has been studied. The effective diffusion coefficients of Cu^{2+} and Zn^{2+} have been determined to be 2.6×10^{-8} and 1.4×10^{-7} cm^2/s , respectively, for the given conditions. The kinetics of Cu^{2+} and Zn^{2+} thermostripping from the resin preequilibrated with a mixture of zinc and copper sulfates at pH 1.8 have been shown to be influenced by the different metal ion diffusivities and by the presence of a third component (H^+) in the system so that an oscillation of ion concentration is observed. This phenomenon is observed more clearly with the increase of resin beds when studying the dynamics of the column thermostripping process. Formation of a concentration wave results in the enrichment of the first halfwave with Zn^{2+} while the second halfwave appears to be enriched with Cu^{2+} . A mathematical model of ion-exchange dynamics of components with dissimilar diffusivities has been developed. The phenomenon of formation of concentration waves is interpreted within the model as a result of the influence of a local electrical field, arising in the resin phase, from the difference on fluxes of exchanging ions. The results of computer simulation of the thermostripping process within the frame of the model proposed are in a good agreement with those obtained in thermostripping experiments. © 1998 Elsevier Science B.V.

Keywords: Concentration waves, thermo-induced; Thermostripping; Ion-exchange dynamics; Copper; Zinc

1. Introduction

Multicomponent ion-exchange systems play an essential role in nature, science and technology. Ion-exchange in soils [1–3], chromatographic separation of ionic substances [4–6], deionization and softening of water [7–9], recovery of valuable mineral com-

ponents from sea water [10,11] and other hydromineral sources [12–14] represent the most clear examples of multi-ionic exchange processes of great theoretical and practical importance. Intensive investigations in this field of ion-exchange science and technology have been carried out within the last decades. Some of the results obtained are summarized in monographs and periodical publications dedicated to the main topics of the multicomponent ion-exchange such as, ion-exchange equilibrium [1,11], kinetics [15,16] and dynamics [17–20].

Several models have been proposed to describe the

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ion-exchange equilibrium in terms of the interaction between a charged surface of the ion-exchanger and the ions under separation. Most of them are based on the Gouy–Chapman–Stern theory for the double electric layer [21–27] and can be classified as electrostatic retention models [27]. Furthermore all these models describe the ion-exchange separation under isothermal conditions and do not account for the dynamic features of the particular ion-exchange system.

The separation of multicomponent ionic mixtures by dual-temperature ion-exchange techniques has attracted scientists since the beginning of the 1960s [28]. The main advantage of this fractionation technique deals with the possibility of designing reagentless and wasteless, as a result, ion-exchange separation processes [10]. Parametric pumping [29–32], thermal ion-exchange fractionation [33,34] and allied dual-temperature ion-exchange processes [10–13,35–37] may be included in the group of separation methods exploiting the differences of the ion-exchanger affinity towards the target ionic species to govern the process of fractionation. Practical application of the above separation techniques is still limited due to the lack of information available on the equilibrium, kinetics and dynamics of multi-ionic ion-exchange systems at different temperatures. This is particularly true for the kinetics and dynamics of multicomponent ion-exchange. Only a few communications report the results obtained in this field [11,12,36–38], but data on nonisothermal dynamics of ion-exchange are practically absent in the literature.

In the preceding communication of this series we reported the results on studying the ion-exchange equilibrium of Cu^{2+} and Zn^{2+} on iminodiacetic (IDA) and aminomethylphosphonic resins at different temperatures [39]. The present paper accomplishes the investigation of the Cu^{2+} – Zn^{2+} exchange on IDA resin system with results obtained by the systematic study of:

1. kinetics of the Zn^{2+} – Cu^{2+} – H^+ exchange on IDA resin;
2. kinetics of thermostripping of metal ions from the resin phase;
3. dynamics of thermostripping in column at different temperatures;
4. mathematical model describing the nonisothermal ion-exchange dynamics;

5. a physical model to explain the phenomenon of formation of concentration waves.

This is the first time that the formation of concentration waves during the dual-temperature thermostripping cycles has been observed. The new phenomenon is discussed and described in terms of the proposed model. The validity of this model is demonstrated by a satisfactory fit with the experimental results.

2. Experimental section

2.1. Reagents, ion-exchangers, and apparatus

Zinc sulfate, copper sulfate, and sulfuric acid of p.a. grade were purchased from Panreac (PA, Barcelona, Spain). Macroporous IDA ion-exchanger, Lewatit TP-207, was kindly supplied by Bayer Hispania Industrial, S.A. (Barcelona, Spain). Doubly distilled water was used in all experiments. Prior to experiments, all solutions were degassed by using an ultrasonic bath (Branson 1200, Danbury, CT, USA) and a vacuum pump. The ratio of Zn^{2+} to Cu^{2+} in stock solution, of a total concentration of $(\text{Cu}^{2+}, \text{Zn}^{2+})\text{SO}_4^{2+}$ of 0.165 ± 0.008 mol/dm³, was kept constant at 8.5 ± 0.5 . The pH of the stock solution was adjusted to 1.9 ± 0.10 with 0.1 M H_2SO_4 and kept constant (see Ref. [31] and note 25 therein.). Standard precautions recommended for handling sulfuric acid solutions [40] were followed when adjusting pH and preparing the 0.1 M H_2SO_4 solution from concentrated acid. The concentrations of metal ions were determined by atomic emission spectroscopy using the inductively coupled plasma (ICP)-AES technique with an ARL Model 3410 spectrometer (Fisons, Valencia, CA, USA) provided with minitorch. The emission lines for the spectrochemical analysis were 224.700 nm for Cu^{2+} and 206.191 nm for Zn^{2+} . The uncertainty of metal ions determination was <1.5%. Determination of H^+ concentration was carried out by potentiometric titration using a Crison pH meter 507 (Barcelona, Spain) provided with a combined glass electrode. Jacketed glass columns of either 1.1 or 1.4 cm I.D. connected with a thermostat (Selecta Ultraterm 6000383, Barcelona, Spain) were used for studying the ion-exchange kinetics and dynamics at different temperatures. The construction of the columns pro-

vided the simultaneous thermostatic conditioning of both resin and entering solution phases.

Narrow granulometric fraction of Lewatit TP-207 resin was obtained by sieving air-dry samples of the ion-exchanger using 0.42 mm mesh so that only the resin beads stuck in the holes of the sieve were collected. An average diameter of the beads in the swollen state was determined by microscopic technique and appeared to be 0.048 ± 0.002 cm. The columns were charged with a certain portion of the resin (0.5 g for the kinetic experiments and either 2.0 or 3.0 g for the dynamic experiments) which was kept constant while the given series of experiments was carried out.

2.2. Procedures

Kinetic experiments to study $H^+ - Zn^{2+}$, $H^+ - Cu^{2+}$, $Zn^{2+} - Cu^{2+}$, and $Cu^{2+} - Zn^{2+}$ exchanges were carried out at 293 K in thermostatic columns applying the shallow bed technique (see Ref. [2], p. 94). A column containing the resin in the desired ionic form (resin bed of ~ 0.5 cm height in a thermostatic column of 1.4 cm I.D.) was preequilibrated with H_2SO_4 solution (pH 1.9) at 293 K and then a solution of either 0.14 M $ZnSO_4$ or 0.016 M $CuSO_4$ at pH 1.9 was passed through the column at a constant flow-rate of $32 \text{ cm}^3/\text{min}^2$ and collected in portions where H^+ , Zn^{2+} and/or Cu^{2+} concentrations were determined. The eluate was collected in portions in preweighed vials, and the volume of the eluate portions was determined by weighing these vials with eluate samples and taking the difference in weight. The accuracy of volume determination was $\pm 0.005 \text{ cm}^3$. The degree of the resin bed conversion, F , was calculated from the data of the analysis as follows:

$$F = \frac{\sum_j^N v_j (c_i^0 - c_i)}{Q_i} \quad (1)$$

where v_j is the volume of eluate portion “ j ”, cm^3 ; c_i^0 and c_i are the concentrations of either Zn^{2+} or Cu^{2+} in the initial solution and in the “ j ” eluate portion respectively, expressed in $\text{mequiv}/\text{cm}^3$; Q_i is the

capacity of the resin bed towards the ionic species under consideration, in mequiv , obtained in separated experiments under appropriate equilibrium conditions; and “ N ” is the number of eluate portions where $c_i^0 - c_i \geq \Delta c$, Δc being the absolute uncertainty on the determination of the metal ion concentration.

Kinetic experiments on thermodesorption (thermostripping) of Cu^{2+} and Zn^{2+} were carried out as follows: the resin portion (resin bed of 0.7 cm height in a thermostatic column of 1.1 cm I.D.) was preequilibrated with the stock solution of Cu^{2+} and Zn^{2+} mixture at 353 K, then, the solution flow was stopped and the excess of the stock solution was removed from the column until its level coincided with that of the resin bed. The column was cooled at 293 K, then cold stock solution (at 293 K) was passed through the resin bed at a high flow-rate ($32 \text{ cm}^3/\text{min}$) and collected in portions where Cu^{2+} and Zn^{2+} concentrations were determined.

Thermostripping experiments were carried out under dynamic conditions by using the following procedure: after equilibration of the resin (resin portion of either 2 or 3 g) with the stock solution containing a $Cu^{2+} - Zn^{2+}$ mixture at certain temperature, the excess of the equilibrium solution was removed from the column as described before. Then, the cooling of the column was started. After reaching the appropriate temperature, the same stock solution was passed through the column and collected in portions followed by determination of Zn^{2+} , Cu^{2+} and H^+ concentrations.

Finally, in the series of experiments for differential thermostripping, a sequential procedure was followed. Thus, after achieving the ion-exchange equilibrium at the second temperature (first cycle), the resin was underwent the second and third thermostripping cycles by following the mentioned procedure for a single thermostripping experiment.

3. Results

3.1. Kinetics of ion-exchange

The typical F versus time kinetic curves of $H^+ - Zn^{2+}$ and $H^+ - Cu^{2+}$ exchange on IDA resin in the H-form from either 0.14 M $ZnSO_4$ or 0.016 M $CuSO_4$ solutions at pH 1.9 are shown in Fig. 1. As

²This value of the solution flow-rate has been shown to fit the conditions of the “shallow bed” technique.

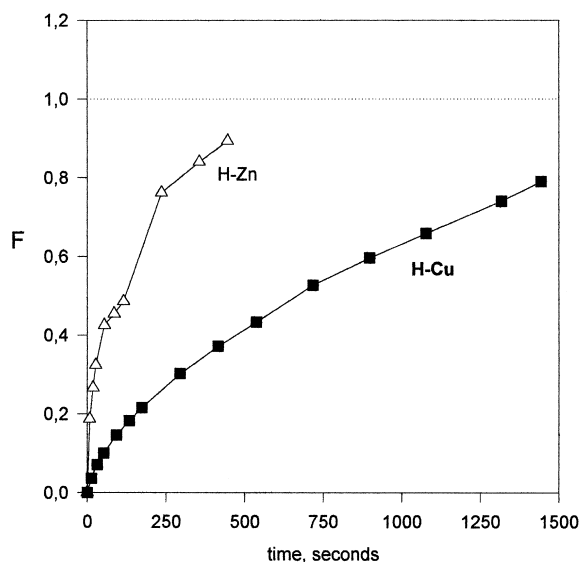


Fig. 1. Kinetic curves of $H^+ - Zn^{2+}$ (triangles) and $H^+ - Cu^{2+}$ (squares) exchanges on Lewatit TP-207 resin at 293 K (see text). Experimental conditions: 0.5 g of resin (~ 0.5 cm of resin height), 0.14 M $ZnSO_4$ (pH 1.9), 0.016 M $CuSO_4$ (pH 1.9), flow-rate of 32 cm^3/min .

seen, the $H^+ - Zn^{2+}$ exchange proceeds much faster than that in the $H^+ - Cu^{2+}$ system. This can be attributed to the difference in IDA resin affinity towards metal ions under study (see below and Refs. [37,39]), which correlates with the order of stability constants of ZnIDA and CuIDA complexes (formed by metal ions and the monomeric IDA) known to be $\log K_{ZnIDA} = 7.27$ and $\log K_{CuIDA} = 10.63$ [41,42] by assuming the stability of Cu^{2+} and Zn^{2+} complexes with IDA resin to be nearly of the same order of magnitude as that of metal complexes with monomeric IDA. This supposition has been confirmed to be valid for the ion-exchange of this particular ion couple on IDA resin [37,39]. The diffusion of complex forming metal ions in the chelating resins is known to proceed by the “relay” mechanism [43]. According to this mechanism, the rate of metal ion diffusion in the resin phase is mainly determined by the time of ion retention by the functional group of the ion-exchanger (in the potential hole), τ_0 , which is proportional to the energy of interaction of metal ion and the functional group. Hence, the higher τ_0 values correspond to the more stable metal ion complex formed (CuIDA in our case) and, consequently, the

slower is the diffusion rate of this particular ion (Cu^{2+}) in the resin phase.

The difference in the IDA complex stabilities also influences the kinetics of the metal ions exchange. The kinetics of the ion-exchange reaction in this case is known to depend on the selectivity of the resin towards exchanging ions, i.e., it depends on the type of the isotherm of ion-exchange so that fast kinetics are observed for the convex isotherm (the resin is more selective for the entering ion than towards the initial one) while for the concave one (the sorbability of the initial counter ion is higher than that of the entering one) the rate of the ion-exchange is much lower [44]. Indeed, as seen in Fig. 2, where the kinetic curves of $Zn^{2+} - Cu^{2+}$ and $Cu^{2+} - Zn^{2+}$ exchanges are shown, the kinetics of the later ion-exchange reaction, which proceeds “against” the resin selectivity [37,39], appears to be far slower than that of the former. In this system, the selectivity of the resin can be easily evaluated from the difference between respective $\log K_{MIDA}$ values (here $M = Cu, Zn$). Then, for $Zn^{2+} - Cu^{2+}$ exchange one obtains: $\log K_{CuIDA} - \log K_{ZnIDA} = 3.36 > 0$, i.e., the isotherm of this ion-exchange reaction is convex. On

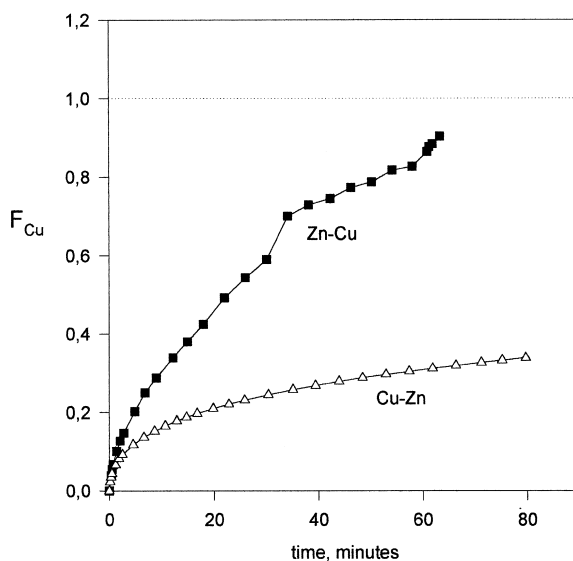


Fig. 2. Kinetic curves of $Zn^{2+} - Cu^{2+}$ (squares) and $Cu^{2+} - Zn^{2+}$ (triangles) exchanges on Lewatit TP-207 resin at 293 K (see text). Experimental conditions: 0.5 g of resin (~ 0.5 cm of resin height), 0.14 M $ZnSO_4$ (pH 1.9), 0.016 M $CuSO_4$ (pH 1.9), flow-rate of 32 cm^3/min . Errors bars for c_i/c_i^0 have been included.

the contrary, the isotherm of the Cu^{2+} – Zn^{2+} exchange is concave.

The typical concentration–time history obtained in studying the kinetics of thermostripping is shown in Fig. 3. As seen in Fig. 3, right after the alteration of the temperature in the column from 353 to 293 K, the release of Zn^{2+} from the resin and sorption of Cu^{2+} are observed. As a result, the first portion of the eluate collected (the volume of the first portion, $v_1 = 4.04 \text{ cm}^3$, significantly exceeds the interbed volume of the resin portion used) appears to be enriched with zinc and depleted with copper. Further elution with the cold stock solution causes the desorption of both metal ions. As one can observe in Fig. 3, the fluctuations of concentrations of both metal ions in the eluate are reminiscent of an oscillation-like pattern. Nevertheless, under the shallow bed conditions these fluctuations lie within the corridor of uncertainties on concentration determination. Hence, to make this effect more clearly pronounced a higher resin bed is required. These fluctuations will be clearly manifested in separate experiments when studying the dynamics of ion-exchange in the system under consideration, as described below.

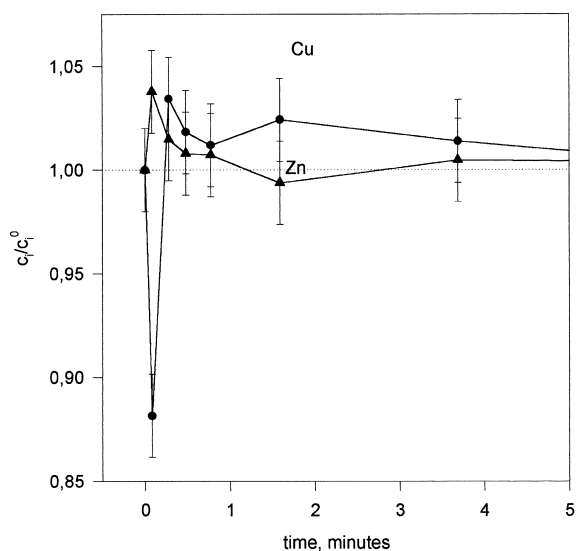


Fig. 3. Kinetics of Cu^{2+} and Zn^{2+} release in thermostripping from Lewatit TP-207 (see text). Experimental conditions: 0.5 g of resin ($\sim 0.7 \text{ cm}$ of resin height), 0.14 M ZnSO_4 , 0.016 M CuSO_4 , pH 1.9, flow-rate of $32 \text{ cm}^3/\text{min}$.

3.2. Dynamics of thermostripping

The thermostripping breakthrough curve obtained by passing cold stock solution at 283 K through the

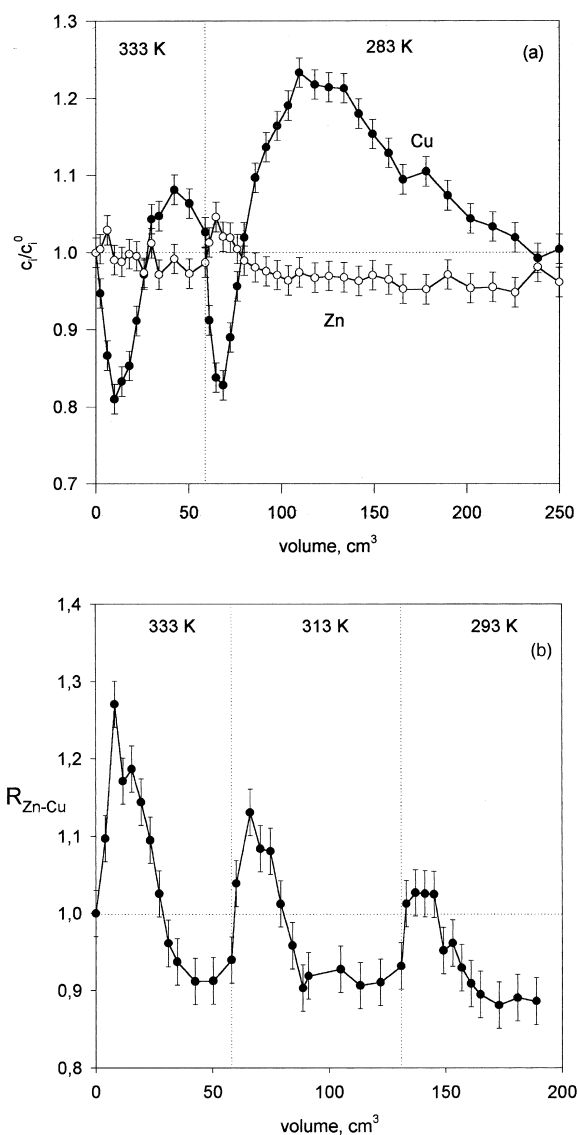


Fig. 4. Differential thermostripping breakthrough curves for Lewatit TP-207 (2 g of resin). (a) Sequential stripping with stock solution at 333 and 283 K from resin preequilibrated with the same solution at 353 K (relative concentration vs. volume history). (b) Sequential stripping with stock solution at 333, 313, and 293 K ($R_{\text{Zn-Cu}}$ vs. volume history) (see text). Experimental conditions: 2.0 g of resin ($\sim 2 \text{ cm}$ of resin height), 0.14 M ZnSO_4 , 0.016 M CuSO_4 , pH 1.9, linear flow-rate of $0.8 \text{ cm}^3/\text{min}$.

resin bed (2 g of the air-dry resin) preequilibrated with the same solution at 333 K, is shown in Fig. 4a. The concentration of Cu^{2+} in the first portions of the stripping solution appears to be lower than that in the stock solution and then grows up. More clearly, the oscillation of metal ion concentrations is seen in Fig. 4b, where the breakthrough curves presented as the ratio of the relative metal ion concentrations ($R_{\text{Zn}-\text{Cu}} = [c_{\text{Zn}}/c_{\text{Zn}}^0] : [c_{\text{Cu}}/c_{\text{Cu}}^0]$) vs. volume histories indicate the formation of successive concentration waves. The curves were obtained in differential thermostripping cycles, carried out at 353→333 K (equilibration→stripping temperatures); 333→313 K, and 313→293 K.

4. Discussion

Interpretation of the results obtained in this study has to first consider the kinetic features of the system under investigation. The qualitative conclusion about the difference in the rates of $\text{H}^+ - \text{Cu}^{2+}$ and $\text{H}^+ - \text{Zn}^{2+}$ ion-exchange reactions (see Section 3) can be confirmed quantitatively. Estimate for this purpose the diffusion coefficients of Cu^{2+} and Zn^{2+} , \bar{D}_{Cu} and \bar{D}_{Zn} , in the resin phase, since the intraparticle diffusion has been shown to be the rate-controlling step in this case [39]. Such an estimation can be done by using the following expression [45,46]:

$$\bar{D}_i = 0.03 \frac{r_0}{t_{0.5}} \quad (2)$$

where r is the radius of the swollen resin bead, cm (see Section 2), and $t_{0.5}$ is the time of the resin half-conversion, s. The $t_{0.5}$ values for $\text{H}^+ - \text{Cu}^{2+}$ and $\text{H}^+ - \text{Zn}^{2+}$ exchanges were determined from the results of respective kinetic experiments (see Fig. 1) and appeared to be 665 and 120 s, respectively. Calculated \bar{D}_{Cu} and \bar{D}_{Zn} values equal 2.6×10^{-8} and $1.4 \times 10^{-7} \text{ cm}^2/\text{s}$, respectively. A comparison of \bar{D}_{Cu} determined in this study (at 293 K) with \bar{D}_{Cu} values reported by Nativ et al. [47] for IDA resin (at higher temperatures) is shown in Fig. 5 and testifies to a good agreement of diffusion coefficients within the $\bar{D}_{\text{Cu}} = f(T)$ dependency presented.

Two factors have to be taken into account to interpret the results shown in Figs. 3 and 4: the

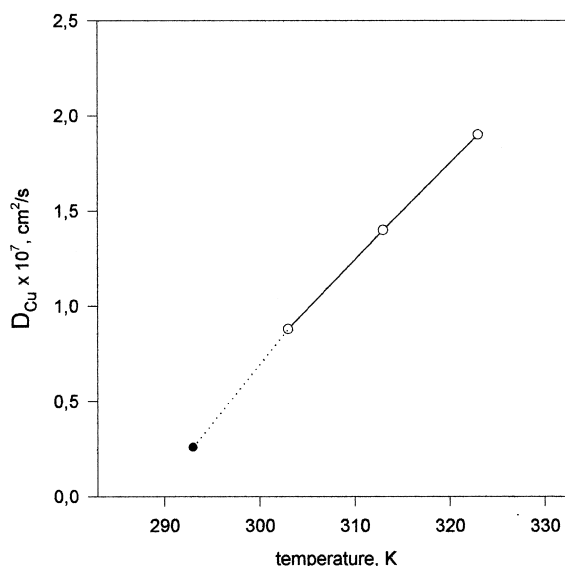


Fig. 5. Temperature dependence of Cu^{2+} diffusion coefficient (\bar{D}_{Cu}) in iminodiacetic resins Dowex A-1 (open points, data taken from Ref. [47]) and Lewatit TP-207 (filled point, this work).

difference in metal ion diffusivities and the effect of the third (H^+) ion. These factors are known to influence both the kinetics [15] and dynamics [38] of ion-exchange, so that concentration extrema on the respective kinetic or dynamic breakthrough curves are observed. A comparison of the results presented in Fig. 3 with those shown in Fig. 4 indicate that the oscillation “signal” obtained on a low resin bed (see Fig. 3) is too weak to exceed the level of the “phone”, i.e., the modulations observed lie within the corridor of uncertainties on concentration determinations. Increase of the resin bed height leads to the “amplification” of the “signal”, see Fig. 4, where Cu^{2+} and Zn^{2+} concentration waves become clearly distinguishable. These results lead to the conclusion that ionic species of dissimilar diffusivities strongly influence the dynamics of ion-exchange and can manifest the appearance of sequential concentration waves. The necessary condition for developing this phenomenon is the presence of a third ionic component in the system, in this case H^+ . Indeed, protons, whose concentration in the stock solution $\approx 0.02 \text{ mol}/\text{dm}^3$, play an active role in the stripping process, as follows from the results, shown in Fig. 6. As seen in this figure, each thermostripping cycle is accompanied by sorption of

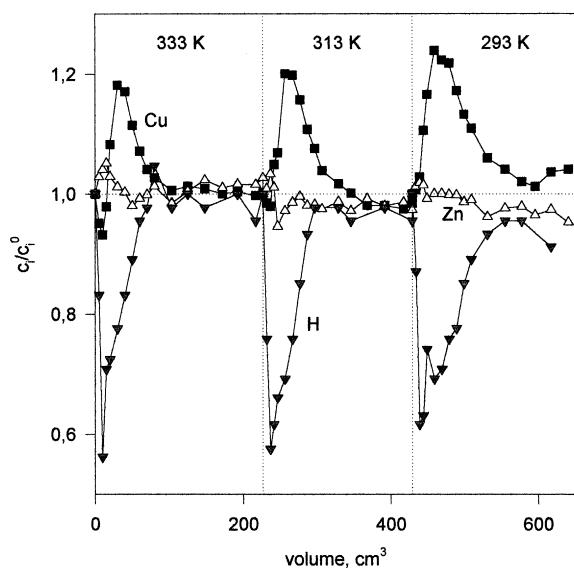


Fig. 6. Differential thermostripping breakthrough curves of Cu^{2+} (squares), Zn^{2+} (triangles), and H^+ (inverted triangles) from Lewatit TP-207. Sequential stripping with stock solution at 333, 313, and 293 K from resin preequilibrated with the same solution at 353 K. Experimental conditions: 3.0 g of resin (~ 3 cm of resin height), 0.14 M ZnSO_4 , 0.016 M CuSO_4 , pH 1.9, linear flow-rate of 0.8 cm/min.

H^+ from the solution passing through the resin bed. The results obtained have allowed us to propose a model for the interpretation of the thermostripping process as described below.

4.1. Model description

The model is based on the following premises, which are mostly accepted as applying to kinetics of ion-exchange [48–57]:

1. Particle diffusion is the kinetic rate determining step;
2. Convective transport is neglected;
3. Solvent uptake or release as well as any shrinking or swelling volumetric variations of the resin beads are neglected;
4. Individual diffusivities of mobile ionic species are assumed to be constant;
5. Local total amount of ionic species in the resin phase is assumed to be constant;
6. Coupling and equalizing of ionic fluxes other than

by local electric field arising in the resin beads are disregarded;

7. The interphase mass exchange coefficients are assumed to be constant throughout each thermostripping cycle;
8. The thermostripping process is assumed to be fast enough, so, the local ion-exchange equilibrium is maintained at all times at any location in the ion-exchanger;
9. The variation of the SO_4^{2-} concentration during one thermostripping cycle is neglected.

Consider an ion-exchange column filled with the ion-exchanger of definite granulation. The resin is preequilibrated with a solution of ions mixture of certain composition at T_1 , then the same solution is passed at a flow-rate V through the column at T_2 . The total concentration of each component of the solution (in the form of both free ions and sulfate complexes) can be expressed through the stability constants of the respective complex species, k_i , as follows:

$$\bar{c}_i = c_i [1 + k_i(T) c_{\text{SO}_4}(T)];$$

$$i = \text{H}^+, \text{Cu}^{2+}, \text{Zn}^{2+}. \quad (3)$$

For the particle diffusion control, the ion-exchange process is known to be described by a model [46,55] which includes the following equations:

mass balance equation:

$$\varepsilon \frac{\partial \bar{c}_i}{\partial t} + V \frac{\partial \bar{c}_i}{\partial z} + \frac{\partial q_i}{\partial t} = 0; \quad (4)$$

general equation of ion-exchange kinetics:

$$\frac{\partial q_i}{\partial t} = f_i(q_i^*; q_i) \quad (5)$$

mass-action law:

$$K_i \left(\frac{c_i}{q_i^*} \right)^{n_i} = K_j \left(\frac{c_j}{q_j^*} \right)^{n_j}; \quad K_i = K_i(T) \quad (6)$$

electroneutrality equations:

$$\sum_1^N q_i^* = \sum_1^N q_i = Q_\Sigma \quad (7)$$

initial and boundary conditions:

$$\begin{aligned} q_i|_{r=0} &= q_i^*|_{r=0}; c_i|_{r=0} = c_i^{\text{init}}; \\ c_i|_{z=0} &= c_i^{\text{bound}} \end{aligned} \quad (8)$$

Considering in more detail the kinetic Eq. (4), some of the ions participating in the ion-exchange interaction are fixed on the functional groups of the ion-exchanger and can be considered as “immobilized” in the resin phase. Other ions, which appear due to the partial dissociation of the resin-counterion complexes, are present in the internal solution in a free state. The particle diffusion proceeds mainly through the intrabead space occupied with the internal solution [44], and leads to the equalizing of local ion concentrations inside the resin bead. Therefore, the higher the degree of ion immobilization, the slower the diffusion process observed, i.e., it corresponds to the lower \bar{D}_i value. In the ion-exchange process under consideration, the equilibrium constants of H^+ , Cu^{2+} or Zn^{2+} binding in the resin phase are substantially different (see below), hence, the effective coefficients of particle diffusion, \bar{D}_i , for these ions must also be different.

The entering ion flux must be equal to that leaving the resin bead throughout the whole ion-exchange process. In the case when interacting ions diffusivities are remarkably different, the last condition can be fulfilled only if the charge redistribution and the appearance of an electric field in the resin phase proceeds [45,46]. The field is directed radially towards bead surface and equalizes the entering and leaving ion fluxes. Numerical estimations show, that the charge redistribution is negligibly small and the medium can be considered neutral with a high degree of accuracy [45]. Furthermore, this field has been shown to influence dramatically the dynamics of the ion-exchange process [38].

When an electric field is absent, Eq. (5) takes the form:

$$\frac{\partial q_i}{\partial t} = \beta_i (q_i^* - q_i) \quad (9)$$

where β_i is the mass-transfer coefficient, which is proportional to the effective diffusion coefficient, \bar{D}_i .

In the presence of an electric field, Eq. (9) takes the form:

$$\begin{aligned} \frac{\partial q_i}{\partial t} &= -S J_i|_{x=r_0} \\ &= S \bar{D}_i \left(\frac{\partial q_i^{\text{loc}}}{\partial x} + \frac{F}{RT} q_i^{\text{loc}} n_i E \right) |_{x=r_0} \end{aligned} \quad (10)$$

where q_i is the average concentration of the component in the resin bead; q_i^{loc} is the local concentration; S is the parameter characterizing the geometry of the bead which, in the simplest case, equals to the ratio of the surface area to the volume of the bead, r_0 is the radius of the resin bead. This equation, is too complex to be applied in the solution of dynamic problems. However, the partial derivative term on the right member of Eq. (10) can be approximated (as it is done in the absence of an electric field) as follows [58]:

$$\frac{\partial q_i^{\text{loc}}}{\partial x} \approx \frac{q_i^* - q_i}{r_0}; q_i^{\text{loc}} \approx \frac{q_i^* + q_i}{2} \quad (11)$$

From Eqs. (10) and (11) one obtains:

$$\begin{aligned} \frac{\partial q_i}{\partial t} &= S \bar{D}_i \left(\frac{q_i^* - q_i}{r_0} + \frac{F}{RT} \frac{q_i^* + q_i}{2} n_i E \right) \\ &= \beta_i (q_i^* - q_i + I (q_i^* + q_i) n_i) \end{aligned} \quad (12)$$

where $\beta_i = S \bar{D}_i / r_0$; $I = 0.5(F/RT)Er$.

Comparison of Eq. (12) with Eq. (9) shows that they differ from each other by the term

$$\beta_i I n_i (q_i^* + q_i) \quad (13)$$

Parameter β_i is used as a fitting parameter. Nevertheless, β_i values for Cu^{2+} and Zn^{2+} correspond quite well to the ratio of their diffusion coefficients determined experimentally, $\bar{D}_{\text{Cu}} = 2.6 \times 10^{-8}$ and $\bar{D}_{\text{Zn}} = 1.4 \times 10^{-7}$ cm^2/s , respectively. Parameter I is in fact the dimensionless density of the electric field and it is estimated from the respective resin characteristics. The E value varies during the ion-exchange cycle, having the maximum value at the beginning (around 5×10^{-2} V/cm). An estimated value of the radial density of the electric field (E) lies in the range of 10^{-1} – 10^{-3} V/cm.

Thus, the model of the process includes Eqs. (3)–(7), where the kinetic Eq. (5) is written in the form of Eq. (12).

4.2. Results of computer simulation

A computer simulation of the thermostripping process dynamics in the tricomponent system, involving H^+ , Cu^{2+} and Zn^{2+} , was carried out by applying the proposed model. The model parameters as well as the boundary and initial conditions used in computer simulation corresponded to those applied

Table 1
Values of Cu^{2+} , Zn^{2+} and H^+ concentrations in resin phase and relative equilibrium constants K_i at different temperatures

T (K)	q_{Cu}^*	q_{Zn}^*	q_{H}^*	K_{Cu}	K_{Zn}	K_{H}
293	3.8	0.42	1.08	9.00	1	46
313	4.0	0.50	0.80	8.50	1	30
333	4.3	0.65	0.35	7.75	1	12
353	4.4	0.90	0	6.63	1	0

in the experiments. The following values of model parameters were used in computations: $m=3$ g; $\varepsilon=0.33$; $Q_{\Sigma}=5.3$ mequiv/g; $V=0.4$ cm/min; $n_{\text{H}}=1$; $n_{\text{Cu}}=2$; $n_{\text{Zn}}=2$; $\beta_{\text{H}}=0.1$ min⁻¹; $\beta_{\text{Zn}}=0.2$ min⁻¹, and $\beta_{\text{Cu}}=0.04$ min⁻¹. The initial and boundary concentrations of system components in the solution phase were constant throughout the process: $c_{\text{H}}^0=0.02$; $c_{\text{Cu}}^0=0.033$, and $c_{\text{Zn}}^0=0.30$ g-equiv/dm³, and were considered to equal each other, i.e., $c_i^{\text{init}}=c_i^{\text{bound}}$. The values of the equilibrium constants K_i (dimensionless) as well as the equilibrium ions content, $q_i^*(0,t)$, in the resin phase at different temperatures are given in Table 1.

A comparison of the experimental results with the results of computer simulation is shown in Fig. 7. As follows from Fig. 7, the results of the process

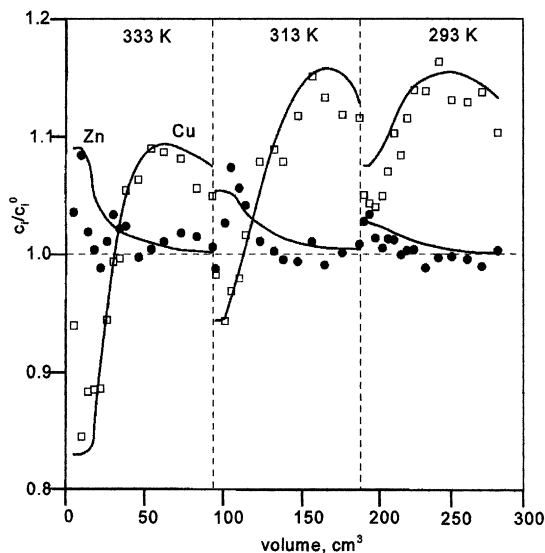


Fig. 7. Computed (curves) and experimental (points) differential thermostripping breakthrough curves. Curves have been computed with model parameters given in text. Experimental conditions: 3.0 g of resin (~3 cm of resin height), 0.14 M ZnSO_4 , 0.016 M CuSO_4 , pH 1.9, linear flow-rate of 0.4 cm/min.

modeling (lines) are in a good qualitative and quantitative agreement with the experimental data (points). This confirms the validity of the model proposed and allows us to interpret the results obtained within the following physical model, which is consistent with the above described. As follows from the data given in Table 1, the decrease of the temperature from T_1 to T_2 in the system under consideration within each differential thermostripping cycle (see Section 2) must result in the desorption of certain amounts of Zn^{2+} and Cu^{2+} , accompanied by the sorption of H^+ , for reaching the ion-exchange equilibrium at T_2 . The kinetic coefficient β_{Cu} (see above) is much lower than that of Zn^{2+} , due to the much higher K_{Cu} values in comparison with K_{Zn} (see Table 1). The process of Zn^{2+} release from the resin phase proceeds rather fast, since β_{Zn} is sufficiently high (see Table 1). The outflowing flux of Zn^{2+} ions throughout the thermostripping cycle must be compensated by an equivalent flux of ions entering the ion-exchanger, namely H^+ . However, H^+ concentration is not sufficient to balance completely Zn^{2+} desorption. This results in the appearance of an electric field in the resin phase, which equalizes ion fluxes. The field “draws” Cu^{2+} into the sorbent, that leads to the drop of copper concentration in the first portions of the eluate, where concentration of Zn^{2+} exceeds that in the stripping solution, i.e., a partial simultaneous separation of Zn^{2+} from Cu^{2+} in the first concentration halfwave is observed. After desorption of the main part of an excessive Zn^{2+} from the resin, the field intensity decreases and Cu^{2+} starts to be desorbed into the solution phase being displaced by H^+ . As a result, the eluate portions corresponding to the second halfwave appear to be enriched with Cu^{2+} .

5. Conclusions

From the results of the present study, the following conclusions can be stated:

(a) Diffusion coefficients of Cu^{2+} and Zn^{2+} in Lewatit TP-207 resin of IDA type have been determined from binary $\text{H}^+ - \text{Cu}^{2+}$ and $\text{H}^+ - \text{Zn}^{2+}$ exchanges at 293 K and appear to be 2.6×10^{-8} and 1.4×10^{-7} cm²/s², respectively.

(b) The difference in Cu^{2+} and Zn^{2+} diffusivities as well as the presence of the third H^+ ion in the

system strongly influences the kinetics of metals thermostripping from IDA resin, so that oscillation of ion concentration is observed. This effect is observed more clearly on higher resin beds, when studying the dynamics of the thermostripping process. The first concentration halfwave appears to be enriched with Zn^{2+} , while the second contains a higher Cu^{2+} content in comparison with that in the stripping solution.

(c) A mathematical model of ion-exchange dynamics of components with different diffusivities has been developed. The phenomenon of formation of concentration waves is considered within the model proposed as the result of the influence of a local electric field arising in the resin phase equalizing the fluxes of exchanging ions. The results of the computer simulation are in a good agreement with those obtained in thermostripping experiments.

6. List of symbols

c_i	Concentration of ion “ <i>i</i> ” in an eluate portion solution (equiv/dm ³)
\bar{c}_i	Total concentration of solution component (equiv/dm ³)
c_i^0	Initial concentration of ion “ <i>i</i> ” in solution (equiv/dm ³)
c_i^{bound}	Boundary conditions
c_i^{init}	Initial conditions
\bar{D}_i	Effective diffusion coefficient of ion “ <i>i</i> ” in resin phase (cm ² /s ¹)
E	Intensity of electric field (V/cm)
F	Degree of the resin bed conversion
J_i	Flux of ion “ <i>i</i> ”
k_i	Stability constant of the sulfate complex of “ <i>i</i> ” ion in solution
K_i	Reduced equilibrium coefficient in mass-action law (relative equilibrium constant)
m	Mass of resin portion (g)
n_i	Charge of ion “ <i>i</i> ”
q_i	Amount of ion “ <i>i</i> ” in resin beads per volume unit of resin bed (equiv/dm ³)
q_i^*	Equilibrium amount of ion “ <i>i</i> ” in resin beads per volume unit of resin bed (equiv/dm ³)
q	Local concentration of ion “ <i>i</i> ” in resin bead (equiv/dm ³)

Q_i	Capacity of resin bed towards ion “ <i>i</i> ” (equiv)
Q_Σ	Total resin capacity (equiv/kg)
r_0	Radius of resin bead (cm)
R	Gas constant (8.34 J mol/K)
S	Geometry parameter of the resin bead (i.e. average ratio between the surface area and volume of the bead)
t	Time
$t_{0.5}$	Time of resin half-conversion (s)
T	Temperature, K
v_j	Volume of eluate portion number “ <i>j</i> ”
V	Solution flow-rate (cm/min)
x	Radial distance from bead center
z	Longitudinal coordinate along ion-exchange column (cm)
β_i	Kinetic parameter of ion “ <i>i</i> ” (min ⁻¹)
ϵ	Resin bed porosity
l	Average intensity of electric field along bead radius

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