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Ion Exchange on Resins with Temperature-Responsive Selectivity. 1. Ion-Exchange Equilibrium of Cu^{2+} and Zn^{2+} on Iminodiacetic and Aminomethylphosphonic Resins

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The ion-exchange equilibrium of Cu^{2+} and Zn^{2+} from sulfate solutions at pH = 1.9 on iminodiacetic (IDA) and aminomethylphosphonic (AMP) resins has been studied in the temperature range between 10 and 80 °C. The values of the equilibrium separation factor α for Zn−Cu exchange demonstrate a strong temperature dependence in the case of IDA resin, while for AMP this dependence is pronouncedly much weaker. A decrease of α at elevated temperatures has been observed for both ion exchangers. The absolute α_{Zn}^{Cu} values for IDA resin lie within between 83.0 (at 10 °C) and 30.0 (at 80 °C). In the case of AMP resin, α values have been shown to vary from 1.67 to 1.4 in the same temperature interval. It has been shown that thermostripping with stock solution at 20 °C from IDA resin pre-equilibrated with the same solution at 60 °C leads to selective desorption of Cu^{2-}, while under the same conditions AMP resin is selectively releasing Zn^{2-}. Thermodynamic interpretation of the temperature dependencies of the separation factors obtained on IDA resin has been shown to allow a comparison of the properties of the ion exchanger with those of iminodiacetic acid in homogeneous solution.

Interphase mass transfer in a pre-equilibrated biphasic system can be provoked by modulating some intensive thermodynamic parameter, such as temperature, ionic strength, pH, etc., which is known to shift the equilibrium in the system under consideration. A group of separation methods, including temperature-swing ion exchange and pressure-swing adsorption, are based upon this physicochemical concept. These methods are attractive because they allow the design of practically reagentless (and, as a result, wasteless) and ecologically clean separation processes.

Parametric pumping techniques,[1−6] dual-temperature ion-exchange processes,[7−9] and thermal ion-exchange fractionation[10,11] can be considered as the typical examples of ion-exchange separation methods which exploit the different resin affinities toward target ions at different temperatures. Besides this potential capability, the main advantage of the above separation techniques is the ability to exclude the resin regeneration step (completely or partially), which is known to be the main source of wastes in ion-exchange processes. In addition, the need for a column conditioning procedure in the adsorption process is also accomplished by this methodology in a straightforward manner. In both cases, the saving of chemical reagents is remarkable. One of the limitations for further development and wider application of parametric pumping and allied techniques is the lack of information available about the types of ion-exchange systems (including both ion exchangers and ion mixtures) which are appropriate for these separation methods. Most of the work has been performed with commercially available ion exchangers of two types: sulfonic resins[10,11] and carboxylic ion exchangers.[12−17] Other ion exchangers, such as, e.g., chelating resins, have found much less use in studies on temperature responsive ion-exchange separation processes.

A high heat of ion exchange is known to serve as a criterion for identifying effective systems applicable to separations based on parametric pumping and other dual-temperature ion-exchange fractionation techniques.[3] Enthalpy changes for ion-exchange processes on the resins of a conventional type are usually small[18,19]

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when no formation of covalent bonds, association, or complex formation is involved. In systems where association equilibria (or complex formation) occur in either the solution or the resin phase, the equilibrium uptake may be shifted markedly,[20-23] so that, as a rule, the selectivity of the ion exchanger decreases with the increase of temperature. For ion-exchange processes of this type, much higher enthalpy values can be expected.

This paper commences a series of investigations on temperature-sensitive ion-exchange systems involving chelating resins of different types and metal ions of economical and ecological concern.[24] The present study was undertaken (1) to obtain information on the $Zn^{2+}-Cu^{2+}$ ion-exchange equilibrium at different temperatures in systems involving two chelating resins of iminodiacetic and aminomethylphosphonic types and (2) to develop a novel approach for predicting temperature dependencies of ion-exchange equilibria on complexing resins on the basis of the enthalpies of the complex formation reaction for metal ions with monomeric analogues of the resin under study. This is the first time that such an approach has been applied successfully to the mentioned prediction. The aim of these investigations includes the application of the same approach for selecting ligands with promising properties for the synthesis of ion-exchange resins with temperature-responsive selectivity.

EXPERIMENTAL SECTION

Reagents, Ion Exchangers, and Apparatus. Zinc sulfate, copper sulfate, and sulfuric acid of analytical grade were from Panreac (PA, Barcelona, Spain). Iminodiacetic ion exchanger, Lewatit TP-207, and aminomethylphosphonic resin, Lewatit R 252-K, were kindly supplied by Bayer Hispania Industrial, S.A. Doubly distilled water was used in all experiments. Prior to experiments, all solutions were degassed by using an ultrasonic bath (Branson 1200) and a vacuum pump. The ratio of Zn^{2+} to Cu^{2+} in stock solution with a total concentration of $(Cu,Zn)SO_4$ of 0.165 ± 0.008 mol/dm^3 was kept constant at 8.5 ± 0.5 level. The pH of the stock solution was adjusted to 1.9 ± 0.05 with H_2SO_4 and kept constant.[25] Standard precautions recommended for handling sulfuric acid solutions[26] were followed when adjusting pH and preparing the 1 M H_2SO_4 solution from concentrated acid. The concentrations of metal ions were determined by the ICP technique using an ARL Model 3410 spectrometer with minitorch. The emission lines used for the spectrochemical analysis were 224.7 nm for Cu^{2+} and 206.191 nm for Zn^{2+}. The uncertainty of metal ions determination was <1.5%. pH was controlled using a Crison pH meter 507 (Barcelona, Spain) supplied with a combined glass electrode. Glass columns (of 1.1 cm i.d. for Lewatit TP-207 and 1.4 cm i.d. for Lewatit R-252) connected with a thermostat (Selecta Ultraterm 6000383; Barcelona, Spain) were used for studying the ion-exchange equilibrium at different temperatures. The construction of the columns permitted the thermostatic conditioning of both resins and entering solution phases.

Narrow granulometric fractions of resins were obtained by dry sieving air-dried samples of ion exchangers using 0.42 mm mesh so that only the resin beads stuck in the holes of the sieve were collected. The columns were charged with 2.00 g of each ion exchanger. The resin portions were kept constant during all series of experiments carried out.

Procedures. Ion-exchange equilibrium was studied under dynamic conditions by using fixed bed columns. The stock solution was passed at constant flow rate (1.6 or 3.0 mL/min) through the columns with resins in H^+-form preconditioned with H_2SO_4 solution at pH = 1.9 and pre-equilibrated at a given temperature. The eluate was collected in portions in preweighted vials, and the eluate sample volume was determined by weighing vials with eluate samples and taking the difference in weight since the density of stock solution was considered to be close to unit. The accuracy of volume determination was ± 0.005 cm^3. The concentrations of both Cu^{2+} and Zn^{2+} were determined in all samples. The achievement of ion-exchange equilibrium in the systems under study was determined by comparison of the metal concentration in the column outlet with that of the initial feed solution. After the eluate sample was collected with concentrations of Cu^{2+} and Zn^{2+} close to those of the initial solution, the flow of solution was stopped and then resumed after a certain period of time. The coincidence of the initial concentration with that of the sample collected after the break was considered as the criterion indicating the equilibrium in the system. After equilibration, the resin was rinsed with twice distilled water, and the metal stripping was carried out with 1 M H_2SO_4, followed by the analysis of Cu^{2+} and Zn^{2+} in the resulting eluate. The results of the stripping solution analysis were used to determine both capacity of the resin toward copper and zinc and the equilibrium separation factor, α, expressed as follows:

$$\alpha_{Zn}^{Cu} = \frac{\bar{x}_{Cu}\,X_{Zn}}{\bar{x}_{Zn}\,X_{Cu}} \qquad (1)$$

where $\bar{x}$ and X are the equivalent fractions of ions under separation in resin and solution phases, respectively. The relative uncertainty on α determination did not exceed 7%.

Thermostripping experiments were carried out as follows. After equilibration of the resin at high temperature (60 °C) with the initial solution, the excess of equilibrium solution was removed from the column so that its level coincided with that of the resin bed. The temperature was then decreased to the preselected value of 20 °C. After equilibration of the system at the lower temperature, the same initial solution was passed through the column at constant flow rate (1.6 mL/min) and collected in portions where concentrations of Cu and Zn were determined. After attainment of the ion-exchange equilibrium, the resin was converted into H^+-form with 1 M H_2SO_4 and prepared for the next run.

RESULTS

Typical effluent concentration histories of Cu−Zn exchange on iminodiacetic (IDA) and aminomethylphosphonic (AMP) resins obtained in equilibration of the ion exchangers with stock solution

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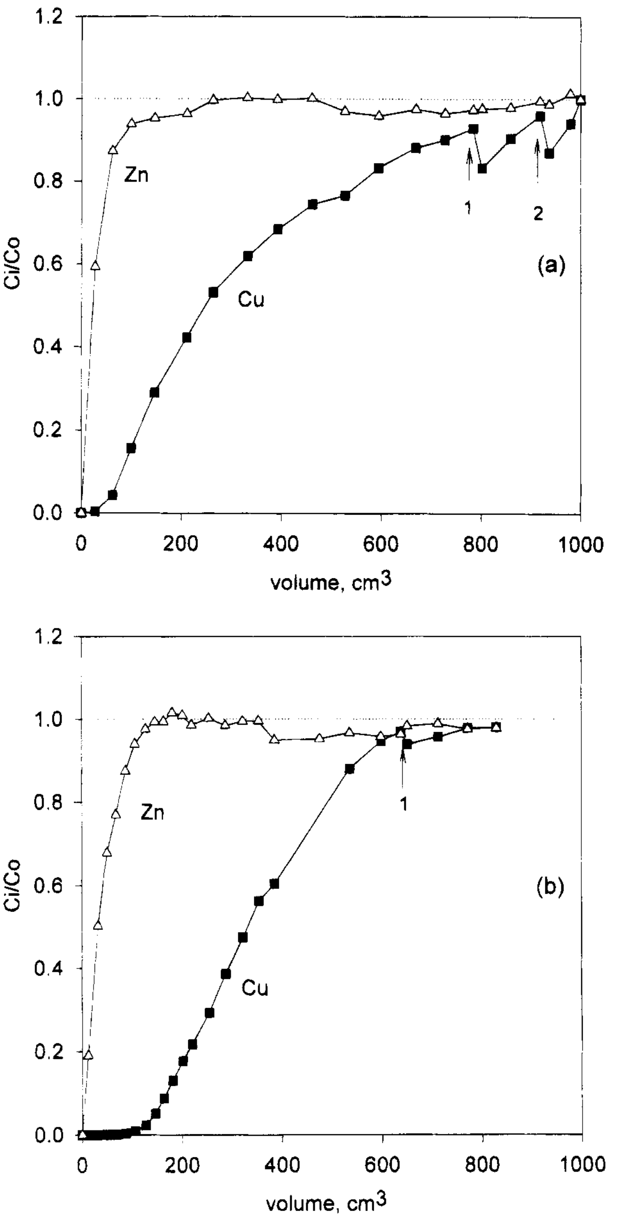

Figure 1. Concentration–volume histories of loading Lewatit TP-207 at 40 (a) and 80 °C (b) with stock solution (see text). Flow rate, 1.6 cm³/min; C_i and C_0 are concentrations of metal ions in *i* solution sample and in stock solution, respectively. Numbered dots indicate moments of temporal solution flow interruptions (each break ≈ 2 h).

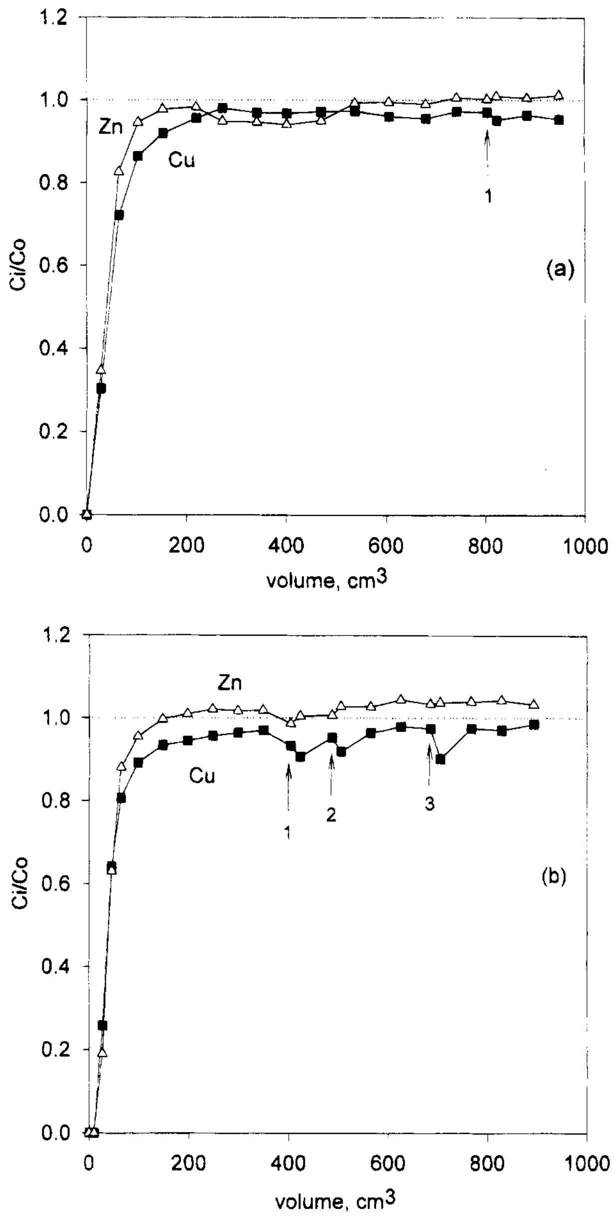

Figure 2. Effluent concentration histories of loading Lewatit R-252-k with stock solution (see text) at 40 (a) and 80 °C (b). Other details are identical to those in Figure 1.

at 40 and 80 °C are shown in Figures 1 and 2, respectively. Comparison of the breakthrough curves presented in Figures 1 and 2 shows that the loading of IDA resin proceeds much faster at high temperature, while in the case of AMP resin, no remarkable influence of temperature on the rate of metal ions sorption can be distinguished. Sorption of Zn^{2+} proceeds faster than that of Cu^{2+} on both types of resins and practically does not depend on temperature. This effect pertains particularly to IDA resin, as is clearly observed in Figure 1. It is also shown in Figure 1 (and in Figure 2 as well) that Cu^{2+}continues being sorbed even after its concentration in the solution leaving the column becomes practically equal to that in the initial one. Indeed, the concentration of Cu^{2+} in the samples withdrawn after the breaks is remarkably lower than that in the previous ones. This effect indicates that sorption of Cu^{2+} continues after temporal interruption of passing the solution through the resin bed and testifies to intraparticle diffusion to be the rate-controlling step in this case.[27] In addition, Figure 1 shows the frontal separation of Zn^{2+} and Cu^{2+} to take place during the loading of IDA resin, and moreover, improving at elevated temperature (cf. Figure 1).[28]

Concentration–volume histories for stripping Cu^{2+} and Zn^{2+} with 1 M H_2SO_4 from IDA resin equilibrated with stock solution at 40 and 80 °C (the stripping was carried out at the same temperatures) are shown in Figure 3. As seen from the elution

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[28] Although the frontal separation of Zn^{2+} and Cu^{2+} is out of the main goal of the present study, it appears to be of practical importance. Indeed, the results shown in Figure 1 have been obtained on a short resin bed (1.5 cm). A far better separation (a wider pure Zn^{2-} zone) can be easily achieved either by increasing the height of the bed or by carrying out the process in a countercurrent column with a moving resin bed. In the last case, the separation proceeds, in fact, on the endless bed of the ion exchanger that allows widening of the zone of the purified component up to the optimum dimensions and collection of the pure product (e.g., pure Zn^{2+}) simultaneously with the separation process.

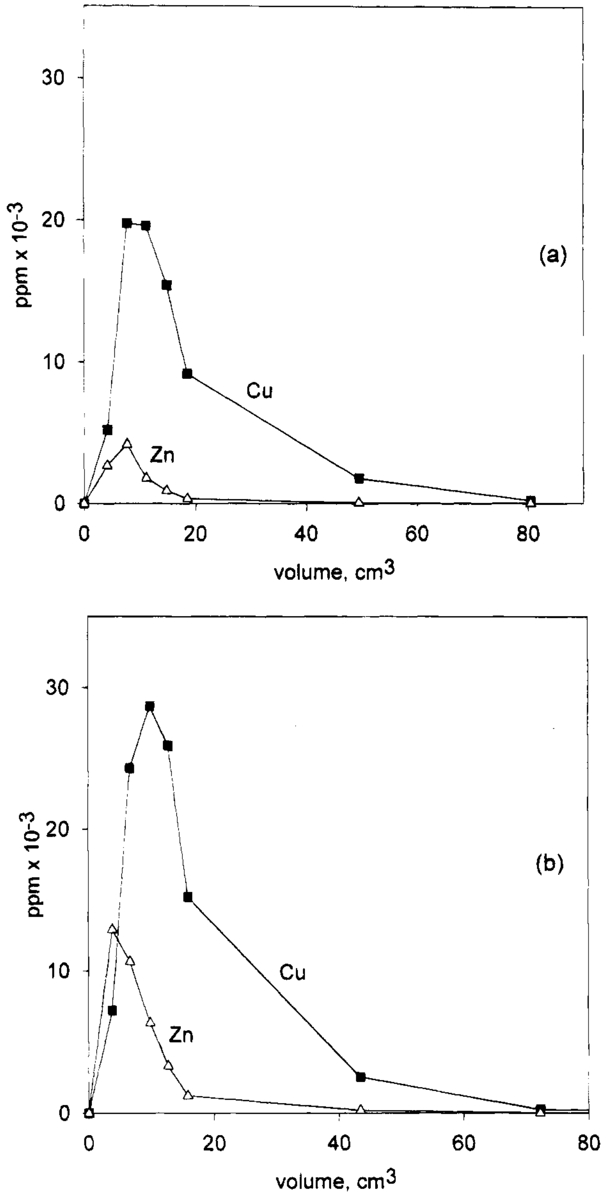

Figure 3. Concentration–volume histories for stripping Cu^{2+} and Zn^{2+} from Lewatit TP-207 with 1 M H_2SO_4 at 40 (a) and 80 °C (b).

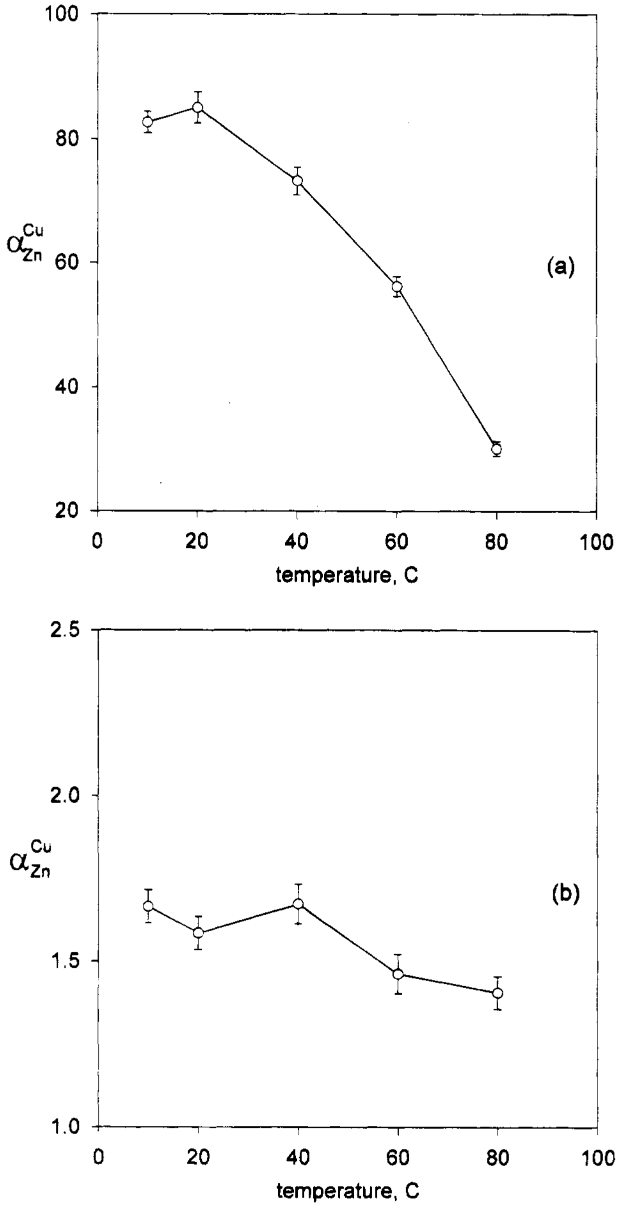

Figure 4. Temperature dependencies of equilibrium separation factor for Zn^{2+}–Cu^{2+} exchange on Lewatit TP-207 (a) and Lewatit R-252-k (b) resins.

curves presented in Figure 3, the partial separation of Cu^{2+} and Zn^{2+} is achieved in the case of the IDA resin. For AMP ion exchanger no separation of metal ions has been observed, at neither 40 nor 80 °C. It is interesting to note that the influence of the temperature on the separation of Cu^{2+} and Zn^{2+} during the stripping follows the opposite trend than that during the loading stage (see Figure 1). Although from data in Figure 3, a partial separation of Cu^{2+} and Zn^{2+} proceeds at both 40 and at 80 °C, a better separation is observed at 40 °C, where the Zn^{2+} contamination is much less than that at 80 °C, and a wide zone of practically pure Cu^{2+} is obtained (see Figure 3a). The temperature increase affect also the sorbabilities of both metal ions on both resins, so that the amounts of Cu^{2+} and Zn^{2+} stripped at 80 °C are remarkably higher than those at 40 °C. This is a consequence of the increased capacities of both resins toward both Cu^{2+} and Zn^{2+} with the increasing temperature.

Temperature dependencies of α_{Zn}^{Cu} for IDA and AMP resins, determined at five different temperatures, are shown in Figure 4, parts a and b, respectively. As shown in Figure 4, both ion exchangers studied are selective toward Cu^{2+} and are characterized by decreasing values of the separation factor with increasing temperature. IDA resin demonstrates a much higher selectivity (higher absolute α_{Zn}^{Cu} values) and a stronger temperature dependence of α than AMP resin.

The capacities of IDA and AMP resins toward Cu^{2+} and Zn^{2+} versus temperature are shown in Figures 5, parts a and b, respectively. As can be seen from the data presented in Figure 5, the resins under study demonstrate different behaviors in terms of their capacities toward Cu^{2+} and Zn^{2+}. Indeed, IDA resin preferentially sorbs copper, while AMP resin gives preference to zinc ions. On the other hand, two temperature intervals with different dependencies of resin capacities (for both IDA and AMP resins) can be clearly distinguished: from 10 to 40 °C and from 40 to 80 °C. The first interval is characterized by a very slight influence of temperature on metal ions sorbability, while a much stronger dependence of resin capacities on temperature is observed in the second. It is interesting to note that the capacity

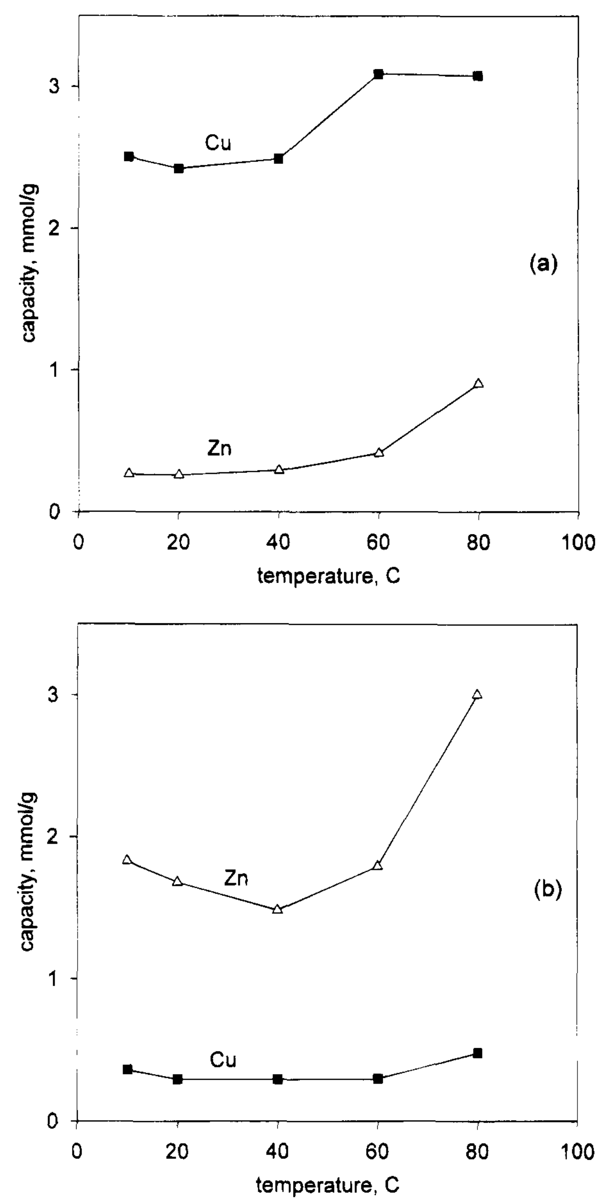

Figure 5. Temperature dependencies of resin capacities toward Cu^{2+} and Zn^{2+} for Lewatit TP-207 (a) and Lewatit R-252-k (b) resins.

of IDA resin toward Cu^{2+} increases in the temperature range between 20 and 60 °C, while that toward Zn^{2+} remains practically constant. AMP resin in the same temperature interval demonstrates absolutely the opposite behavior, i.e., its capacity increases toward Zn^{2+} and does not change toward Cu^{2+}. These results allow for carrying out selective thermostripping of copper against zinc from the IDA resin and zinc against copper from the AMP resin, as is shown in Figures 6 and 7, respectively, where the thermostripping elution curves are presented.

DISCUSSION

The results of this study must be interpreted from two viewpoints: theoretical and practical. Theoretical considerations of the temperature dependencies of α_{Zn}^{Cu} presented in Figure 4 can be based on thermodynamics of the ion-exchange reactions under study. For IDA resin, this reaction can be written as follows:

$$RCH_2N(CH_2COO^-)_2Zn^{2+} + Cu^{2+} \rightleftharpoons RCH_2N(CH_2COO^-)_2Cu^{2+} + Zn^{2+} \quad (2)$$

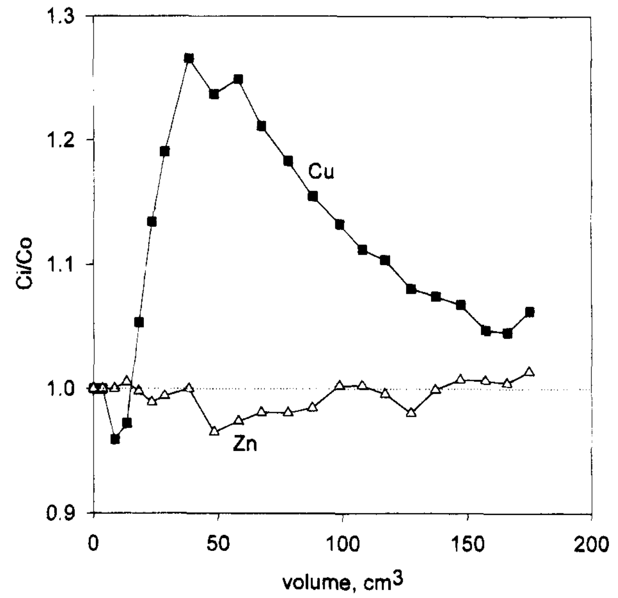

Figure 6. Thermostripping breakthrough curves for Lewatit TP-207. Stripping with stock solution at 20 °C from resin pre-equilibrated with the same solution at 60 °C; C_i and C_0 have the same meaning as in Figure 1.

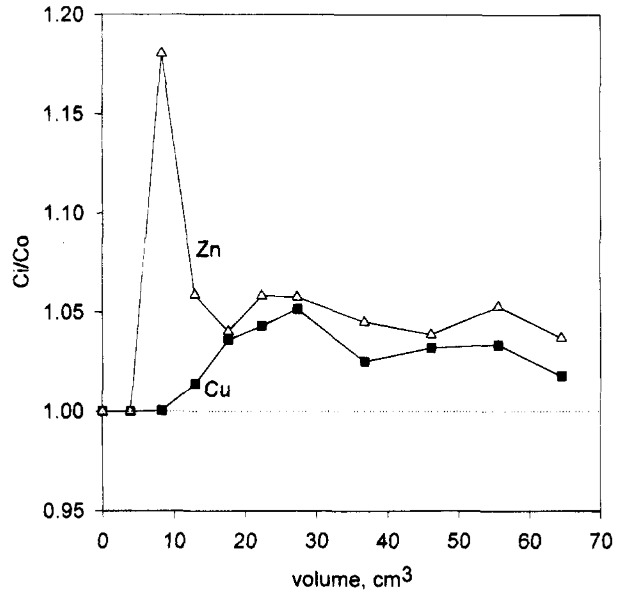

Figure 7. Thermostripping breakthrough curves for Lewatit R-252-k. Stripping with stock solution at 20 °C from resin pre-equilibrated with the same solution at 60 °C; C_i and C_0 have the same meaning as in Figure 1.

Reaction 2 can be represented as a superposition of the following equilibria:

$$RCH_2N(CH_2COOH)_2 + Zn^{2+} \rightleftharpoons RCH_2N(CH_2COO^-)_2Zn^{2+} + 2H^+ \quad (3)$$

$$RCH_2N(CH_2COOH)_2 + Cu^{2+} \rightleftharpoons RCH_2N(CH_2COO^-)_2Cu^{2+} + 2H^{2+} \quad (4)$$

which describe complexation of a single ionic metal species by the resin phase. Reactions 3 and 4 are analogous to those of complexation of the respective metal ions with iminodiacetic acid, which is in fact the monomeric analog of the IDA resin.

Table 1. Separation Factors for Zn–Cu Exchange on IDA Resin at Different Temperatures

T, K	$\alpha_{\rm Zn}^{\rm Cu}$	$\ln \alpha_{\rm Zn}^{\rm Cu}$	$\bar{X}_{\rm Cu}$
293	85.0 ± 5.1	4.44	0.90
313	73.3 ± 4.4	4.29	0.90
333	56.2 ± 3.9	4.03	0.88

The thermodynamics of formation of copper and zinc complexes with iminodiacetic acid was studied by Andereg[29] and Bonomo et al.[30] They reported the following enthalpy values for complex formation reactions: −18.6 (CuIDA), −9.2 (ZnIDA),[29] and −16.6 kJ/mol (CuIDA).[30] Since ion-exchange reaction 2 can be obtained by subtracting eq 3 from eq 4, it can be considered to be analogous with the following complex exchange reaction:

$$\mathrm{HN(CH_2COO^-)_2Zn^{2+} + Cu^{2+} \rightleftharpoons HN(CH_2COO^-)_2Cu^{2+} + Zn^{2+}} \qquad (5)$$

The corresponding differential enthalpy of reaction 5 is calculated to be $\Delta(\Delta H)_{\rm Cu-Zn} = -9.4$ kJ/mol[29] or −7.4 kJ/mol.[29,30]

Now, the differential enthalpy of ion-exchange reaction 2 is estimated from the temperature dependencies of $\alpha_{\rm Zn}^{\rm Cu}$ for IDA resin shown in Figure 4a. Although the separation factor α is not a thermodynamically meaningful parameter, it can be associated with the thermodynamic equilibrium constant (k) of the ion-exchange reaction (e.g., reaction 2) as follows:[31,32]

$$\log k = \int_0^1 \log \alpha(\bar{x})\, {\rm d}\bar{x} \qquad (6)$$

where $\bar{x}$ is the equivalent fraction of the larger sorbed ion in the resin phase ($\mathrm{Cu^{2+}}$ in our case). The standard enthalpy of the ion-exchange reaction can be determined as follows:

$$\Delta H^\circ = \int_0^1 \Delta H_{\rm ap}\, {\rm d}\bar{x} \qquad (7)$$

where $\bar{x}$ is the same as in eq 6 and $\Delta H_{\rm ap}$ is the apparent enthalpy[33,34] depending on $\bar{x}$.

Substitution of k for α in the van't Hoff equation makes it possible to determine $\Delta H_{\rm ap}$ from the temperature dependence of α through the use of the following equation:

$$\Delta H_{\rm ap} = -R\left[\frac{\delta \ln \alpha}{\delta(1/T)}\right]_{\bar{x}_i} \qquad (8)$$

Since the differentiation in eq 8 must be carried out at a fixed $\bar{x}_i$ value, this condition has to be fulfilled by the practical application of eq 8 to determine $\Delta H_{\rm ap}$ values from the experimental data. The values of $\alpha_{\rm Zn}^{\rm Cu}$ determined for IDA resin at 20, 40, and 60 °C are given in Table 1, where the $\bar{x}_{\rm Cu}$ values are also shown. $\bar{x}_{\rm Cu}$ values were determined from the results obtained on stripping $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$ from the resin (see, e.g., Figure 3).

Table 2. Calculated and Experimentally Determined ln(α_i/α_j) Values for Zn–Cu Exchange on IDA Resin at Different Temperatures

	$\ln((\alpha_i/\alpha_j)$		
$T_i - T_j$, K	exptl	calcd[a]	calcd[b]
333–293	0.41 ± 0.06	0.47	0.36
333–313	0.26 ± 0.06	0.22	0.17
313–293	0.15 ± 0.07	0.25	0.19

[a] $\Delta(\Delta H) = -9.6$ kJ/mol. [b] $\Delta(\Delta H) = -7.4$ kJ/mol (see eq 9 and text).

As follows from the data collected in Table 1, the $\bar{x}_{\rm Cu}$ values are practically constant in the temperature range between 20 and 60 °C. This indicates that the α values given in Table 1 can be used to estimate the $\Delta H_{\rm ap}$ value from the slope of ln α vs $1/T$, assuming the usual Arrhenius dependencies of α on temperature. This estimation gives a value of −8.6 kJ/mol, which agrees well with the average of the $\Delta(\Delta H)_{\rm Cu-Zn}$ values given above ($\Delta(\Delta H)_{\rm av} = -8.5$ kJ/mol).

From the coincidence of the apparent enthalpy of ion-exchange reaction 2 with the value of the differential standard enthalpy of reaction 5, one can assume a slight $\Delta H = f(\bar{x})$ dependence (see eq 7) of Zn–Cu exchange on IDA resin, and one can also propose the following approach for predicting temperature dependencies of ion-exchange equilibrium on chelating resins.

The prediction is based on applying literature data on the heats of complex formation[35] for different metal ions with ligands of the same type as the chelating resin under interest (e.g., IDA in our case). The influence of the temperature on the equilibrium constant k can be described by the following relationship:

$$\ln\frac{k_2}{k_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (9)$$

which is valid when ΔH is independent of the temperature in the given temperature interval.

As follows from eqs 7 and 8, in the case when ΔH does not depend on the composition of the resin phase, k in eq 9 can be substituted by α, and the logarithms of α_i/α_j (the ratio of α values determined at T_i and T_j, respectively) can be calculated from the ΔH value for different temperature intervals. A comparison of calculated α_i/α_j values with the corresponding experimental values from Table 1 is presented in Table 2.

As can be seen from the results given in Table 2, the calculated $\ln(\alpha_i/\alpha_j)$ values demonstrate a satisfactory fit with those determined experimentally.

An estimation of $\Delta H_{\rm ap}$ for Zn–Cu exchange on AMP resin, in a fashion similar to the above estimated for IDA ion exchanger, gives $\Delta H_{\rm ap} = -0.3$ kJ/mol for $\bar{x}_{\rm Cu} = 0.16$, which is far lower than the $\Delta H_{\rm ap}$ determined for IDA resin. This result is consistent with the much weaker temperature dependence of $\alpha_{\rm Zn}^{\rm Cu}$ in the case of AMP resin in comparison with that for IDA ion exchanger (cf. Figure 4, parts a and b), and it confirms the conclusion by Tondeur

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Table 3. Differential Enthalpies of Complexation for Hypothetic Chelating Resins with Selectivity Dependent on Temperature (Ratios of Equilibrium Constants at Different Temperatures)

		$-\Delta H$, kJ/mol[a]		
$k(T_1)/k(T_2)$	$\ln[k(T_1)/k(T_2)]$	333–290 K	343–290 K	353–290 K
1.3	0.262	4.89	4.09	3.54
1.5	0.405	7.56	6.32	5.47
1.7	0.431	9.91	8.29	7.17
2.0	0.693	12.94	10.81	9.36
2.5	0.916	17.10	14.29	12.38
3.0	1.099	20.52	17.15	14.85
4.0	1.386	25.88	21.63	18.72
5.0	1.609	30.04	25.11	21.74
7.0	1.946	36.34	30.37	26.29
10.0	2.303	43.00	35.94	31.1

[a] Temperatures are T_2-T_1.

and Grevillot[3] that high heats of ion-exchange reactions are the key for identifying temperature-responsive ion-exchange systems which can be applied for, e.g., efficient parametric pumping separation.

From this viewpoint, eq 9 seems useful for estimating the values of enthalpy changes for some hypothetical ion exchangers (e.g., of chelating type) characterized by changes of their selectivities toward some metal ion couples (in values of equilibrium constants) in a given temperature interval. For this purpose, it is convenient to rewrite eq 9 in the following form:

$$-\Delta H = \left(\ln \frac{k_1}{k_2}\right) R \frac{T_2 T_1}{T_2 - T_1} \tag{9a}$$

The result of such an estimation is shown in Table 3, where the heats of ion-exchange reactions of chelating ion exchangers with different temperature dependencies of their selectivities (expressed as the corresponding ratios of equilibrium constants at given intervals of temperatures) are presented.

The data shown in Table 3 illustrate, on the one hand, the range of enthalpy changes characterizing the resins with remarkable temperature dependencies of their selectivities (e.g., $k(T_1)/k(T_2) > 2$) toward a certain ion couple; on the other hand, the data allow one to preselect the ion exchangers suitable for separation of certain ion mixtures in applying temperature-responsive ion-exchange fractionation techniques (e.g., parametric pumping and others).

This preselection can be based on $\Delta(\Delta H)$ values for complexation of metal ions with the respective resin analogues. For example, as follows from the heats of IDA complex formation with Co^{2+} (−8.95 kJ/mol), Ni^{2+} (−21 kJ/mol), Cd^{2+} (−6.11 kJ/mol), and Pb^{2+} (−13.97 kJ/mol),[29] IDA resin can be expected to demonstrate a quite strong temperature dependence of α for the exchange of the following ion couples: Co^{2+}–Cu^{2+} ($\Delta(\Delta H) = -9.8$ kJ/mol), Co^{2+}–Ni^{2+} (−12.2 kJ/mol), Ni^{2+}–Cd^{2+} (−15.0 kJ/mol),; Cd^{2+}–Pb^{2+} (−7.9 kJ/mol), and Zn^{2+}–Ni^{2+} (−11.9 kJ/mol) (this series can be easily extended). For ion couples such as Cd^{2+}–Zn^{2+} (−3.1 kJ/mol), Cd^{2+}–Co^{2+} (−2.8 kJ/mol), and Ni^{2+}–Cu^{2+} (−2.3 kJ/mol), a far weaker temperature dependence of α values can be predicted for the same ion exchanger. Finally, for Co^{2+}–Zn^{2+} (−0.25 kJ/mol), practically no influence of temperature on the ion-exchange equilibrium on IDA resin can be expected.

The validity of the proposed approach and its predictive ability have been demonstrated above and can be illustrated by the results presented in Table 2. All other predictions done must be confirmed by the respective experimental data, and we intend to follow this further. As follows from the comparison of the data shown in Tables 2 and 3, the efficiency of separation by the dual-temperature ion-exchange technique depends on two parameters: the absolute value of the differential enthalpy of complexation and the value of the corresponding temperature interval. The efficiency in this case is known to be directly proportional to the ratio $k(T_1)/k(T_2)$[3]. As can be clearly seen from Table 3, higher values of this ratio (i.e., higher separation efficiency) at a fixed $\Delta(\Delta H)$ can be achieved by widening the temperature range. For aqueous solutions, the temperature range may be chosen within the scale from 273 to 353 K. It seems useful to analyze the influence of $\Delta T = T_2 - T_1$ and its position on the temperature scale (which can be determined by T_1 value) on the $k(T_1)/k(T_2)$ ratio. Consider for this purpose again eq 9, which can be rewritten as follows:

$$\ln \frac{k_2}{k_1} = \frac{\Delta H}{T_1 R}\left(\frac{\Delta T}{T_1 + \Delta T}\right) \tag{10}$$

As follows from eq 10, at a fixed ΔT, the value of the term in parentheses increases when T_1 decreases.

It seems reasonable to mention one more possible application of the predicting data shown in Table 3. These data allow one to preselect the ligands having greater promise to be used for the purposeful synthesis of chelating ion exchangers with temperature-responsive selectivity. This preselection must be based on the fact that the differential heat of the complex formation reaction between the chosen ligand and a certain metal ion couple should not be less than 15–20 kJ/mol, which can provide a sufficient variation of the synthetic resin affinity toward the target ion in a suitably narrow temperature range. The synthesis of ion exchangers of this type has to stimulate the wider application of the reagentless ion-exchange separation techniques, which can allow for designing the wasteless and ecologically clean ion-exchange technologies.

Lastly, we will consider the results obtained in this study in practical application to the separation of Cu^{2+} and Zn^{2+} from the mixture under consideration.

As can be seen in Figures 1 and 3, Zn^{2+} and Cu^{2+} can be separated on IDA resins by frontal and reverse frontal separation techniques, respectively. The frontal separation improves at elevated temperatures (see Figure 1a), which is, in fact, the result of two temperature effects acting in opposite directions. The former effect deals with the influence of temperature on ion-exchange equilibrium and may be considered as "negative" since α_{Zn}^{Cu} significantly decreases with increasing temperature (see Figure 4). The latter is connected with the rate of Cu^{2+} uptake by IDA resin, which is positively affected by the temperature increase, as demonstrated by Schmuckler et al.[36] The total separation effect observed testifies to the dominant role of the "kinetic effect of temperature" in this case. A contrary conclusion can be derived from the results presented in Figure 3, where a better reverse frontal separation is observed at low temperature,

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(36) Nativ, M.; Goldstein, S.; Schmuckler, G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1951.

which can be ascribed now to the dominating "equilibrium effect of temperature" (higher $\alpha_{\mathrm{Zn}}^{\mathrm{Cu}}$ value).

Another possibility for separation of Cu^{2+} and Zn^{2+} on IDA resin is illustrated by the results shown in Figure 6, from which it follows that this ion exchanger can be used for dual-temperature fractionation of the ion couple under consideration in applying, e.g., the parametric pumping technique.

As can be seen from the data shown in Figure 7, AMP resin also demonstrates the potential to be applied for dual-temperature fractionation of Cu^{2+} and Zn^{2+} mixtures. This result is interesting, since neither during the loading (see Figure 2) nor in the stripping has remarkable separation of the mixture components been observed; this can be attributed to strong temperature dependence of AMP resin capacity toward Zn^{2+}. This leads to the conclusion that not only α vs T but also capacity vs T dependencies have to be taken into account for selecting appropriate conditions for carrying out dual-temperature ion-exchange fractionation.

CONCLUSIONS

From the results of the present study, the following can be concluded:

(a) Lewatit TP-207 resin of iminodiacetic type demonstrates a strong temperature dependence of the equilibrium separation factor for Zn–Cu exchange from sulfate solutions at pH = 1.9 with a $[Zn^{2+}]/[Cu^{2+}]$ ratio around 8.5. Such dependencies agree with values predicted on the basis of the differential enthalpies of complex exchange reactions between the metal ions under study and the monomeric analog of the resin (iminodiacetic acid in our case).

(b) A simple thermodynamic approach for preselection of ion-exchange systems (including ion exchanger and metal ion mixtures), applicable for separations by dual-temperature fractionation techniques, such as, e.g., parametric pumping, has been proposed, based on the heats of related ion-exchange reactions, which are considered practically constant in a relatively narrow range of temperature. The same approach is thought to be applicable for selecting ligands which would be promising for the synthesis of ion-exchange resins with temperature-responsive selectivity.

(c) Thermostripping with stock solution at 20 °C from IDA resin pre-equilibrated with the same solution at 60 °C results in selective desorption of Cu^{2+}, while under the same conditions, AMP resin selectively releases Zn^{2+}, despite the fact that both resins demonstrate preferential selectivity toward Cu^{2+}.

(d) Temperature dependencies of resin capacities toward certain metal ions allow for preselection of conditions for selective thermostripping of the given ionic species that can be applied for separation of the metal ions mixture by the parametric pumping technique.

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