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Ion exchange on resins with temperature-responsive selectivity III. Influence of complex formation stoichiometry on temperature dependence of resin selectivity

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Abstract

The influence of temperature ($293 < T < 353$ K) on $\text{Cu}^{2+}-\text{Ni}^{2+}$; $\text{Zn}^{2+}-\text{Co}^{2+}$, and $\text{Cu}^{2+}-\text{Co}^{2+}$ ion-exchange equilibrium at $\text{pH}=1.55-3.0$ from either aqueous sulfate or aqueous nitrate media on iminodiacetic (IDA) resin Lewatit TP-207 was studied. A novel approach for evaluation of the resin phase composition from α versus T dependencies has been proposed and the validity of such an approach is demonstrated. The temperature dependence of the equilibrium separation factor, α , in the $\text{Cu}^{2+}-\text{Ni}^{2+}$ exchange varies from nitrate to sulphate medium and it depends on the formation of different IDA complexes with the minor component (Ni^{2+}) in the resin phase. In the nitrate medium, formation of $(\text{IDA})_2-\text{Ni}$ complex is prevailing at $293 < T < 308$ K, while at $T > 308$ K 1:1 IDA: Ni^{2+} complex is dominating. The $\text{Cu}^{2+}-\text{Ni}^{2+}$ exchange equilibrium from sulfate medium is characterized by the formation of nickel complexes of both stoichiometries within the whole temperature range studied. The dependence of α on T in $\text{Zn}^{2+}-\text{Co}^{2+}$ exchange system has been shown to be weaker than that in the $\text{Cu}^{2+}-\text{Ni}^{2+}$ system. This result is in a good agreement with the predictions made in the first communication of this series. The results of thermostripping experiments carried out for $\text{Cu}^{2+}-\text{Co}^{2+}$ exchange have shown that the efficiency of the thermostripping process depends on both the interval of working temperatures (ΔT) and its position on the temperature scale. The efficiency of thermostripping rises with an absolute ΔT value and also increases following the shift of temperature interval to the lower temperature range. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Complex formation stoichiometry; Resin selectivity; Temperature dependence

1. Introduction

The group of ion-exchange (IE) separation methods based on the shift of IE equilibrium to the

desired direction due to the modulation of temperature (or some other intensive thermodynamic parameters), involves parametric pumping [1–3], dual-temperature IE processes [4], and thermal IE fractionation [5–7]. Most of the work in this field has been performed with commercially available ion-exchangers of two types: sulfonic resins [5,6] and carboxylic ion-exchangers [7–11]. Other ion-exchangers, such as, e.g., chelating resins, known to be highly selective towards, e.g., heavy metal ions, find

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much less use in studies on temperature responsive IE separation processes. However, their applicability for dual temperature IE fractionation of complex ionic mixtures has been recently demonstrated [12–14]. The necessary condition for IE systems, where dual-temperature separation methods can be applied, is a high heat of IE reaction [3,7]. This requirement is met when the IE reaction is coupled with some additional interactions such as, e.g., association and complex formation (in the resin or in the solution phase), which result in a high heat of the overall process [7,15–17].

A new approach for the prediction of temperature dependencies of IE equilibrium on chelating resins has been reported in the first communication of this series [18]. This approach can be applied to select commercially available chelating ion-exchangers suitable for separation of different ionic mixtures by using dual-temperature IE fractionation techniques, and also to pre-select ligands for the tailored synthesis of novel IE resins with temperature-dependent selectivity [7,18,19]. The efficiency of thermostripping (thermodesorption) process has been predicted [18] to depend on the differential enthalpy of complexes formation of ions to be separated, the width of interval of working temperatures (the difference between the loading and stripping temperatures) and the position of this interval on the temperature scale. In the second paper of this series [20], a model describing the formation of thermo-induced concentration waves in an IE column in the course of thermostripping processes has been developed.

The present communication is addressed to the further development of the proposed approach by both confirming the above mentioned predictions and accounting for the chemistry of the metal complex formation in the resin phase. The present study was undertaken; (1) to obtain information on the Cu^{2+} – Ni^{2+} ; Co^{2+} – Zn^{2+} , and Cu^{2+} – Co^{2+} IE equilibria on iminodiacetic resin at different temperatures; (2) to elucidate the influence of complexation characteristics in the resin phase on temperature dependence of the resin selectivity, and (3) to study the effect of the position of the temperature interval in the temperature scale on the thermostripping process of Co^{2+} – Cu^{2+} mixture from iminodiacetic resin.

2. Experimental section

2.1. Reagents and apparatus

All chemicals of analytical grade were purchased from Panreac (P.A., Barcelona, Spain). Iminodiacetic (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. A Perkin Elmer 16 PC FTIR (Norwalk, CT, USA) spectrometer was used to record infrared spectra of the resin phase in the range of 4000 to 400 cm^{-1} . The concentrations of metal ions were determined by the ICP technique using the ARL Model 3410 spectrometer (Valencia, CA USA) provided with minitorch. The emission lines used for the spectrochemical analysis were 324.754 nm for Cu^{2+} , 227.021 nm for Ni^{2+} , 206.200 nm for Zn^{2+} and 228.616 nm for Co^{2+} . The uncertainty of metal ions determination was $<1.5\%$. The pH was controlled using Crison pH meter 507 (Barcelona, Spain) supplied with a combined glass electrode. Glass columns of 1.4 and 1.1 cm I.D. connected with a thermostat (Selecta Ultraterm 6000383, Barcelona, Spain) were used to study the IE equilibrium at different temperatures and to carry out the thermostripping experiments. The construction of the columns permitted a simultaneous thermostatic conditioning of both resin and entering solution phase. The columns were charged with 2.0 g of the ion-exchanger. The resin portions were kept constant during all series of experiments carried out. The uncertainty on the results obtained has been determined from data of three replicates.

2.2. Procedure

The IE equilibrium at different temperatures was studied under dynamic conditions by following the procedure described elsewhere [18]. The results of determination of equilibrium concentrations of ions in solution and resin phases were used to calculate both capacity of the resin towards metal ions and the equilibrium separation factors, α , expressed as follows:

$$\alpha_{\text{A}}^{\text{B}} = \frac{\bar{X}_{\text{B}}}{\bar{X}_{\text{A}}} \frac{X_{\text{A}}}{X_{\text{B}}} = \frac{q_{\text{B}}}{q_{\text{A}}} \frac{C_{\text{A}}^*}{C_{\text{B}}^*} \quad (1)$$

where \bar{X} and X are the equivalent fractions of ions (A and B) under separation in the resin and the solution phases, respectively, q is the partial capacity of the resin towards each ion, C^* is the equilibrium concentration of ions in the solution phase and B denotes the better sorbed ion. The relative uncertainty on α determination did not exceed 6%.

Thermostripping experiments were carried out as described elsewhere [20] with temperature decrement, $\Delta T = T_2 - T_1 = 50$ K (where T_2 is the loading and T_1 is the thermostripping temperature). The position of ΔT on the temperature scale was varied so that in one of the experiments $T_2 = 333$ K and $T_1 = 283$ K, while in the other one, T_2 and T_1 were 353 and 303 K, respectively. Differential thermostripping experiments were carried out by following the previously described procedure [20].

Preparation of the resin for the spectral analysis was performed as follows: 0.100 g of the resin in the H-form was pre-conditioned at 293 K with either HNO_3 (for System 1, see Table 1) or H_2SO_4 (for System 2) solution at pH=1.7. The loading of the resin portion with Cu^{2+} – Ni^{2+} mixture was carried out under batch conditions by vigorous agitation of the resin with 100 cm³ of the stock solution at a given temperature in a thermostatic flask supplied with a reflux system during 5 h. This time was shown to be sufficient for complete equilibration of the resin with Cu^{2+} – Ni^{2+} mixture. After equilibra-

tion, the resin was separated from the solution phase by filtration and then rinsed with three portions of 2 ml of bidistilled water. The resin was then dried, mixed with KBr (Fluka, for IR-spectroscopy) and ground in an agate mortar followed by preparation of pellets and recording of the IR spectra.

3. Results

The main parameters of system under studied are collected in Table 1. Systems 2–5 were studied to confirm the predictions previously made [18] (see Introduction). System 2 and 3 were expected to characterise moderate and weak α versus T dependencies, respectively. Systems 1 and 2 differ from each other by the nature of co-ions (ionic media) and, as the result, by different complexation conditions in the resin phase (see below). Systems 4 and 5 were studied to demonstrate the dependence of thermostripping efficiency on the position of ΔT interval on the temperature scale.

3.1. Systems 1 and 2

The $\alpha_{\text{Ni}}^{\text{Cu}}$ versus T dependencies and partial capacities of the resin in Systems 1 and 2 towards Cu^{2+} , Ni^{2+} and H^+ at different temperatures are shown in Tables 2 and 3, respectively, where X_{Cu} and $q_{\text{H}}/q_{\text{Ni}}$ values for both systems studied are also presented. As seen, $\alpha_{\text{Ni}}^{\text{Cu}}$ versus T dependencies are different for the nitrate and sulphate media, although the absolute

Table 1
Main parameters of systems under study

System	M_1	M_2	C_0, M^{a}	M_1/M_2^{b}	pH	Media	Study
1	Cu	Ni	0.100	1:1	1.7	NO_3^-	Equilibrium at different temperatures (293–353 K)
2	Cu	Ni	0.100	1:1	1.7	SO_4^{2-}	Equilibrium at different temperatures (293–353 K)
3	Co	Zn	0.100	1:1	3.0	NO_3^-	Equilibrium at different temperatures (283–353 K)
4	Cu	Co	0.100	1:1	1.55	NO_3^-	Thermostripping experiment: $T_1 = 283$ and 303 K, $\Delta T = 50$ K
5	Cu	Co	0.100	1:9	1.55	NO_3^-	Differential thermostripping experiment: $T_1 = 333, 313, 293$ K, $\Delta T = 20$ K

^a Total concentration of stock solution.

^b Molar ratio.

Table 2

$\alpha_{\text{Ni}}^{\text{Cu}}$ values and partial capacities of Lewatit TP-207 towards Cu^{2+} , Ni^{2+} and H^+ at different temperatures in nitrate medium, meq/g

T , K	q_{Cu}	q_{Ni}	q_{H}	$q_{\text{H}}/q_{\text{Ni}}$	\bar{X}_{Cu}	$\alpha_{\text{Ni}}^{\text{Cu}}$
293	3.63	0.187	1.50	8.02	0.95	19.1 ± 0.4
298	3.56	0.189	1.57	8.31	0.95	18.5 ± 0.4
303	3.66	0.230	1.43	6.22	0.94	15.5 ± 0.3
308	3.57	0.227	1.52	6.70	0.94	15.4 ± 0.5
313	3.85	0.236	1.23	5.21	0.94	16.5 ± 0.5
333	4.05	0.231	1.04	4.50	0.95	17.2 ± 0.5
353	4.27	0.242	0.81	3.3	0.95	18.1 ± 0.4

$\alpha_{\text{Ni}}^{\text{Cu}}$ values are similar in both cases. In both systems, IDA resin preferentially sorbs Cu^{2+} against Ni^{2+} ($\alpha_{\text{Ni}}^{\text{Cu}} \gg 1$), which correlates with stability constants of copper and nickel complexes with IDA ligand in the aqueous solution [21] ($\log \beta_{\text{IDA}\text{Cu}} = 10.6$ and $\log \beta_{\text{IDA}\text{Ni}} = 8.2$). For the nitrate media, two different zones of $\alpha_{\text{Ni}}^{\text{Cu}}$ versus T dependencies can be distinguished (see Table 2): (1) between 293 and 308 K where α value decreases, and (2) between 308 and 353 K where it increases with T . On the contrary, for sulphate media a smooth decrease of α is observed within the whole temperature range studied (see Table 3).

As also seen from Tables 2 and 3, the capacities of the resin towards Ni^{2+} (at the same temperatures) when determined from different ionic media are similar to each other, while those towards Cu^{2+} are higher for the nitrate medium in comparison with the

Table 3

$\alpha_{\text{Co}}^{\text{Zn}}$ values and partial capacities of Lewatit TP-207 towards Cu^{2+} , Ni^{2+} and H^+ at different temperatures in sulfate medium, meq/g

T , K	q_{Cu}	q_{Ni}	q_{H}	$q_{\text{H}}/q_{\text{Ni}}$	\bar{X}_{Cu}	$\alpha_{\text{Ni}}^{\text{Cu}}$
293	3.05	0.160	2.11	13.2	0.95	19.3 ± 0.6
298	3.22	0.162	1.94	12.0	0.95	20.1 ± 0.6
303	3.36	0.212	1.75	8.25	0.94	16.1 ± 0.3
308	3.47	0.208	1.64	7.89	0.94	16.6 ± 0.3
313	3.18	0.212	1.93	9.09	0.94	15.4 ± 0.3
323	3.76	0.271	1.29	4.76	0.93	14.0 ± 0.4
333	3.88	0.298	1.14	3.83	0.93	13.1 ± 0.4
353	4.21	0.290	0.82	2.8	0.93	14.2 ± 0.3

sulfate one. For both systems under consideration an increase of the resin capacity towards both nickel and copper with temperature is observed. The capacity of this resin has been previously determined by a potentiometric method to be 5.32 ± 0.23 meq/g [22]. The maximum resin capacities towards both metal ions ($q_{\text{Cu}} + q_{\text{Ni}}$)_{max} are observed at $T = 353$ K and equal to 4.51 (System 1) and 4.53 (System 2) meq/g indicating that even at high temperature not all functional groups are loaded with metal ions. The partial resin capacities towards H^+ , q_{H} , shown in Table 2 were calculated as follows:

$$q_{\text{H}} = 5.32 - (q_{\text{Cu}} + q_{\text{Ni}}) \quad (2)$$

The carboxylic groups of IDA resin are partially protonated at all temperatures but their deprotonation degree increases at elevated temperature resulting in higher metal capacities at high temperature. This is substantiated by the IR spectra of the resin phase pre-equilibrated with Cu^{2+} and Ni^{2+} mixture in Systems 1 and 2 at 293 and 353 K, shown in Fig. 1b and c, respectively. The IR spectrum of the completely protonated IDA resin is presented in Fig. 1a. A comparison of the spectra presented in Fig. 1b and c with that shown in Fig. 2a, testifies to the diminishing of the band at 1716 cm^{-1} , corresponding to the C=O stretching of the carboxylic acid at $T = 293$ K and to the remarkable decrease of this band at 353 K in both systems under study. The difference in the q_{H} values determined in Systems 1 and 2 (see Tables 2 and 3) can be attributed to the stronger complexation properties of SO_4^{2-} ions with metal ions in comparison with NO_3 ion [23]. The presence of stronger sulfate complexes in the solution shifts the IE equilibrium in the system that increases the content of protonated groups in the resin phase.

3.2. System 3

In this system the resin manifests a higher affinity towards Zn^{2+} . The resin selectivity in this case is lower, than that observed in Systems 1 and 2 what correlates with the lower difference between stability constants of Co–IDA and Zn–IDA complexes: $\log \beta_{\text{IDA}\text{Zn}} = 7.3$ and $\log \beta_{\text{IDA}\text{Co}} = 7.0$ [21]. As the result, $\alpha_{\text{Co}}^{\text{Zn}}$ values lie within the range $1.32 < \alpha_{\text{Co}}^{\text{Zn}} < 1.72$, as shown in Table 4. The influence of temperature on $\alpha_{\text{Co}}^{\text{Zn}}$ is far weaker than that observed in the

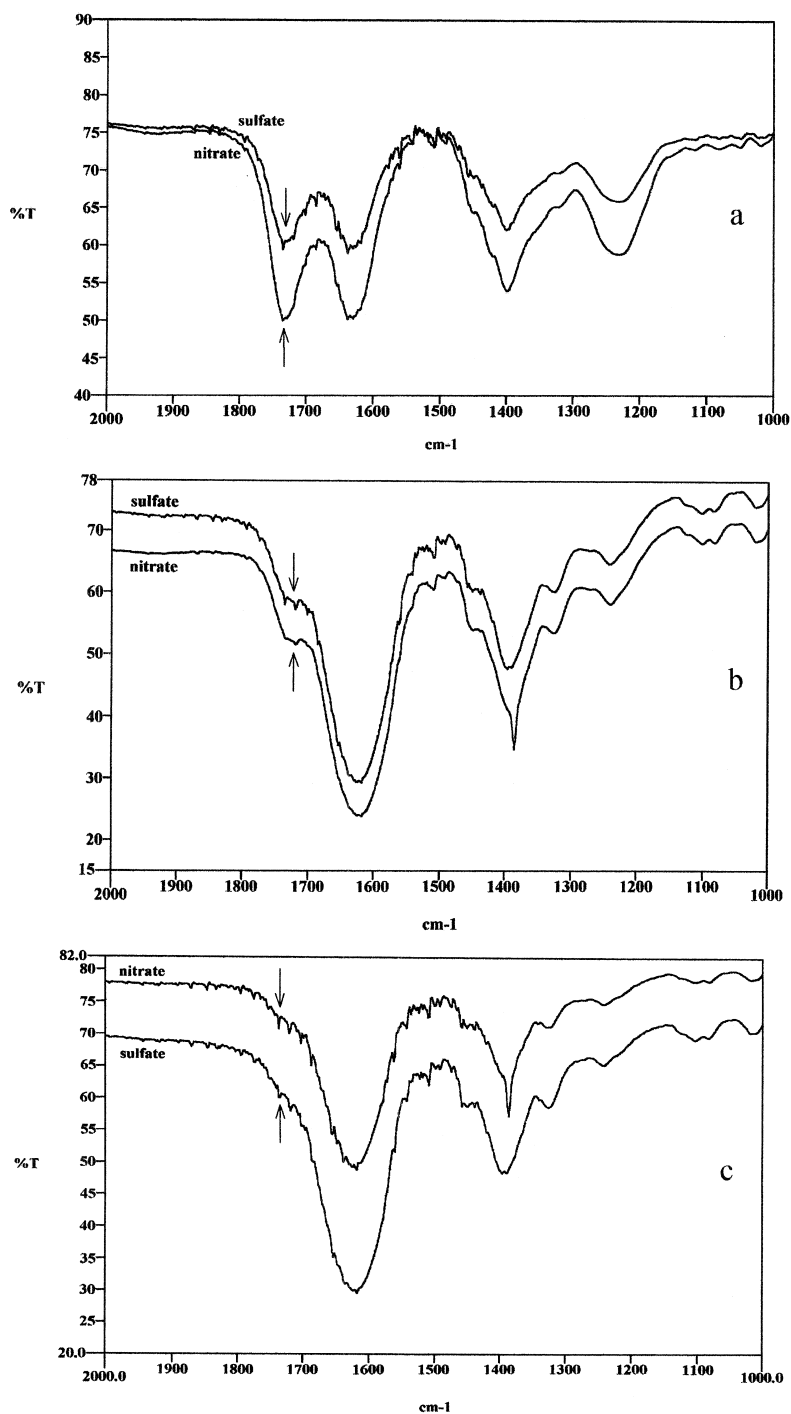


Fig. 1. IR spectra of Lewatit TP-207 resin samples: (a) Completely protonated resin equilibrated with nitric and sulfuric acid solutions; (b) resin pre-equilibrated with Cu²⁺ and Ni²⁺ mixture at 293, and (c) 353 K from nitrate and sulfate media (see text).

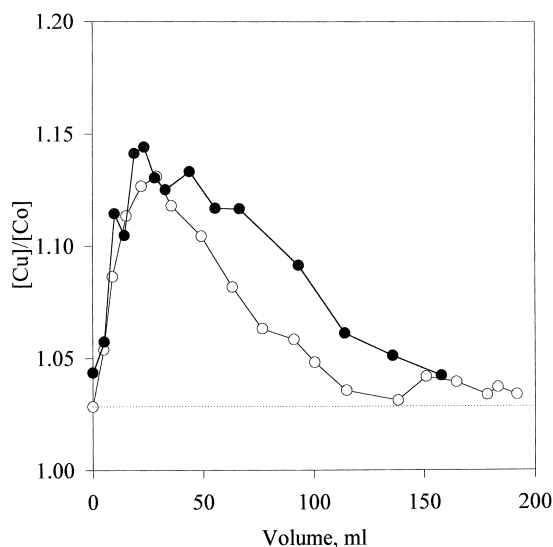


Fig. 2. Variation of Cu:Co ratio in eluate samples collected during first thermostripping cycle ($T_1=303$ K; $\Delta T=50$ K, open points) and second thermostripping cycle ($T_1=283$ K; $\Delta T=50$ K, filled points). Conditions: Feed solution – equimolar Cu^{2+} and Co^{2+} mixture of 0.05 mol/l at pH=1.55; flow-rate=0.4 ml/min; resin bed height=3.2 cm; column diameter=1.4 cm.

previous systems. As it is also seen from Table 4, both q_{Zn} and q_{Co} values increase with temperature, but this increase is more remarkable for Zn^{2+} than that for Co^{2+} .

3.3. Systems 4 and 5

The preferential sorption of Cu^{2+} versus Co^{2+} is observed in System 4. This is consistent with the difference in stability constants of IDA-Cu^{2+} and

IDA-Co^{2+} complexes, which equal to $\log \beta_{\text{IDACu}} = 10.63$ and $\log \beta_{\text{IDACo}} = 6.97$, respectively [21]. The $\alpha_{\text{Co}}^{\text{Cu}}$ values determined at different temperatures equal: 19.7 (293 K); 20.4 (313 K); 22.9 (333 K), and 26.9 (353 K). A stronger temperature effect of sorbability of copper ion makes it possible to carry out a selective thermostripping of this ion against cobalt from the resin pre-loaded with Cu^{2+} – Co^{2+} mixture at high temperature by using the same mixture at low temperature. The breakthrough thermostripping curves obtained by studying Systems 4 and 5 are shown in Figs. 2 and 3, respectively. In both cases, a selective increase of copper content in solution samples collected is observed.

4. Discussion

The results obtained by studying Systems 1–3 provide an additional support to the novel approach for predicting temperature dependencies of IE equilibrium on chelating resins [18]. The approach is based on pre-calculation of α versus T dependencies from the enthalpies of complex formation for metal ions with monomeric analogues of the resin under study (e.g., IDA ligand in solution and IDA resin). The IE reactions (the IE interaction in this case can be identified as ion exchange accompanied by complex formation) proceeding in Systems 1 and 2 (see Table 1) are written as follows:

(a) Deprotonated resin

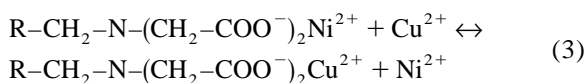


Table 4

$\alpha_{\text{Co}}^{\text{Zn}}$ values and partial capacities of Lewatit TP-207 towards Zn^{2+} , Co^{2+} and H^+ at different temperatures, meq/g

T , K	q_{Zn}	q_{Co}	q_{H}	$q_{\text{H}}/q_{\text{Zn}}$	\bar{X}_{Zn}	$\alpha_{\text{Co}}^{\text{Zn}}$
283	1.396	1.052	2.87	2.06	0.570	1.32±0.04
293	1.537	1.120	2.66	1.73	0.579	1.39±0.04
298	1.603	1.200	2.52	1.57	0.572	1.34±0.04
303	1.821	1.321	2.18	1.20	0.580	1.35±0.04
313	1.958	1.374	1.99	1.02	0.588	1.42±0.04
323	2.101	1.423	1.80	0.86	0.596	1.51±0.05
333	2.391	1.485	1.44	0.60	0.617	1.63±0.05
353	2.344	1.377	1.60	0.68	0.630	1.72±0.05

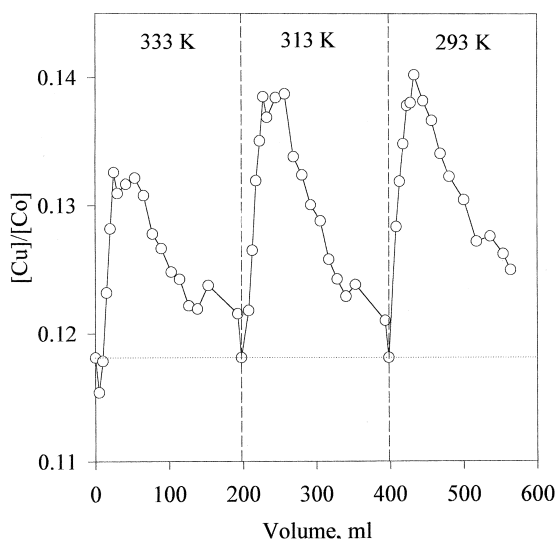
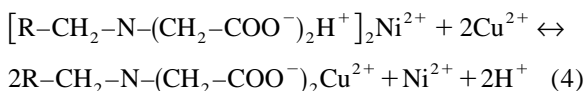


Fig. 3. Variation of Cu:Co ratio in eluate samples collected during differential thermostripping experiment ($\Delta T=20$ K) carried out with feed solution containing 0.01 mol/l of Cu^{2+} and 0.09 mol/l of Co^{2+} at $\text{pH}=1.55$. Other conditions are same as in Fig. 2.

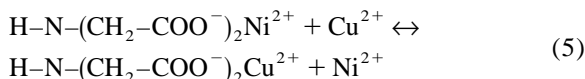
(b) Partially protonated resin



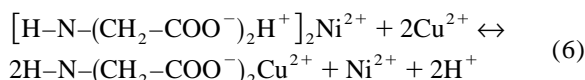
In System 1, the existence of two temperature intervals with different α versus T dependencies (see Table 2) can be attributed to the predominance of different Ni–IDA complexes in the resin phase in respective temperature ranges: $\text{Ni}(\text{IDA})_2$ at $293 < T < 308$ K and $\text{Ni}(\text{IDA})$ $308 < T < 353$ K. The probability of Ni–(IDA)₂ complex formation against Ni–IDA in System 1 is higher at low temperatures ($T < 308$ K) due to the higher content of protons in the resin phase (high values of $q_{\text{H}}/q_{\text{Ni}}$ ratio, see Table 2). Under these conditions interaction of Ni^{2+} (as a minor component) must proceed mainly with semi-protonated IDA functional groups leading to the formation of Ni–IDA complex with 1:2 stoichiometry. Similar reasoning leads to the conclusion that in System 2 (see Table 3) formation of $\text{Ni}(\text{IDA})_2$ complexes can be expected in a wider temperature range as sufficiently high values of $q_{\text{H}}/q_{\text{Ni}}$ ratio are observed in this case up to the maximal temperatures.

The formation of mixed M–IDA and M–(IDA)₂ complexes in IDA resin has been recently reported by Waki [24] (for $\text{M}=\text{Ni}^{2+}$) and by Pesavento et al. [25] (for $\text{M}=\text{Zn}^{2+}$ and Cd^{2+}). Furthermore, the IE reactions (3) and (4) can be considered to be analogous to the following IDA–complex-exchange reactions:

(a) Deprotonated IDA ligand



(b) Partially protonated IDA ligand



The differential enthalpies of reactions (5) and (6) ($\Delta(\Delta H)_{\text{Ni}-\text{Cu}}$) can be easily evaluated from the respective thermodynamic data available in the literature [23] and compared with the apparent enthalpies, ΔH_{ap} , of the IE reactions (3) and (4), which can be calculated using the following equation [18]:

$$\Delta H_{\text{ap}} = -R \left[\frac{\partial \ln \alpha}{\partial (1/T)} \right] \overline{X}_{\text{B}} \quad (7)$$

where \overline{X}_{B} is the same as in Eq. (1). Eq. (7) is derived from the van't Hoff equation by taking into account the relationships connecting α with thermodynamic equilibrium constant, K [26]:

$$\log K = \int_0^1 \log \alpha(\overline{X}_{\text{B}}) d\overline{X}_{\text{B}} \quad (8)$$

and standard and apparent enthalpies of the IE reaction:

$$\Delta H^0 = \int_0^1 \Delta H_{\text{ap}}(\overline{X}_{\text{B}}) d\overline{X}_{\text{B}} \quad (9)$$

Eq. (7) can also be used to estimate α versus T dependencies from respective literature data on $\Delta(\Delta H)_{\text{A}-\text{B}}$ values [18]. Thus, for Cu^{2+} – Ni^{2+} couple a moderate temperature dependence of IE equilibrium on IDA resin was predicted from $\Delta(\Delta H)_{\text{CuIDA}-\text{NiIDA}} = +2.33$ kJ/mol [21], and essentially no temperature effect for Co^{2+} – Zn^{2+} equilibrium on IDA resin ($\Delta(\Delta H)_{\text{ZnIDA}-\text{CoIDA}} = -0.25$ kJ/mol [21]) was expected. A comparison of the results obtained for Cu^{2+} – Ni^{2+} , and Co^{2+} – Zn^{2+} couples

(see above) testifies to the correctness of the predictions made.

As follows from the data collected in Tables 2 and 3, \overline{X}_{Cu} values remain practically constant within the whole temperature interval studied for both ionic media. This makes it possible to estimate ΔH_{ap} values for the systems under study from the slopes of respective $\ln \alpha$ versus $1/T$ plots assuming the usual (Arrhenius-like) dependencies of α on temperature. Such an estimation made for System 1 for temperature intervals, $\Delta T_1 = 293\text{--}303$ K, and $\Delta T_2 = 308\text{--}353$ K, which are characterized by different α versus T dependencies (see Table 2) gives $\Delta H_{\text{ap}}(\Delta T_1) = -15.7$ kJ/mol, and $\Delta H_{\text{ap}}(\Delta T_2) = +2.9$ kJ/mol. The $\Delta H_{\text{ap}}(\Delta T_2)$ value agrees well with $\Delta(\Delta H)_{\text{CuIDA-NiIDA}} = +2.33$ kJ/mol (see above), calculated through the use of Eq. (5). Calculation of $\Delta(\Delta H)_{\text{CuIDA-Ni(IDA)}_2}$ by using Eq. (6) from the data taken from [20] gives a value of -18.8 kJ/mol, which satisfactory agrees with $\Delta H_{\text{ap}}(\Delta T_1)$ value obtained. The enthalpy of Ni(IDA)₂ complex formation in solution refers to completely deprotonated ligand since the thermodynamic data for the corresponding protonated species are not available. Nevertheless, the enthalpy values for formation of Ni(IDA)₂ complexes with deprotonated (L) and semiprotonated (HL) IDA species can be assumed to be close to each other. The correctness of this hypothesis is confirmed by the literature data for IDA–Cu complexes reported by Bonomo et al. [27]: $\Delta H_{\text{CuL}} = -16.6$ and $\Delta H_{\text{Cu(HL)}} = -19$ kJ/mol at 298 K. These values can be considered to be nearly identical within the conventionally acceptable uncertainty of ΔH determination ($\sim 20\%$). The same similarity of enthalpy values can be expected for NiL and Ni(HL)₂ complexes. This confirms the correctness of the above supposition about formation of different Ni²⁺–IDA complexes in the resin phase at different temperatures. Note that evaluation of the mechanism of complex formation in the resin phase from α versus T dependencies is carried out for the first time and it reveals a simple method to model the resin phase composition. To confirm this conclusion, let us consider the results obtained by studying System 2 within the framework of such an approach.

The ΔH_{ap} value estimated from the slope of $\log \alpha$ versus $1/T$ plot for the temperature range from 293 to 333 K in System 2 (see Table 1) equals to -8.4 kJ/mol, i.e. appears to be in between

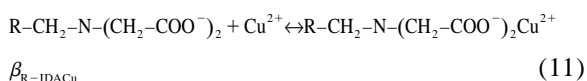
$\Delta(\Delta H)_{\text{CuIDA-NiIDA}}$ and $\Delta(\Delta H)_{\text{CuIDA-Ni(IDA)}_2}$ values (see above). In this situation one can expect a coexistence of both Ni–IDA and Ni–(IDA)₂ complexes in the resin phase and, moreover, to estimate an average content of each nickel-complex form for the overall temperature interval studied. Such estimation is based on the assumption about the additivity of heat effects of reactions (3) and (4), and can be carried out by using the following equation:

$$\Delta H_{\text{ap}} = \overline{X}_{\text{NiIDA}} \Delta(\Delta H)_{\text{CuIDA-NiIDA}} + (1 - \overline{X}_{\text{NiIDA}}) \Delta(\Delta H)_{\text{CuIDA-Ni(IDA)}_2} \quad (10)$$

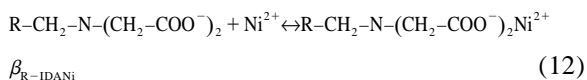
where $\overline{X}_{\text{NiIDA}}$ is the molar fraction of 1:1 Ni²⁺–IDA complexes in the resin phase. An average $\overline{X}_{\text{NiIDA}}$ value calculated from Eq. (10) equals 0.5, i.e. the equimolar quantities of both NiIDA and Ni(IDA)₂ complexes coexist in the resin in System 2 at $T = 293\text{--}333$ K.

The weak influence of temperature on IE equilibrium in System 3 correlates well with the predictions made previously [18] (see above). Estimation of ΔH_{ap} from α values determined at $283 < T < 313$ K gives a value of 0.45 kJ/mol, which correlates with $\Delta(\Delta H)_{\text{ZnIDA-CoIDA}} = -0.25$ kJ/mol [23] (this value refers to 293 K) within the uncertainty on ΔH_{ap} determination exceeding 100% in this case. The further increase of temperature in this system does not lead to substantial variation α values. Hence, no remarkable changes in the stoichiometry of metal complexes formed in the resin phase can be expected. On the other hand, relatively low values of $q_{\text{H}}/q_{\text{Zn}}$ ratio permit to assume the predominant formation of Zn(IDA) complexes with 1:1 stoichiometry.

The IE reaction (3) can be represented by a simultaneous combination of two independent equilibria, which describe the complexation of a single ionic species by IDA resin:



and



where stability constants, β , are defined as follows:

$$\beta_{R-IDACu} = \frac{q_{Cu}}{C_{IDA}^* C_{Cu}^*} ; \beta_{R-IDANi} = \frac{q_{Ni}}{C_{IDA}^* C_{Ni}^*} \quad (13)$$

Here q_{Cu} and q_{Ni} are the same as in Table 2, and C_{IDA}^* and $C_{Cu,Ni}^*$ are the equilibrium concentrations of free (uncomplexed) IDA groups in the resin phase and metal ions in the solution phase, respectively.

Since Eq. (3) can be obtained by subtracting Eq. (12) from Eq. (11) and taking into account Eqs. (13) one can rearrange Eq. (1) as follows:

$$\alpha_{Ni}^{Cu} = \frac{\beta_{R-IDACu}}{\beta_{R-IDANi}} \quad (14)$$

Taking logarithm of Eq. (14) one obtains:

$$\log \alpha_{Ni}^{Cu} = \log \beta_{R-IDACu} - \log \beta_{R-IDANi} \quad (15)$$

Similar equations can be derived for other ionic couples studied. Stability constants of metal complexes in the resin phase, β_{R-IDAM} (here M=metal ion under consideration), are known to be proportional to the β_{IDAM} values of IDA ligand complexes in the solution phase [28]. Substantiation of this conclusion is demonstrated in Fig. 4, where $\log \alpha$ for

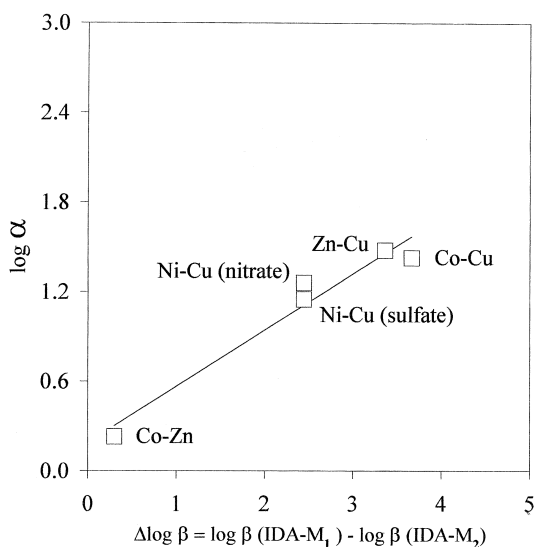


Fig. 4. Correlation between $\log \alpha$ and $\Delta \log \beta$ for different metal ion pairs.

different ion couples are plotted against respective $\Delta \log \beta_{IDAM}$ values taken from [23]. As seen in Fig. 4, $\log \alpha$ versus $\Delta \log \beta$ dependence is satisfactorily approximated by a straight line. Note, that all α values used to plot Fig. 4 refer to $T=353$ K, where the formation of 1:1 IDA–M complexes predominate (see above). The corresponding $\Delta \log \beta$ values also refer also to complexes of the same type. A good correlation between $\log \alpha$ and $\Delta \log \beta$ values, shown in Fig. 4 provide an additional confirmation of validity of conclusions derived by studying Systems 1 and 2 (see above).

The results, obtained by studying systems 4 and 5 (see Figs. 2 and 3) illustrate the influence of ΔT value on the efficiency of thermostripping process, which is directly proportional to the ratio of $K(T_2)/K(T_1)$ [3], depending, in turn, on the differential enthalpy of IE reaction under consideration [18]:

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{RT_1} \left(\frac{\Delta T}{T_1 + \Delta T} \right) \quad (16)$$

where $\Delta T = T_2 - T_1 > 0$, and T_1 assigns the position of ΔT on the temperature scale. As follows from Eq. (16), at fixed ΔT and ΔH , the value of $K(T_2)/K(T_1)$ ratio increases when T_1 decreases. The confirmation of this conclusion is seen in Figs. 2 and 3. Indeed, when thermostripping is carried out in a wide temperature interval ($\Delta T=50$ K, see Fig. 2), the decrease of T_1 from 303 to 283 K leads to the broadening of copper concentration peak indicating that a higher amount of copper is desorbed from the resin.

On the other hand, in experiments on differential thermostripping carried out in a more narrow temperature interval ($\Delta T=20$ K), the decrease of T_1 results in an increase of the height of copper peak (see Fig. 3). This indicates an enhancement of selective concentration of copper against cobalt in the stripping solution.

5. Conclusions

The following conclusions can be derived from the results obtained in this study:

1. Temperature dependence of the equilibrium separation factor for $Zn^{2+}-Co^{2+}$ and $Cu^{2+}-Ni^{2+}$ exchanges on Lewatit TP-207 resin of im-

- inodiacetic type from sulphate solutions agree well with those predicted from the differential enthalpies of complex exchange reactions between metal ions under study and iminodiacetic acid (monomeric analog of IDA resin).
2. Estimation of composition of the resin phase from temperature dependencies of separation factor for Ni–Cu exchange on IDA indicates the formation of both 1:1 and 1:2 Ni–IDA complexes in the resin phase. This result is consistent with the IR spectra of the resin pre-loaded with the Cu^{2+} – Ni^{2+} mixtures at 293 and 353 K and, thus, confirms the validity of the proposed approach.
 3. The efficiency of thermostripping process carried out in the Cu–Co system has been shown to be influenced by the width of interval of working temperatures and on its position on the temperature scale, so that the efficiency rises when ΔT increases and when it is shifted to the lower temperatures.
 4. Logarithms of α values determined for different metal ion couples on IDA resin at 353 K appear to be directly proportional to the difference in respective $\log \beta_{\text{IDAM}}$ values referred to the 1:1 IDA–M complexes.

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