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Aqua-Impregnated Resins. 1. Mass Transfer Active Interfaces in Bi- and Triphase Systems Involving Solid Polymer and Two Immiscible Liquid Phases

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The ion-exchange and extraction equilibria of Cu^{2+} and Zn^{2+} from aqueous sulfate solutions at pH = 1.9 in bi- and triphase systems (Resin–Organic solution of extractant–Aqueous solution) involving solid resins (either iminodiacetic (IDA) or (aminomethyl)phosphonic (AMP)) and an organic solution of extractant in heptane (either LIX 860, phosphoric acid bis(2-ethylhexyl) ester (DEHPA), or dithiophosphoric acid bis(2-ethylhexyl) ester (DEHDTPA)) have been studied at 22 °C. The values of the equilibrium separation factor α for Zn^{2+} – Cu^{2+} exchange and the degree of Cu^{2+} extraction, E , in triphase R–Org–Aq systems depend on the relative selectivity of the resin over the extractant (or vice versa) toward the ion couple under study. The ion-exchange interaction in the triphase system proceeds via three interfaces representing three possible routes for the mass transfer. Each interface can be characterized by the corresponding ion-exchange reaction and related α value. A comparison of the extraction behavior of DEHPA and DEHDTPA toward Cu^{2+} – Zn^{2+} mixtures in the bi- and triphase systems of different types has shown that the presence of the resin significantly facilitates the solvent extraction of the ionic species that are not extracted in the liquid–liquid systems. The maximum extraction degree of the “nonextractable” metal ion is observed in a resin–organic solution of extractant biphasic systems (aqua–impregnated resin (AIR) systems), which can be attributed to the changes of both hydration of metal ions and pH in the resin phase. Taking into account these characteristics, one-stage extractive purification of Cu^{2+} from a Cu^{2+} – Zn^{2+} mixture in a DEHPA–IDA resin AIR system has resulted in the rise of the product (CuSO_4) purity from 98.1 to 99.8%. Purification of Zn^{2+} from a Cu^{2+} – Zn^{2+} mixture in an AIR system involving DEHDTPA and AMP resin has allowed the purity of ZnSO_4 to be increased from 52.5 to 99.3%. The results of this study are the first successful demonstration of the applicability of the AIR concept to enhance the selectivity of metal ion separation.

Introduction

Biphasic systems involving a solid or liquid ion exchanger and a liquid (basically aqueous) solution are the systems most conventionally investigated in the field of ion exchange. The presence of a third phase in the biphasic ion-exchange system (by either addition or its formation during ion-exchange interaction) is usually used for shifting the ion-exchange equilibrium in the desired direction.¹ The new system may offer some advantages in comparison with the traditional variant of the ion-exchange process.

Triphase solid–solid–liquid (S–S–L) systems most often applied in practice are mixed beds of ion exchangers widely used for water deionization^{2–4} and in ion-exchange synthesis.^{5,6} S–S–L systems, where the ion-exchange process is accompanied by the formation of slightly soluble substances, have been applied in precipitation chromatography,⁷ for modifying ion-exchange resins^{8,9} and for some other purposes.^{10,11}

Triphase S–L–L systems including solid resin and two immiscible liquid phases (aqueous and organic) are known

in the literature mainly as triphase catalytic systems.^{12,13} Phase-transfer catalysis with ion-exchange resins^{14,15} and reactive extraction with ion-exchange membranes^{16,17} are comparable to the mass-transfer process proceeding in S–L–L systems. Two versions of S–L–L systems including either ion-exchange membranes¹⁷ or granulated ion-exchange resins^{18–20} simultaneously contacting both organic and aqueous phases have been shown to be applicable in mass-exchange reactions. Moreover, similar intrinsic rates of exchange reactions are observed in both cases.¹⁹ Recently it has been shown that S–L–L systems can be effectively applied for carrying out the hydrogen–deuterium, H–D, exchange reaction on (trimethylamino)–borane dissolved in water–immiscible solvents.^{17–20} In this case, the isotope-exchange reaction has been demonstrated

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to occur at the interface between the water-swollen (aqua-impregnated) ion-exchange material and the organic phase. It has also been shown that the aqueous phase (D_2O) can be withdrawn from S–L–L systems in such a way that it is substituted by the D_2O taken up in the swollen polymer.^{19,20} This has been shown to allow for transforming triphase S–L–L systems into the corresponding biphasic ones where the aqua-impregnated resins (AIR)²⁰ phase is in contact with the organic solution of the substrate, and thus providing the conditions to modify the batch mode of operation (deuteration) to the dynamic one and, thus, to obtain the spectroscopically pure deuterated product in two stages.²⁰ On the other hand, the mechanism of the mass transfer in the AIR systems is not studied yet in detail, although this information may be of particular importance for the further development and practical application of the AIR concept.

The present study has been focused on the further development of the AIR approach and represents its first successful application to the selective separation of metal ions. The main objectives of this work are addressed (1) to obtain information on the Zn^{2+} – Cu^{2+} distribution equilibria in bi- and triphase systems involving solid resin, organic solution of extractant, and aqueous solution of metal ions, (2) to elucidate the mutual influence of contacting phases in the equilibrium state and the possible pathways (active interfaces) of mass transfer in systems under study, and (3) to demonstrate a possibility of selective separation of Cu^{2+} and Zn^{2+} using the AIR technique.

Experimental Section

Reagents, Ion Exchangers, and Extractants. Copper sulfate, zinc sulfate, and sulfuric and hydrochloric acids of analytical grade were from Panreac (P.A., Barcelona, Spain). Iminodiacetic acid ion exchanger (IDA), Lewatit TP-207, and (aminomethyl)phosphonic acid resin (AMP), Lewatit R-252-k, were kindly supplied by Bayer Hispania Industrial, S.A. Phosphoric acid bis(2-ethylhexyl) ester (DEHPA) 99% was purchased from Carlo Erba R.S. (Milano, Italy). LIX 860 (solution of 5-dodecylsalicylaldehyde in kerosene) was kindly supplied by Henkel KGaA (Germany). Dithiophosphoric acid bis(2-ethylhexyl) ester (DEHDTPA) was synthesized from phosphorus pentasulfide and 2-ethylhexanol as described elsewhere.²¹ Further purification of DEHDTPA was carried out by following a previously reported procedure.²² The purity of the final product determined by potentiometric titration of samples dissolved in a water–ethanol mixture with 0.05 M NaOH appeared to be $95 \pm 0.2\%$. Doubly distilled water was used in all experiments. Prior to experiments, solutions were degassed by using an ultrasonic bath (Branson 1200) and a vacuum pump. The pH of the stock solution of the Cu^{2+} and Zn^{2+} sulfate mixture was adjusted to 1.9 ± 0.05 with 0.2 M H_2SO_4 .²³ Standard precautions recommended for handling sulfuric acid solutions²⁴ were followed for adjusting the pH and preparing the 0.2 M H_2SO_4 solution from concentrated acid. The concentrations of metal ions were determined by the ICP-AES technique using an ARL Model 3410 spectrometer. The emission lines used for the spectrochemical analysis were 224.7 nm for Cu^{2+} and 206.91 nm for Zn^{2+} . The relative uncertainty of metal ion determination was $<1.5\%$. The pH was controlled using a Crison pH meter 507 (Barcelona, Spain) supplied with a combined glass electrode. Glass columns (of 1.0 cm i.d.) with two-way polycarbonate flow adaptors (Bio-Rad, Richmond, CA) were used for the ion-exchange equilibrium experiments. A 0.036 M solution (indicated otherwise) of a given

extractant in heptane (99%, Aldrich, Steinheim, Germany) was employed as the organic phase. In the case of LIX 860 the above concentration referred to the 5-salicylaldehyde content.^{25,26} A rotary mixer, SBS, ABT-4, was used to carry out agitation in batch experiments in an air-conditioned room at $22 \pm 0.5^\circ C$.

Procedure. Experiments on studying extraction and ion-exchange equilibria in triphase and biphasic systems involving solid resin (R), organic solution of extractant (Org), and aqueous solution (Aq) were carried out in batch mode by agitating equal volumes of Org and/or Aq with 0.25 g of R (in H^+ -form) preconditioned with H_2SO_4 solution at pH = 1.9. In all the cases, the equilibration was carried out by using stoppered glass tubes fixed on a continuously rotating rack at 55 rpm during 14 h, which was sufficient time to reach equilibrium in both extraction and ion-exchange processes under the experimental conditions. After equilibration, the resin phase was transferred quantitatively into a column (1.0 cm i.d.) and separated from the Aq and/or Org by blowing them away with compressed air. The resin was rinsed with ethanol to remove the film of organic phase from the surface of the beads (when necessary). Then, metal stripping was carried out using 50 mL of 2.2 M HCl followed by the analysis of Cu^{2+} and Zn^{2+} in the resulting eluate and equilibrium aqueous solution. The concentration of metal ions in the Org was calculated for Org–Aq systems as the difference between concentrations of the respective ionic species in stock and in equilibrium aqueous solutions. In the case of R–Org–Aq triphase systems, the metal content in the Org was calculated as the difference between concentrations of metal ions in stock solution and the sum of their concentrations in equilibrium and stripping solutions.

Ion-exchange equilibria in biphasic systems of R–Aq types were also studied under dynamic conditions in columns. The resin was equilibrated with stock solutions of a Cu^{2+} – Zn^{2+} mixture of composition similar to those used in batch experiments with the respective R–Org–Aq triphase systems followed by stripping of metal ions and determination of the composition of both the stock solution and the eluate obtained.

The data for the equilibrium and stripping processes were used to determine both the capacity of the resin toward copper and zinc and the equilibrium separation factor, α , expressed as follows:

$$\alpha_{R(Org)} = \alpha_{Zn}^{Cu} = \frac{\bar{X}_{Cu} X_{Zn}}{\bar{X}_{Zn} X_{Cu}} = \frac{\bar{X}_{Cu}}{1 - \bar{X}_{Cu}} \frac{1 - X_{Cu}}{X_{Cu}} \quad (1)$$

where \bar{X} and X are the equivalent fractions of metal ions in the resin (R) or organic solution of extractant (Org) and aqueous solution, respectively. The relative uncertainty on α determination did not exceed 7%. The degree of copper or zinc extraction, E_i , was determined for Org–Aq and R–Org–Aq systems from the data of the stock, equilibrium, and stripping solution analyses as follows:

$$E_i = \frac{C_{Org} V_{Org}}{C_0 V_{Aq}} \quad (2)$$

where $i = 2$ or 3 denotes the number of phases, C_{Org} is the equilibrium concentration of either Cu^{2+} or Zn^{2+} in the organic phase (mmol/cm³), C_0 is the initial concentration of Cu^{2+} or Zn^{2+} in the stock solution (mmol/cm³), and V_{Org} and V_{Aq} are the volumes of the organic and the aqueous phases, respectively (cm³). The sorption degree E_i^R was also determined for the R phase in R–Aq and R–Org–Aq systems as follows:

$$E_i^R = \frac{q_M m}{C_0 V_{Aq}} \quad (3)$$

where $M = Cu^{2+}, Zn^{2+}$, q_M is the capacity of the R toward the respective metal ion (mmol/g), and m is the mass of the resin portion used (g).

In R–Org systems, the degrees of metal ion extraction, E_M , and sorption, E_M^R , were determined by using the following

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Table 1. Specific Capacities (q) of the AMP Resin (Lewatit R-252) toward Cu^{2+} and Zn^{2+} in Bi- and Triphase Systems Involving LIX 860 at Different Metal Concentrations (C_{tot}) and Compositions (X_{Cu}) of CuSO_4 – ZnSO_4 Mixtures

C_{tot} , mol/L	X_{Cu}	q_{Cu} , mmol/g		q_{Zn} , m mol/g		$Q = q_{\text{Cu}} + q_{\text{Zn}}$	
		bi ^a	tri	bi ^a	tri	bi ^a	tri
0.25	0.002	0.004	0.004	0.74	0.67	0.74	0.67
0.38	0.011	0.017	0.012	0.82	0.68	0.84	0.69
0.51	0.027	0.046	0.032	0.88	0.77	0.93	0.80
0.67	0.040	0.059	0.048	0.95	0.90	1.01	0.95

^a Determined under dynamic conditions.

Table 2. Specific Capacities (q) of the IDA Resin (Lewatit TP-207) toward Cu^{2+} and Zn^{2+} in Bi- and Triphase Systems Involving LIX 860 at Different Metal Concentrations (C_{tot}) and Compositions (X_{Cu}) of CuSO_4 – ZnSO_4 Mixtures

C_{tot} , mol/L	X_{Cu}	q_{Cu} , mmol/g		q_{Zn} , m mol/g		$Q = q_{\text{Cu}} + q_{\text{Zn}}$	
		bi ^a	tri	bi ^a	tri	bi ^a	tri
0.25	0.001	0.02	0.18	0.48	0.28	0.50	0.46
0.41	0.003	0.07	0.30	0.54	0.31	0.61	0.61
0.52	0.012	0.24	0.46	0.53	0.32	0.77	0.78
0.74	0.029	0.54	0.69	0.54	0.34	1.08	1.03

^a Determined under dynamic conditions.

expressions:

$$E_{\text{M}} = \frac{C_{\text{Org}} V_{\text{Org}}}{q_{\text{M}} m} \quad E_{\text{M}}^{\text{R}} = \frac{q_{\text{M}}^{\text{m}}}{C_{\text{Org}} V_{\text{Org}}} \quad (4)$$

The uncertainty on E determination was $\leq 8\%$.

Results

The experimental data corresponding to the ion-exchange equilibrium of Cu^{2+} and Zn^{2+} on either (aminomethyl)phosphonic acid (AMP) or iminodiacetic acid (IDA) resins in biphasic (R–Aq) and triphasic (R–Org–Aq) systems involving LIX 860 have been expressed in terms of specific sorption capacities, q , and selectivity factors, α . Tables 1 and 2 collect the results of sorption capacities for AMP and IDA, respectively.

Comparison of data given in Table 1 with those presented in Table 2 shows that the introduction of the extractant phase into the biphasic R–Aq system modifies AMP and IDA resin capacities in a different manner. As follows from Table 1, the capacities of AMP resin toward both metal ions, q_{Cu} and q_{Zn} , in biphasic, R–Aq, systems are higher than those determined in the presence of LIX 860. On the contrary, as seen in Table 2, the IDA resin manifests an absolutely different behavior. Addition of the Org leads to a significant increase of q_{Cu} , whereas the capacity toward Zn^{2+} decreases. In this case, the total capacity of the resin, Q , remains practically constant when determined in either bi- or triphase systems while for AMP resin, Q , appears to be lower in presence of the Org in comparison with the value determined in the biphasic R–Aq system (see Table 1). The observed differences in AMP and IDA resins in the triphase system (including LIX 860) can be attributed to the difference in resin selectivities toward Cu^{2+} and Zn^{2+} against the selectivity of the extractant. Thus, q_{Cu} values for R–Aq given in Tables 1 and 2 demonstrate that IDA resin has a much higher affinity for copper than AMP, which correlates well with our previous results.²⁷ Furthermore, LIX 860 is also

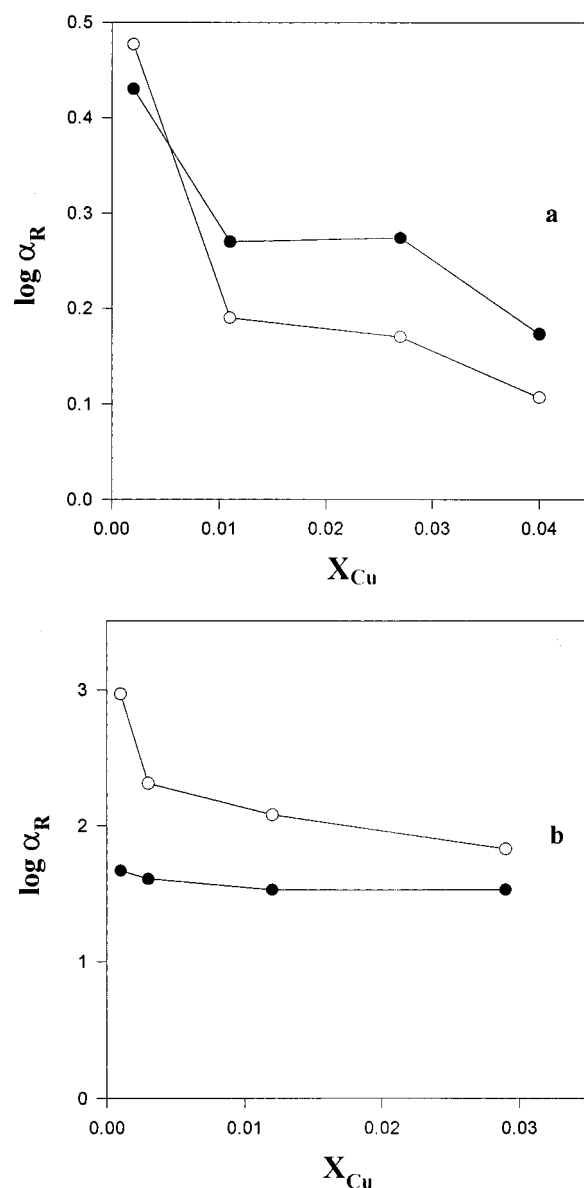


Figure 1. $\log \alpha_{\text{R}}$ vs X_{Cu} for AMP (Lewatit R-252) (a) and $\log \alpha_{\text{R}}$ vs X_{Cu} for IDA (Lewatit TP-207) (b) in bi- (filled points) and triphase (empty points) systems, involving LIX 860. Conditions: $m = 0.25$ g, $V_{\text{Org}} = 10$ cm³, $V_{\text{Aq}} = 10$ cm³.

known to be highly selective toward copper.^{25,28} Introduction of the Org into the biphasic R–Aq system creates conditions for a "competitive" sorption-extraction process. Then, in the case of R–Org–Aq systems involving AMP resin, LIX 860 manifests a stronger affinity toward both metal ions and "wins the competition"; so, it extracts them from both the aqueous and the resin phases, leading to a lower resin capacity (see Table 1). As follows from the data given in Table 2, the IDA resin shows an opposite behavior toward Cu^{2+} ; i.e. IDA sorbs this ion from both the Aq and Org, whereas a higher affinity of LIX 860 toward Zn^{2+} leads to the extraction of this metal from the R and Aq.

The above qualitative explanations are supported by the following quantitative relationships presented in Figures 1 and 2. Figure 1 presents $\alpha_{\text{Zn}}^{\text{Cu}}$ vs X_{Cu} dependencies for AMP (Figure 1a) and IDA (Figure 1b) resins determined in bi- and triphase systems. Figure 2 shows the extraction degree of Cu^{2+} for LIX 860 in the presence

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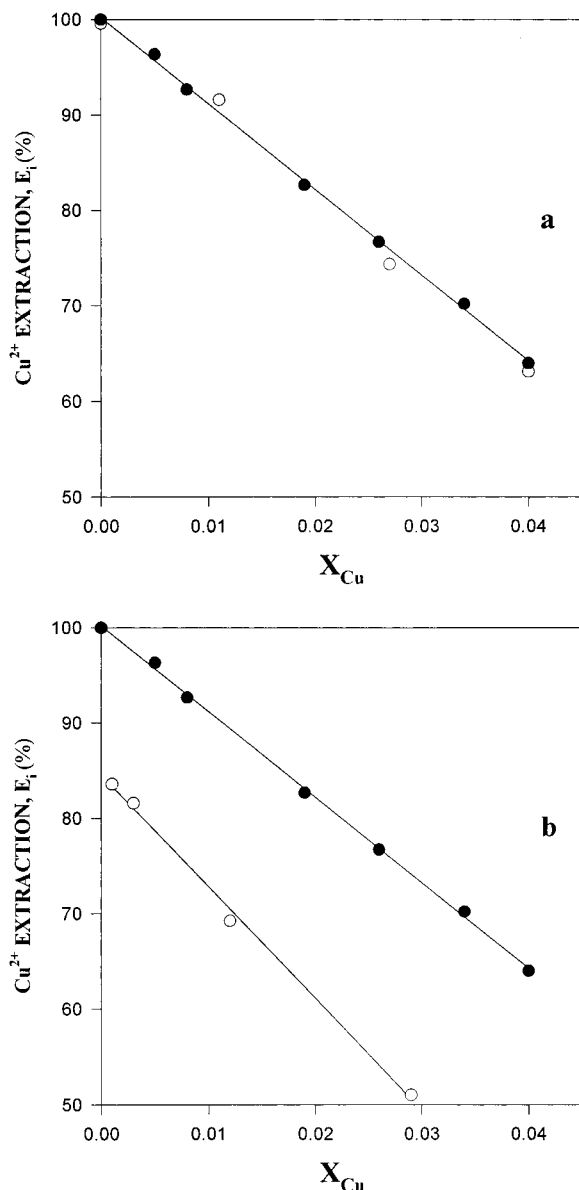


Figure 2. Extraction degree of Cu^{2+} vs X_{Cu} for LIX 860 in bi- (filled points) and triphase (empty points) systems involving AMP (Lewatit R-252) (a) and IDA (Lewatit TP-207) (b) resins. Conditions are the same as in Figure 1.

and absence of AMP (Figure 2a) and IDA (Figure 2b) resins. In Figure 1a, α_R values for the AMP resin in the biphasic systems are higher than those determined in the presence of Org. A much stronger influence of the Org on the R selectivity is developed in the LIX 860–IDA resin system, as is clearly seen in Figure 1b where, moreover, this influence leads to a higher resin selectivity in the triphase LIX 860–IDA system that is opposite to the results for the LIX 860–AMP system (Figure 1a).

The influence of the R on the Org behavior is illustrated by Figure 2. As seen in Figure 2a, LIX 860 is not “feeling” the presence of the AMP resin, since E (percent extraction) values determined in bi- and triphase systems are practically the same (within the uncertainty on E determination, see below) for the Aq of the same composition. On the contrary, LIX 860 appears to be more sensitive toward the presence of the IDA resin (see Figure 2b), which follows from the decrease of E values in the triphase system. These results can be correlated with data shown in Figure 3, where the degree of Cu^{2+} extraction (sorption), E_i^R , by the IDA resin in R–Aq and R–Org–Aq systems is presented. The E_i^R vs X_{Cu} dependencies shown in Figure

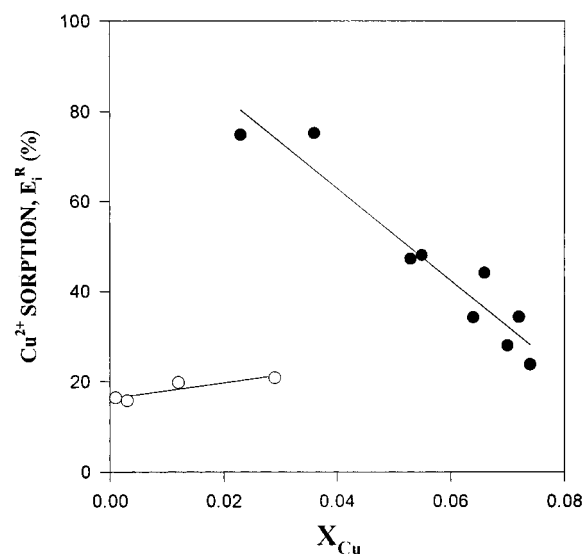


Figure 3. Sorption degree of Cu^{2+} vs X_{Cu} for IDA (Lewatit TP-207) resin in bi- (filled points) and triphase (empty points) systems, involving LIX 860.

3 for the triphase systems were calculated from the equilibrium data given in Table 2 using eq 3. As follows from Figure 3, Cu^{2+} sorption decreases when X_{Cu} increases in the biphasic R–Aq system, while much lower E_i^R values with an opposite trend are observed in the presence of the Org phase. Note that the difference of E_i values for LIX 860 in the bi- and triphase systems approximately equals the Cu^{2+} sorption values for the IDA resin in the respective R–Org–Aq systems.

The results obtained by studying the ion-exchange and extraction equilibria in bi- and triphase systems involving AMP resin and DEHDTPA (known to be copper selective extractant^{29–31}) are shown in Figures 4 and 5. This series of experiments was carried out by varying the composition of a CuSO_4 – ZnSO_4 mixture (in Aq) in a wide range, while C_{tot} was kept constant at the 0.40 ± 0.01 M level. The plots of α_R vs X_{Cu} for the AMP resin obtained in the presence and absence of the Org are shown in Figure 4. Comparison of the results given in Figure 4 with those shown in Figure 1 indicates the good correlation between the AMP resin behavior in the presence of two different copper selective extractants. Indeed, as seen in Figure 4, the selectivity factor does not vary dramatically in the presence of the Org (DEHDTPA); nevertheless, a sharper trend of decreasing α_R values in the triphase system can be seen. This indicates the weak influence of the Org on the selectivity of the resin toward the ion couple under study. A similar conclusion on affecting the Org by the R can be derived from the results shown in Figure 5, where $E_i(\text{Cu}^{2+})$ values for DEHDTPA measured in the presence and absence of the R (AMP resin) are presented. As follows from Figure 5, the Org does not practically “feel” the presence of the R; nevertheless, a definite increase of copper extraction in R–Org–Aq (versus Org–Aq) systems with X_{Cu} in the range from 0.2 to 0.6 can be observed. This correlates with the above assumption about extraction of metal ions (Cu^{2+} in this case) from the resin phase.

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(32) In S_3 the resin phase was pre-equilibrated with a solution of Cu^{2+} and Zn^{2+} mixture then rinsed with water followed by introduction of the resin into S_3 . The resin prepared in the above manner was also used to study S_4 .

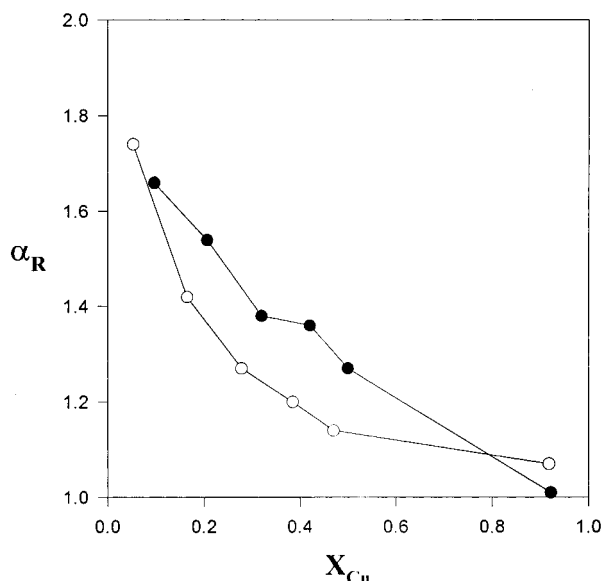


Figure 4. α_R vs X_{Cu} for AMP (Lewatit R-252) resin in bi- (filled points) and triphase (empty points) systems, involving DEH-DTPA.

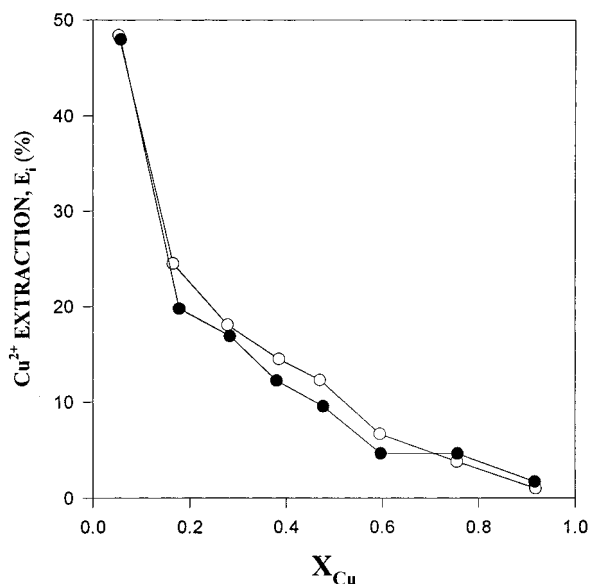


Figure 5. Extraction degree of Cu^{2+} vs X_{Cu} for DEHDTPA in bi- (filled points) and triphase (empty points) systems, involving AMP (Lewatit R-252) resin.

Discussion

The meaning of the results of this study may be understood first by viewing the mutual influence of the contacting phases on each other in the R–Org–Aq systems studied. For this purpose it is convenient to consider $E_{2,3} = f(X_{Cu})$ dependencies of two types presented in Figure 2a,b. In the biphasic Org–Aq systems E_2 vs X_{Cu} dependencies can be described by eq 2, which can be rewritten as follows:

$$E_2 = \frac{C_0 - C_{eq}}{C_0} = 1 - \frac{C_{tot}}{C_0} X_{Cu} \quad (5)$$

where C_0 and C_{tot} are the initial copper concentration and the total concentration of metal ions in the aqueous phase, respectively (mol/dm^3).

For the triphase systems, including also the solid R, one can write

$$E_3 = 1 - \frac{C_{eq} V_{aq} + q_{Cu} m}{C_0 V_{aq}} \quad (6)$$

where q_{Cu} and m are the same as above (see Experimental Section).

The ion-exchange equilibrium in the triphase system can be better described in terms of α_R values. Consider first R–Org–Aq systems involving the AMP resin, which is characterized by low selectivity toward Cu^{2+} (see Figure 1a). As follows from eq 1, at low α values and low copper content in the Cu^{2+} – Zn^{2+} mixture both $(1 - X_{Cu})$ and $(1 - \bar{X}_{Cu})$ tend to 1 (i.e., at $X_{Cu} \rightarrow 0$, $(1 - X_{Cu}) \rightarrow 1$ and $(1 - \bar{X}_{Cu}) \rightarrow 1$). Therefore, in this case α_R can be approximated by

$$\alpha_R \approx \frac{\bar{X}_{Cu}}{X_{Cu}} \quad (7)$$

where

$$\bar{X}_{Cu} = \frac{q_{Cu}}{Q} \quad (8)$$

and $Q = q_{Cu} + q_{Zn}$ (see Tables 1 and 2) is the total specific capacity of the resin in the triphase system under study (mmol/g). Combining eqs 7 and 8 with 6, one obtains

$$E_3 = 1 - \frac{\alpha_R Q_R + C_{tot} V_{aq}}{C_0 V_{aq}} X_{Cu} \quad (9)$$

where $Q_R = Qm$ is the resin portion capacity in the triphase system (mmol). Comparison of eq 9 with eq 5 shows that the equality of the slopes of $E_2 = f(X_{Cu})$ and $E_3 = f(X_{Cu})$ lines (see Figure 2a) can be observed only if $\alpha_R Q_R \ll C_{tot} V_{aq}$. As follows from the data presented in Table 1, Q values for the AMP resin in the presence of LIX 860 lie within the range from 0.17 to 0.24 mmol . As seen in Figure 1a, α_R values for the AMP resin in R–Org–Aq systems lie between 2.0 and 1.3. Thus an estimation of $\alpha_R Q_R / C_{tot} V_{aq}$ ratios against the E_3 values presented in Figure 2a shows that they do not exceed 8%, which corresponds to the uncertainties on E_3 determination.

The data for the IDA resin (see Figure 2b) can be treated in a way similar to that above. The q_{Cu} value in eq 6 for the triphase systems involving LIX 860 and the IDA resin can be expressed using another approximation for α_R . As follows from eq 1, at low X_{Cu} and high α_R (see Figure 1b) $\bar{X}_{Cu} \gg 0$ (see Table 2) and the approximation (7) is not valid. Hence, in this case eq 1 can be rewritten as follows:

$$\alpha_R \approx \frac{\bar{X}_{Cu}}{(1 - \bar{X}_{Cu}) X_{Cu}} \quad (10)$$

From eqs 8 and 10 one obtains

$$q_{Cu} = \frac{\alpha_R Q X_{Cu}}{1 + \alpha_R X_{Cu}} \quad (11)$$

Substituting eq 11 into (6) and neglecting the term that contains X_{Cu}^2 (since at $X_{Cu} \rightarrow 0$, $X_{Cu}^2 \approx 0$) gives

$$E_3 = 1 - \frac{\alpha_R Q_R + C_{tot} V_{aq}}{C_0 V_{aq} (1 + \alpha_R X_{Cu})} X_{Cu} \quad (12)$$

Comparison of eqs 9 and 12 shows that the term determining the slope of the $E_3 = f(X_{Cu})$ line in the last equation differs from that in (9) by the term $(1 + \alpha_R X_{Cu})$, which can be rewritten after rearrangement of eq 10 as

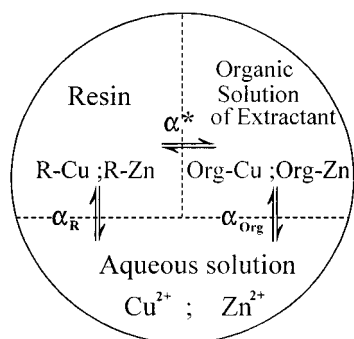


Figure 6. Scheme of triphase system involving solid resin, organic solution of extractant, and aqueous solution of metal ions.

follows:

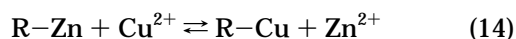
$$1 + \alpha_R X_{Cu} = \frac{1}{1 - \bar{X}_{Cu}} = \frac{1}{\bar{X}_{Zn}} \quad (13)$$

By using $1/\bar{X}_{Zn}$ values, the term $(1 + \alpha_R X_{Cu})$ can be determined experimentally with higher accuracy ($\sim 1.5\%$).

As seen in Figure 2b, the slopes of the lines $E_3 = f(X_{Cu})$ and $E_2 = f(X_{Cu})$ differ from each other and results are consistent with this difference since $E_3 < E_2$, which corresponds to a higher negative slope of $E_3 = f(X_{Cu})$ in eq 12. Interpretation of such a difference can be based upon reasonings similar to those given above for the LIX 860–AMP resin systems. Indeed, as seen in Figure 1b, α_R values for the IDA resin are much higher than those determined for the AMP ion exchanger (see Figure 1a); therefore, the value of the term $\alpha_R Q_R$ now becomes comparable with that of $C_{tot} V_{aq}$.

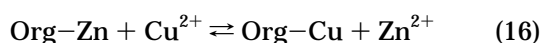
As follows from the above discussion, the distribution of metal ions between the R and Org phases depends on the *competitive affinity* of each phase toward ionic species under consideration. The meaning of this parameter may be understood by viewing all distribution equilibria in the R–Org–Aq system shown schematically in Figure 6. As seen in Figure 6, the triphase systems of this type are characterized by three interfaces: one liquid–liquid (Org–Aq) and two solid–liquid (R–Aq and R–Org). Each interface represents a possible pathway for the mass transfer in the system and therefore can be associated with the respective ion-exchange reaction and with the corresponding α values as follows:

R–Aq interface



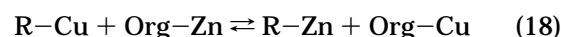
$$\alpha_R = \frac{[Cu^{2+}]_R [Zn^{2+}]_{Aq}}{[Zn^{2+}]_R [Cu^{2+}]_{Aq}} \quad (\text{see eq 1}) \quad (15)$$

Org–Aq interface



$$\alpha_{Org} = \frac{[Cu^{2+}]_{Org} [Zn^{2+}]_{Aq}}{[Zn^{2+}]_{Org} [Cu^{2+}]_{Aq}} \quad (\text{see eq 1}) \quad (17)$$

R–Org interface



$$\alpha^* = \frac{[Zn^{2+}]_R [Cu^{2+}]_{Org}}{[Cu^{2+}]_R [Zn^{2+}]_{Org}} \quad (19)$$

Here and above R, Org, and Aq subscripts denote the resin, organic solution of extractant, and aqueous phases, respectively.

The aqueous solution in contact with the R and Org phases in the triphase systems is the same, therefore substituting equations (15) and (17) into (19) one obtains:

$$\alpha^* = \frac{\alpha_{Org}}{\alpha_R} \quad (20)$$

As follows from eq 20 all ion-exchange equilibria in the triphase systems under consideration are inter-related with each other. Separation factor α^* in this context can be considered as not only a quantitative characteristics of the organic solution–resin equilibrium but also a measure of the *competitive affinity* of the extractant against the resin (at $\alpha^* > 1$ or vice versa otherwise) toward certain ionic species (Cu^{2+} in our case). The α_R , α_{Org} , and α^* values for triphase systems studied are given in Tables 3 and 4.

As seen in Table 3, α^* values in the triphase systems involving the AMP resin and LIX 860 are sufficiently high within the range of X_{Cu} studied. This correlates with the data given in Table 1 and testifies to the possibility of Cu^{2+} extraction from the R phase via the R–Org interface (see above). An opposite situation is observed in Table 4, where α^* values in LIX 860–IDA resin systems appear to be < 1 . As follows from Table 2, the direction of the Cu^{2+} transfer through the R–Org interface in this system changes to the contrary; i.e., the IDA resin sorbs this ionic species from the Org.

An additional substantiation of the observed results was obtained within the series of experiments carried out with bi- and triphase systems involving different combinations of heptane solution of extractants (either DEHDTPA, LIX 860, or DEHPA) with the resins (either IDA or AMP). In these systems, the distribution equilibria of Cu^{2+} and Zn^{2+} from a 0.4 M mixture of $CuSO_4$ and $ZnSO_4$, with $Cu^{2+}:Zn^{2+} = 1:1$ at pH = 1.9, was studied under batch conditions (see Experimental Section). The results of this series of experiments are collected in Tables 5–7.

As seen in Table 5, DEHDTPA does not extract Zn^{2+} in the biphasic system S_1 . Note that the same result has been observed in experiments on liquid–liquid extraction with the same Org for Cu^{2+} – Zn^{2+} mixtures of different compositions (see the curve with filled points in Figure 5). This indicates that DEHDTPA gives greater preference to Cu^{2+} when extracting from aqueous solutions of Zn^{2+} – Cu^{2+} mixtures, which is consistent with the extraction constants (K_{ex}) of the corresponding metal ions reported by Lewin et al.^{29–31} corresponding $\log K_{ex}$ values for Zn^{2+} and Cu^{2+} by DEHDTPA in octane are 2.25 and 12.3, respectively. Introduction of the third R phase into an Aq–Org system (see S_2) results in a substantial increase of Zn^{2+} extraction, $E_{Zn\%} = [Zn]_{Org} \times 100/[Zn]_{Aq}$, which may be explained by the creation of an additional active interface, i.e., an additional pathway for the mass transfer into the Org phase. This allows us to assume that in S_2 the R–Org interface is in fact “responsible” for the transfer of Zn^{2+} into the Org phase; i.e., this interface is “penetrable” for Zn^{2+} while the Org–Aq interface is not (cf. S_1 and S_2). This assumption is reinforced by comparison of the results

Table 3. α^* , α_R , and α_{Org} for the Triphase System AMP (Lewatit R-252) Resin–LIX 860–Aqueous Solution of Cu^{2+} – Zn^{2+} Mixtures

X_{Cu}	α_R	α_{Org}	α^*
0.011	1.55	57	37 ± 5.55
0.027	1.48	43	29 ± 4.35
0.040	1.28	15	14 ± 2.10

Table 4. α^* , α_R , and α_{Org} for the Triphase System IDA Resin (Lewatit TP-207)–LIX 860–Aqueous Solution of Cu^{2+} – Zn^{2+} Mixtures

X_{Cu}	α_R	α_{Org}	α^*
0.003	204	287	0.71 ± 0.11
0.012	120	109	0.88 ± 0.13
0.029	68	73	1.07 ± 0.16

Table 5. Extraction of Zn^{2+} by DEHDTA in Bi- and Triphase Systems of Different Characteristics^a

system (no. of phases)	S_1 (2)	S_2 (3)	S_3 (3)	S_4 (2)
type of contacting phases	Aq–Org	R_1 –Org–Aq	R^* –Org–W	R^* –Org
active interface	Aq–Org	Aq–Org or R–Org	R–Org	R–Org
E_{Zn} , %	0	4.6	57	63

^a Aq = 0.4 M ($CuSO_4 + ZnSO_4$) with $Cu^{2+}:Zn^{2+} = 1:1$ at pH = 1.9 (10 mL). W = water (10 mL). R_1 = AMP resin (Lewatit R-252) (0.3 g) and R^* = resin preequilibrated with Aq under dynamic conditions. Org = 0.036 M DEHDTA in heptane (10 mL).

Table 6. Extraction of Zn^{2+} by LIX 860 in Bi- and Triphase Systems of Different Characteristics^a

system (no. of phases)	S_1 (2)	S_2 (3)	S_3 (3)	S_4 (2)
type of contacting phases	Aq–Org	R_1 –Org–Aq	R^* –Org–W	R^* –Org
active interface	Aq–Org	Aq–Org or R–Org	R–Org	R–Org
E_{Zn} , %	2	2.6	56.5	60.6

^a Aq = 0.4 M ($CuSO_4 + ZnSO_4$) with $Cu^{2+}:Zn^{2+} = 1:1$ at pH = 1.9 (10 mL). W = water (10 mL). R_1 = AMP resin (Lewatit R-252) (0.3 g) and R^* = resin preequilibrated with Aq under dynamic conditions. Org = 0.036 M DEHDTA in heptane (10 mL).

obtained in S_2 and S_3 .³² In the triphase system where the Aq has been substituted by water (S_3) the Aq–Org interface is in fact “inactive” since the aqueous phase is not bearing any metal ions. Hence, the mass transfer in this case can proceed only via the R–Org interface. As seen in Table 5, a significant increase of Zn^{2+} content in the organic phase is observed in S_3 . The mass transfer in S_3 occurs during the collisions of the organic solution of extractant droplets and micelles with resin beads, which proceed in the aqueous phase (in W). The organic solution of extractant micelles under these conditions is of the normal structure, i.e., the hydrophilic functional groups of DEHDTA are facing toward W. A similar structure can be ascribed to the extractant droplets. This type of ion-exchange mechanism has been studied for the first time by Muraviev and Omarova³³ and is known as a “contact granulo-micellar exchange”, which can be considered as a version of a “contact ion exchange” (ion exchange between contacting resin beads in different ionic forms) investigated by Nikolaev and Bogatyrev et al.^{34–36} and later by Bunzl and Schultz.³⁷ As seen in Table 5, E_{Zn} achieves the maximum value in S_4 , where the value of the R–Org interface is also reaching a maximum since the

water phase is absent. Similar conclusions can be derived from the data collected in Table 6, where the results on Zn^{2+} extraction by LIX 860 are shown.

The results shown in Table 7 follow the same trend as observed above. Indeed, extraction of Cu^{2+} by DEHPA in bi- and triphase systems involving AMP and IDA resins increases in R–Org systems (S_6 and S_5) against Aq–Org (S_1). Also, the different influences of the two resins studied on the extraction of Cu^{2+} with DEHPA can be attributed to the difference in their affinities toward this ion (see above). Thus, the IDA resin binds Cu^{2+} much stronger than the AMP ion exchanger and remarkably lower E_{Cu} values are observed in S_3 and S_5 in comparison with those determined in S_4 and S_6 , respectively.

The results presented in Tables 5–7 identify in fact the active interface in the mass transfer of the metal, and, on the other hand, they allow us to distinguish two additional parameters affecting this process, i.e., hydration of metal ion and pH in the resin. Thus, a comparison of results for S_1 and S_6 systems in Table 7 determines that this process may be considered as somewhat “immobilization” of the Aq in the R. From this viewpoint S_6 can be regarded as the AIR analogue of S_1 (see Introduction). Immobilization of the Aq in the R (or impregnation of the R with the Aq) leads to the remarkable changes in the chemistry of the metal ions when sorbed by the IDA resin. Firstly, both Cu^{2+} and Zn^{2+} appear to be far less hydrated in the R than in the respective Aq (in S_1) since water molecules can only occupy the coordination vacancies of metal ions that are unsaturated with the ligand groups of the ion exchanger.³⁸ Less hydrated ions will be easier transported via the R–Org interface. Secondly, the pH in the R is higher than that in the equilibrium Aq, as has been reported by Szabadka for the IDA resin.³⁹ Therefore, the shift to higher pH in the resin will also lead to the rise of Cu^{2+} extraction from the R phase. Similar reasonings may be applied for the interpretation of the other results shown in Tables 5–7.

The results obtained allowed us to carry out separate test experiments addressing the extractive purification of either Cu^{2+} or Zn^{2+} from Cu^{2+} – Zn^{2+} mixtures by applying the corresponding AIR process. The purification was based on the following procedure: 0.25 g of the resin (AMP or IDA) was loaded with 0.4 M solution of $CuSO_4$ and $ZnSO_4$ mixture with $Cu^{2+}:Zn^{2+}$ molar ratio = 1:1 and pH = 1.9. After equilibration, the resin was separated from the equilibrium solution and rinsed with bidistilled water. Finally, the resin was wiped between sheets of filter paper and placed in contact with 5 mL of 0.036 M heptane solution of the extractant (DEHPA, DEHDTA or LIX 860) for 14 h under vigorous agitation followed by separation of phases and stripping of metal ions from the resin with 1 M H_2SO_4 . The initial composition of each resin (Cu^{2+} and Zn^{2+} content) was determined in parallel by stripping of metal ions from the resin with H_2SO_4 followed by the resin equilibration stage. The results of this series of experiments are shown in Tables 8–10.

As follows from the results shown in Table 8, LIX 860 completely extracts Cu^{2+} from the resin phase, so that the purity of $ZnSO_4$ yielded appears to be >99.9%. As seen

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Table 7. Extraction of Cu²⁺ by DEHPA in Bi- and Triphase Systems of Different Characteristics^a

system (no. of phases)	S ₁ (2)	S ₂ (3)	S ₃ (3)	S ₄ (3)	S ₅ (2)	S ₆ (2)
type of contacting phases	Aq–Org	R _{1,2} –Org–Aq	R ₁ –Org–W	R ₂ –Org–W	R ₁ –Org	R ₂ –Org
active interface	Aq–Org	Aq–Org and R–Org	R–Org	R–Org	R–Org	R–Org
E _{Cu} , %	0	>0.2	9.9	28	13.4	33.8

^a R₁ = IDA resin (Lewatit TP-207) (0.3 g) and R₂ = AMP resin (Lewatit R-252) (0.3 g). Org = 0.036 M DEHPA in heptane (10 mL). Other details are identical to those in Tables 5 and 6.

Table 8. Extractive Purification of Zn²⁺ from a Cu²⁺–Zn²⁺ Mixture by the AIR Process Involving the AMP Resin (Lewatit R-252) and LIX 860

phase	composition				purity of ZnSO ₄ , %	
	initial ^a		final ^b		initial ^a	final ^b
AMP resin	Cu, mg	Zn, mg	Cu, mg	Zn, mg		
LIX 860	12.31	10.54	<0.01	4.15	46	>99.9
			12.30	6.39		

^a After stripping from the resin with 1 M H₂SO₄. ^b After extraction with LIX 860 and stripping with 1 M H₂SO₄.

Table 9. Extractive Purification of Cu²⁺ from a Zn²⁺–Cu²⁺ Mixture by the AIR Process Involving the IDA Resin (Lewatit TP-207) and DEHPA

phase	composition				purity of CuSO ₄ , %	
	initial ^a		final ^b		initial ^a	final ^b
IDA resin	Cu, mg	Zn, mg	Cu, mg	Zn, mg		
DEHPA	20.9	0.4	18.1	0.05	98.1	99.8
			2.8	0.35		

^a After stripping from the resin with 1 M H₂SO₄. ^b After extraction with DEHPA and stripping with 1 M H₂SO₄.

Table 10. Extractive Purification of Zn²⁺ from a Cu²⁺–Zn²⁺ Mixture by the AIR Process Involving the AMP Resin (Lewatit R-252) and DEHDTA

phase	composition				purity of ZnSO ₄ , %	
	initial ^a		final ^b		initial ^a	final ^b
AMP resin	Cu, mg	Zn, mg	Cu, mg	Zn, mg		
DEHDTA	12.31	10.54	0.04	5.09	46	99.2
			12.27	5.45		

^a After stripping from the resin with 1 M H₂SO₄.

from the data presented in Table 9, DEHPA quantitatively extracts Zn²⁺ admixture from the R, which results in an increase of CuSO₄ purity from 98.1 to 99.8%. Approximately 15% of Cu²⁺ is also extracted by DEHPA;

therefore, the yield of the purified CuSO₄ appears to be around 85%. The results given in Table 10 indicate that one-stage extraction of a Cu²⁺ admixture with DEHDTA from IDA resin yields ZnSO₄ of 99.3% purity from 52.5% initial product. As seen in Table 10, Zn²⁺ is also coextracted by DEHDTA, which does not allow us to obtain the product at sufficiently high yield. The same concerns coextraction of Zn²⁺ by LIX 860 from AMP resin (see Table 8).

Finally, we would like to view the results obtained in this study in comparison with the model of solvent-impregnated resins (SIR).^{18,19} Immobilization of the aqueous component of an extraction system in a resin phase to form an AIR was considered as a “symmetrical reflection” of the classical SIR concept, based upon immobilization of the organic part of an extraction system in a solid phase.^{40–42} As follows from the results obtained, the necessary conditions of such a “symmetry” must be an absence of any chemical interactions of the immobilized liquid (either organic or aqueous solution) with the solid phase. When immobilization of an electrolyte solution in the resin phase is accompanied by changes of metal ion hydration, pH, and some other system parameters, the extraction of metal ions from the polyelectrolyte media (resin phase) may differ dramatically from that in the liquid–liquid extraction system.

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