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Comparative Equilibrium Studies on the Sorption of Metal Ions with Macroporous Resins Containing a Liquid Ion-Exchanger

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ABSTRACT

The distribution of five metal ions (M^{m+}) including Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) between dilute sulfate solutions and macroporous resins containing di(2-ethylhexyl)phosphoric acid (D2EHPA, HR) was investigated. Experiments were carried out as a function of aqueous pH, D2EHPA concentration in the resin phase, and temperature. The equilibrium data were numerically analyzed. It was shown that the sorption reaction could be described by assuming the formation of metal complexes with a general composition $MR_m(HR)_n$ in the resin phase. For several systems a change of complex stoichiometry with temperature was observed and discussed. The apparent thermodynamic data for the formation of these complexes were also calculated.

INTRODUCTION

Extractant-impregnated resins (EIRs) have been shown to be effective media for the separation and recovery of species from dilute solutions. The EIRs can bridge the gap between solvent extraction and resin ion-exchange processes (1). They combine not only the advantages of resin ion-exchange for processing very dilute liquors with the specific properties of extractants, but also the high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplic-

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ity of equipment and operation characteristic of solid ion-exchange technology.

A significant number of studies on the sorption and separation of metal ions with EIRs have been carried out (2–24). The impregnated extractants include acidic and neutral organophosphorus compounds like di(2-ethylhexyl)phosphoric acid (D2EHPA) (2–11), di(2-ethylhexyl)dithiophosphoric acid (12), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (2, 3, 13, 14), di(2,4,4-trimethylpentyl)phosphinic acid (15–17), bifunctional carbarmoylmethylphosphine oxide (18), and organophosphonate (19). Also, some extractants such as tri-*n*-octylamine (20, 21), quaternary alkylammonium salts (22), crown ethers (23), and hydroxyquinoline (24) have often been adopted. It was well recognized that the impregnated extractants can exhibit strong affinity for the polymeric matrix but still behave as if in the liquid state (5, 16). Thus, the possible applications of EIRs for the recovery and separation of metal ions from dilute solutions could be understood in both analytical (13, 14, 18, 22–24) and practical fields (2–11, 15–17, 19–21, 23).

Of these extractants, D2EHPA is particularly suitable for the sorption of single metal ions from acidic media due to its good chemical stability, extremely low water solubility, and high distribution ratio for metal ions (2–4). Recently, Cortina et al. (6, 7) found that the compositions of some metal complexes in the D2EHPA-EIR systems are different from those obtained in the solvent extraction systems. The extracted species in the EIR systems are generally less solvated than those in the organic solvents, probably because D2EHPA is less associated in the EIR media. However, systematic studies on this subject have not been done. The main aim of this work is to investigate the sorption equilibria of five metal ions including Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) from sulfate solutions with D2EHPA-EIRs. Experiments were performed as a function of aqueous pH and D2EHPA concentration in the resin phase. The reaction stoichiometries were numerically determined by the modified LETAGROP-DISTR program. In addition, the effect of temperature on the complex composition was examined and the apparent thermodynamic data were determined.

EXPERIMENTAL

Reagents, Resins, and Solutions

Deionized water produced by a Millipore Milli-Q Water System was used in this work. D2EHPA was a product of Merck Co. It had a purity of about 98.5% and was used as received. Metal sulfate, *n*-hexane, and other inorganic chemicals were also supplied by Merck Co. as analytical reagent grade, and all were used without further purification.

The macroporous resins used, Amberlite XAD-2 and XAD-4, were supplied by Merck Co. They both were comprised of styrene–divinylbenzene copolymer with a high aromatic content. On a dry basis, they had a specific surface area of 330 and 780 m^2/g, a porosity of 0.42 and 0.51, a mean pore diameter of 9 and 5 nm, and a pore volume of 0.693 and 0.998 cm^3/g, respectively (24, 25). The particle size of both resins was 0.3–0.9 mm (20–50 mesh). Prior to impregnation, these resins were washed with deionized water several times to remove Na_2CO_3 and NaCl, followed by acetone and *n*-hexane to remove organics, and then dried at 323 K in a vacuum for 2 hours.

The aqueous solution consisted of 0.5 mol/dm^3 $(Na,H,M)SO_4$. The total sulfate concentration was kept constant. The aqueous pH was adjusted by changing different fractions of H_2SO_4 and Na_2SO_4. It should be noted that in this work the concentrations of D2EHPA and metals sorbed in the resin phase were expressed on the basis of dry fresh resin.

Preparation of the D2EHPA-EIRs

The D2EHPA-impregnated resins were prepared using a batch method as follow (8–11). An aliquot of D2EHPA (3.5–5.0 g) was first diluted in a precalculated amount of *n*-hexane (20 cm^3). The resulting *n*-hexane solution was then contacted with fresh resins (10 g) until all organic solution was absorbed by the resins. This step was normally accomplished within 12 hours in a drying oven at 333 K. Finally, these resins were evaporated to completely remove the solvent at 323 K in a vacuum for 2 hours. The concentration of D2EHPA held in the resin phase was determined by potentiometric titration with NaOH in ethanol of the amount of D2EHPA eluted from a packed column with *n*-hexane.

Procedures

In each sorption run the D2EHPA-EIR (1 g) and aqueous solution (50 cm^3) were placed in a 125-cm^3 glass-stoppered flask and shaken at 110 rpm for at least 12 hours using a thermostated shaker (Firstek Model B603, Taiwan). Preliminary experiments had shown that the sorption was complete after 6 hours. After standing for 1 hour, the aqueous phase was separated from the resin phase and its pH was measured with a Radiometer PHM82 pH meter. The concentration of metal ions was analyzed with a GBC atomic absorption spectrophotometer (Model 932). The concentrations of metals sorbed and unreacted D2EHPA in the resin phase were calculated from a mass balance. Each experiment was duplicated under identical conditions.

RESULTS AND DISCUSSION

Properties of the D2EHPA-EIRs

As indicated earlier (8, 10), the amount of D2EHPA transferred from the organic solution to the resin was more than 99.5% by using the present impregnation method. In this study the concentration of D2EHPA analyzed by titration agreed well with that calculated from the changes in the weight of the resins before and after impregnations. In addition, the resulting XAD-2/EIR and XAD-4/EIR become adhesive after drying when the concentrations of D2EHPA exceed about 2.17 and 2.52 mol/kg, respectively. Because the swelling ratio, defined as the ratio of the volume of the resin immersed in a solvent to that in the dry state, is equivalent for the XAD-2 and XAD-4 resins (24), it seems that the swelling of the resins has no significant contribution on this difference. It is probably affected by such properties as the pore volume, surface area, and pore size distribution of the resins (24, 26).

From the measured density of pure D2EHPA at 298 K (0.96 cm^3/g), the above saturated concentrations correspond to 0.73 and 0.85 cm^3 of D2EHPA adsorbed per gram of fresh XAD-2 and XAD-4 resins, respectively. Because the pore volumes of XAD-2 and XAD-4 are 0.693 and 0.998 cm^3/g, respectively (24, 25), this likely means that the impregnation of D2EHPA on XAD-4 is mainly due to pore filling, whereas on XAD-2 it is due to a combination of pore filling and surface adsorption. In fact, Jerabek et al. (12) recently studied the relation between impregnation process and polymer support morphology for XAD resins containing di(2-ethylhexyl)dithiophosphoric acid (DEHTPA). They indicated that in the adsorption process DEHTPA fills the pore space gradually from the smallest pores up to pores with a diameter of about 10 nm. This is probably connected with strong cohesion forces between DEHTPA molecules, as evidenced by the extremely low volatility of DEHTPA during the drying of the EIRs. From the residual surface area measurements before and after impregnations, they nevertheless found that the sorbed DEHTPA fills almost all its porous system for the XAD-4 resins. On the other hand, the EIRs made from the XAD-2 resins exhibit a substantial residual surface area, for which the pores with a diameter greater than 10 nm are probably responsible. The different impregnation mechanisms may relate to the different equilibrium behaviors for the sorption of metal ions, as discussed later.

Because the loss of D2EHPA from the resin phase was reported to be negligibly small when the D2EHPA concentrations range from 0.9 mol/kg to their saturated values (8, 10), in this study the concentration of D2EHPA in the resin phase was kept higher than 0.9 mol/kg. In addition, it was proven by experiments that at our selected shaker speed of 110 rpm, the loss of D2EHPA from the resin phase was less than 2 wt% (10, 11).

Effect of pH and D2EHPA Concentration on Metal Sorption

The distribution of metal ions between the aqueous phase and the resin phase containing D2EHPA can be directly obtained as (6, 17)

$$D = [\overline{\mathrm{M}}]_t/[\mathrm{M}^{m+}]_t \tag{1}$$

where $[\overline{\mathrm{M}}]_t$ is the total concentration of metals in the resin phase in mol/kg of dry fresh resin and $[\mathrm{M}^{m+}]_t$ is the total concentration in the aqueous phase. Alternatively, the amount of metals extracted can be expressed as

$$\text{Metal extracted (\%)} = 100D(W/V)/\{1 + D(W/V)\} \tag{2}$$

where V is the volume of aqueous phase and W is the mass of dry fresh resin.

Figures 1 and 2 show the distributions of metal ions as a function of equilibrium pH in the XAD-2/EIR and XAD-4/EIR systems, respectively. It is found that the distribution increases with aqueous pH. The order of metals extracted, in terms of $\mathrm{pH}_{1/2}$ (the pH at which 50% of a given metal is extracted), is Fe(III) < Zn(II) < Cu(II) < Co(II) < Ni(II). Similar trends of $\mathrm{pH}_{1/2}$ are reported in the solvent extraction systems (27). As in the case of solvent extraction, it must be understood that comparison of the percent of metals extracted is useful only as an indication of the pH range over which metal extraction occurs, since these curves can shift with the concentrations of metal ions and extractant. The cause for the abnormal behavior of Fe(III) in the XAD-4/EIR system remains unclear at this stage, but it is possibly related to the steric hindrance of the Fe(III)–D2EHPA complex formed within the more restricted XAD-4 pores.

As clearly shown in Figs. 1 and 2, the distribution of metal ions in the XAD-2/EIR system is somewhat larger than that in the XAD-4/EIR system under the same conditions. Factors leading to such a difference remain unclear. The smaller porosity and specific pore volume for XAD-2 resins may be probable reasons which affect the distribution of D2EHPA within the pores and on the internal surfaces of the resins.

The effect of free D2EHPA concentration in the resin phase, $[\overline{\mathrm{HR}}]$, on the distribution ratios is plotted in Figs. 3 and 4. The values of $[\overline{\mathrm{HR}}]$ are

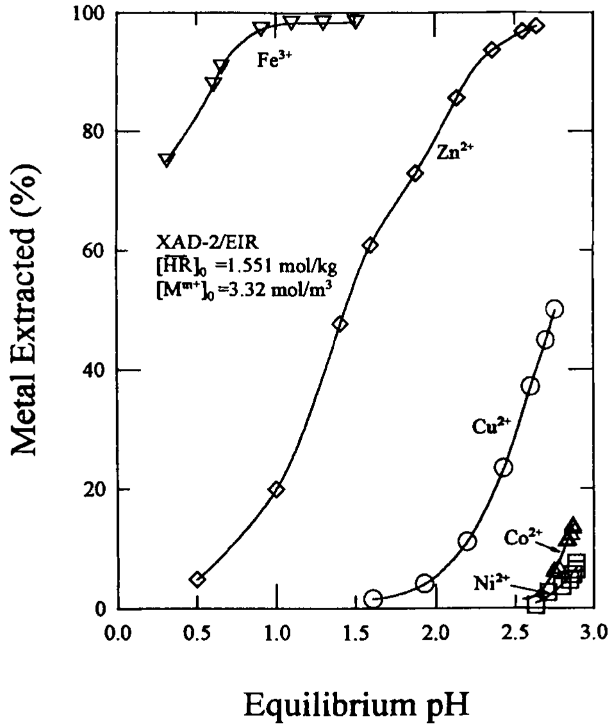

FIG. 1 Effect of aqueous pH on the amount of metals sorbed in the XAD-2/EIR systems at 298 K.

calculated from the mass balance given in Eq. (9), omitting the terms for metal complexes, because in this study the concentration of metals sorbed in the resin phase is much less than that of D2EHPA. It follows from Figs. 3 and 4 that the equilibrium distribution increases with D2EHPA concentration. Such types of plots are usually adopted to determine the reaction stoichiometry in the solvent extraction systems. In this paper a more accurate method is adopted, as observed later.

Stoichiometry of Metal Sorption

It is well known that D2EHPA mainly forms dimers in nonpolar or low polar organic solvents due to the strong intermolecular hydrogen-bonding. In the aqueous phase, on the other hand, it exists mainly as monomers because the intermolecular hydrogen-bonding between the acids is de-

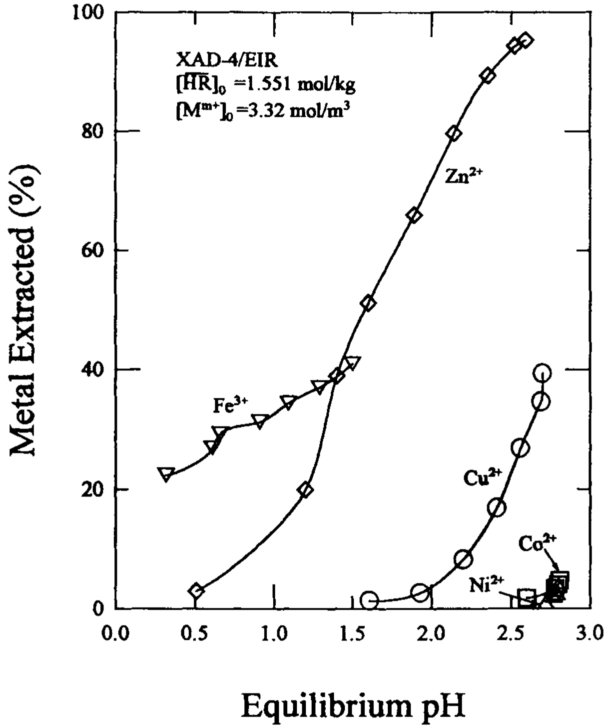

FIG. 2 Effect of aqueous pH on the amount of metals sorbed in the XAD-4/EIR systems at 298 K.

stroyed by the preferential hydrogen-bonding with water molecules. Hence, for the present systems we have:

$$\mathrm{HR} \Leftrightarrow \overline{\mathrm{HR}}; \qquad K_d \tag{3}$$

$$2\overline{\mathrm{HR}} \Leftrightarrow \overline{(\mathrm{HR})_2}; \qquad K_2 \tag{4}$$

$$\mathrm{HR} \Leftrightarrow \mathrm{H}^+ + \mathrm{R}^-; \qquad K_a \tag{5}$$

where the overbar refers to the resin phase.

The equilibrium constants for the distribution of D2EHPA molecules between the XAD-2 resins and aqueous phase were found to be $\log K_d = 4.72$, $\log K_2 = -0.52$, and $pK_a = 2.90$ at 298 K (5). In contrast to the corresponding constants reported when D2EHPA is dissolved in the organic solvents (27), as expected, K_a is equivalent. On the other hand, K_d is significantly greater, indicating that the distribution of D2EHPA is

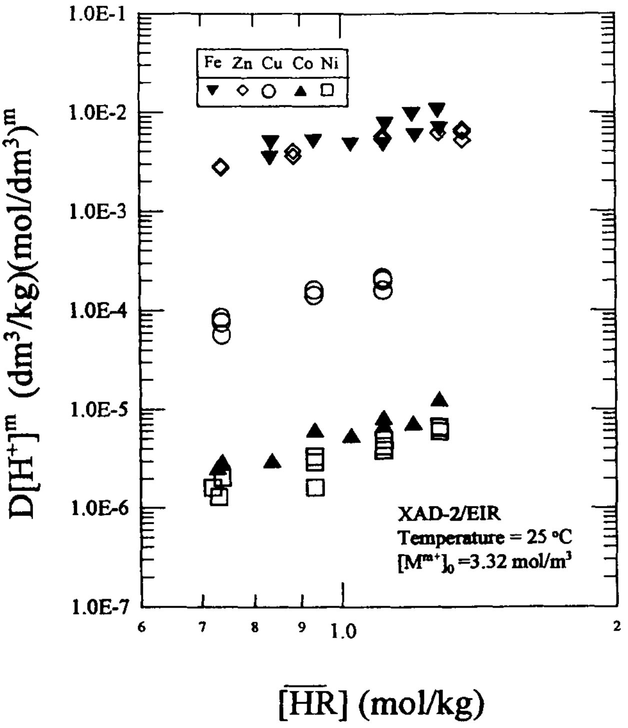

FIG. 3 Effect of D2EHPA concentration in the resin phase on the distribution of metal ions in the XAD-2/EIR systems at 298 K.

shifted more toward the resin phase, probably due to the interaction of D2EHPA with the support (5). Moreover, the constant K_2 is considerably smaller, which means that D2EHPA molecules mainly exist as monomers rather than dimers in the resin phase.

As stated above, the mechanism of metal sorption with EIRs is basically similar to the case of solvent extraction (6–8, 17), although the extracted complexes in the EIR system may be less solvated than in the organic solvents (6, 7, 17). Hence, the extraction of metal ions with D2EHPA–EIRs can be expressed by the following stoichiometric relation:

$$M^{m+} + (m + n)\overline{HR} \Leftrightarrow \overline{MR_m(HR)_n} + mH^+; \qquad K_{mn} \qquad (6)$$

where n is the number of free D2EHPA molecules involved in the extracted species. The corresponding equilibrium constant K_{mn} is given by

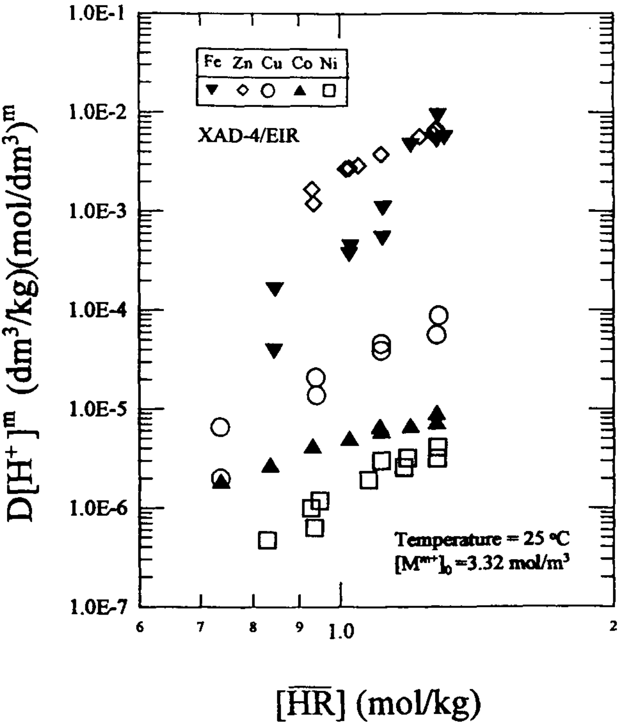

FIG. 4 Effect of D2EHPA concentration in the resin phase on the distribution of metal ions in the XAD-4/EIR systems at 298 K.

$$K_{mn} = [\overline{MR_m(HR)_n}][H^+]^m/\{[M^{m+}][\overline{HR}]^{m+n}\} \tag{7}$$

Now, the total concentration of metal ions in the resin phase is

$$[\overline{M}]_t = \sum_n [\overline{MR_m(HR)_n}] = \sum_n K_{mn}[M^{m+}][H^+]^{-m}[\overline{HR}]^{m+n} \tag{8}$$

The term $[\overline{HR}]$ in Eq. (8) is calculated by the following equation.

$$\begin{aligned}[\overline{HR}]_0 &= [R^-] + [HR] + [\overline{HR}] + 2[\overline{(HR)_2}] + \sum_n n[\overline{MR_m(HR)_n}] \\ &= \{1 + (1/K_d) + (K_a/K_d[H^+])\}[\overline{HR}] + K_2[\overline{HR}]^2 \\ &\quad + \sum_n nK_{mn}[M^{m+}][H^+]^{-m}[\overline{HR}]^{m+n}\end{aligned} \tag{9}$$

For the present systems the use of the conventional slope analysis method for determining the stoichiometry may lead to somewhat erroneous results because the concentrations of D2EHPA in the resin phase are limited to a narrow range (0.95–1.92 mol/kg) as indicated above (28). Also, in some cases the straight line obtained from Figs. 3 and 4 (not shown) gives a noninteger slope. This leads to certain difficulty in determining the value of K_{mn}. Hence, numerical analysis based on the least-squares error concept is highly desired for this purpose.

Numerical Analysis of the Distribution Data

The computer program LETAGROP-DISTR was originally developed to analyze the distribution data of a component between two phases using the least-squares error method (29). The "best" equilibrium constants for the formation of a set of complexes with up to four components can be obtained. This program has been modified to five-component systems in C-language and successfully used to treat equilibrium data in the extraction of metal ions with some organophosphoric acids (30–33). In this work we further employ this program to analyze the distribution data of metal ions between the macroporous resins containing D2EHPA and aqueous solutions.

In this calculation the computer searches for the best set of equilibrium constants for a given model that minimizes the error squares sum, defined by

$$U = \sum (\log D_{\mathrm{expt}} - \log D_{\mathrm{calc}})^2 \qquad (10)$$

where D_{expt} is the measured distribution ratio and D_{calc} is the one calculated by the program considering the above mass-balance equations (Eqs. 8 and 9). This program also calculates the standard deviation $\sigma(\log D)$ defined by

$$\sigma(\log D) = (U/N_{\mathrm{p}})^{1/2} \qquad (11)$$

where N_{p} is the degree of freedom, i.e., the difference between the total number of data points and the total number of equilibrium constants calculated.

The value of n tried was $n = 0$–4, inferred from the literature results of solvent extraction (30–38). The equilibrium constants shown in Eqs. (3)–(5) in the XAD-4 systems are directly adopted from those obtained in the XAD-2 systems for simplicity, because the two resins have similar polymeric matrices and structures. Table 1 gives typical calculation results for Zn(II)–XAD-2/EIR system at 298 K.

It follows from Table 1 that only a single Zn(II)–D2EHPA complex is formed on the macroporous resins at 298 K. As shown in Tables 2 and 3, this is the case for all metal-D2EHPA complexes. The simultaneous formation of binary or multimodel species is rejected for all EIR systems investigated. The best-fit formulation for the metal–D2EHPA complexes, together with the calculated equilibrium constants, are listed in Tables 2 and 3 for the XAD-2/EIR and XAD-4/EIR systems, respectively.

The present results for Cu(II) and Zn(II) in the XAD-2/EIR systems are somewhat different from those obtained previously (6) under comparable

TABLE 1
Results of Numerical Calculation Obtained in the $\overline{\text{Zn(II)/XAD}}$-2 System at 298 K for Various Model Species $\overline{ZnR_2(HR)_n}$

Model	Species (2,*n*)	log K_{2n}[a,b]	U_{min}	σ(log *D*)	Rejected[c]
I	(2,0)	−2.443 ± 0.031	0.051	0.049	
II	(2,1)	−2.373 ± 0.078	0.299	0.119	
III	(2,2)	−2.305 ± 0.132	0.888	0.206	
IV	(2,3)	−2.168 ± 0.189	1.937	0.304	
V	(2,4)	−2.162 ± 0.263	3.106	0.384	
VI	(2,0) (2,1)	−2.443 ± 0.031	0.051	0.049	(2,1)
VII	(2,0) (2,2)	−2.443 ± 0.031	0.051	0.049	(2,2)
VIII	(2,0) (2,3)	−2.443 ± 0.031	0.051	0.049	(2,3)
IX	(2,0) (2,4)	−2.443 ± 0.031	0.051	0.049	(2,4)
X	(2,1) (2,2)	−2.412 ± 0.188 max −2.471	0.714	0.223	
XI	(2,1) (2,3)	−2.415 ± 0.064 max −2.773	0.339	0.141	
XII	(2,1) (2,4)	−2.419 ± 0.064 max −2.887	0.341	0.142	
XIII	(2,2) (2,3)	−2.388 ± 0.097 max −2.526	1.037	0.242	
XIV	(2,2) (2,4)	−2.390 ± 0.097 max −2.532	1.045	0.244	
XV	(2,3) (2,4)	−2.366 ± 0.127 max −2.142	2.203	0.351	

[a] The error given corresponds to 3σ(log *K*).

[b] The value after max corresponds to log [*K* + 3σ(*K*)].

[c] The species were rejected by the program because the equilibrium constants were set equal to zero.

TABLE 2
Complex Formulation and Equilibrium Constant K_{mn} Determined in the XAD-2/EIR Systems at Different Temperatures[a]

Metal ions	T = 288 K		T = 298 K		T = 308 K		T = 318 K	
	(m,n)	log K_{mn}	(m,n)	log K_{mn}	(m,n)	log K_{mn}	(m,n)	log K_{mn}
Fe(III)	(3,0)	−0.71	(3,0)	−0.60	(3,0)	−0.24	(3,0)	−0.13
Co(II)	(2,0)	−5.29	(2,0)	−5.22	(2,0)	−5.06	(2,1)	−4.86
Ni(II)	(2,1)	−5.67	(2,1)	−5.18	(2,4)	−5.53	(2,4)	−5.42
Cu(II)	(2,1)	−4.48	(2,1)	−4.11	(2,1)	−4.02	(2,1)	−3.97
Zn(II)	(2,0)	−2.80	(2,0)	−2.44	(2,0)	−2.24	(2,0)	−2.17

[a] Unit of K_{mn}: $(\mathrm{dm}^3/\mathrm{mol})(\mathrm{mol/kg})^{1-m-n}$.

conditions. This difference may partly result from the different sources of XAD resins (Merck Co. vs Rohm & Haas). Presumably, some modifications on the resin surface or during synthesis are made by Merck Co. In our laboratory, in fact, experimental results had shown that the amount of citric acid extracted by tri-*n*-octylamine-impregnated Rohm & Haas XAD-4 resins is about 20% greater than that extracted using XAD-4 resins from Merck Co. The different aqueous media used (sulfate vs nitrate or chloride) are another possible source of these discrepancies, because in separate papers (6, 7) Cortina et al. proposed different complex compositions for a given metal/EIR sorption system with different aqueous media.

In the case of solvent extraction of metal traces with D2EHPA, the values of *n* reported in the literature are 3 for Fe(III) (34, 35), 2–3 for

TABLE 3
Complex Formulation and Equilibrium Constant K_{mn} Determined in the XAD-4/EIR Systems at Different Temperatures[a]

Metal ions	T = 288 K		T = 298 K		T = 308 K		T = 318 K	
	(m,n)	log K_{mn}	(m,n)	log K_{mn}	(m,n)	log K_{mn}	(m,n)	log K_{mn}
Fe(III)	(3,3)	−1.44	(3,3)	−1.14	(3,3)	−0.62	(3,3)	−0.04
Co(II)	(2,0)	−5.49	(2,1)	−5.48	(2,1)	−5.15	(2,2)	−4.96
Ni(II)	(2,4)	−5.73	(2,4)	−5.48	(2,3)	−5.56	(2,3)	−5.45
Cu(II)	(2,4)	−4.92	(2,4)	−4.23	(2,3)	−4.42	(2,3)	−4.24
Zn(II)	(2,4)	−3.02	(2,4)	−2.52	(2,3)	−2.36	(2,2)	−2.16

[a] Unit of K_{mn}: $(\mathrm{dm}^3/\mathrm{mol})(\mathrm{mol/kg})^{1-m-n}$.

Co(II) (31, 36, 37), 2–4 for Ni(II) (30, 36), 2 for Cu(II) (36, 38), and 1–2 for Zn(II) (32, 36). In this respect the extracted species formed in the XAD-2/EIR phase at 298 K are indeed less solvated than those in the organic solvents, as indicated earlier (6, 7, 17). In the XAD-4/EIR phase, on the other hand, the extracted complexes contain either equivalent or more D2EHPA solvating molecules. For a given metal ions, the more D2EHPA molecules solvated in the complexes in the XAD-4/EIR systems, compared to the XAD-2/EIR systems, may be a result of its less steric hindrance within the resin pores since the impregnation of D2EHPA on XAD-4 is carried out by pore filling, as stated above.

Determination of the Thermodynamic Data

The influence of temperature on the sorption of metal ions is illustrated in Figs. 5 and 6. Evidently the distribution ratio increases with tempera-

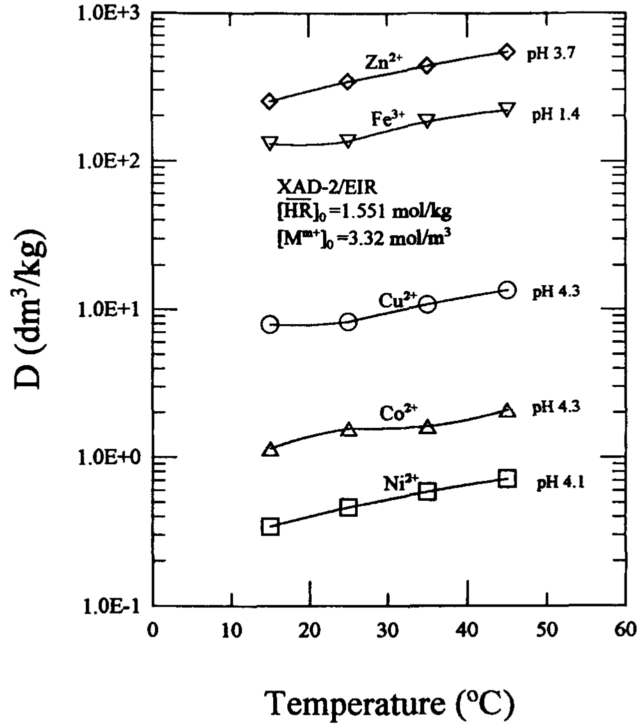

FIG. 5 Effect of temperature on the distribution ratio of metal ions in the XAD-2/EIR systems.

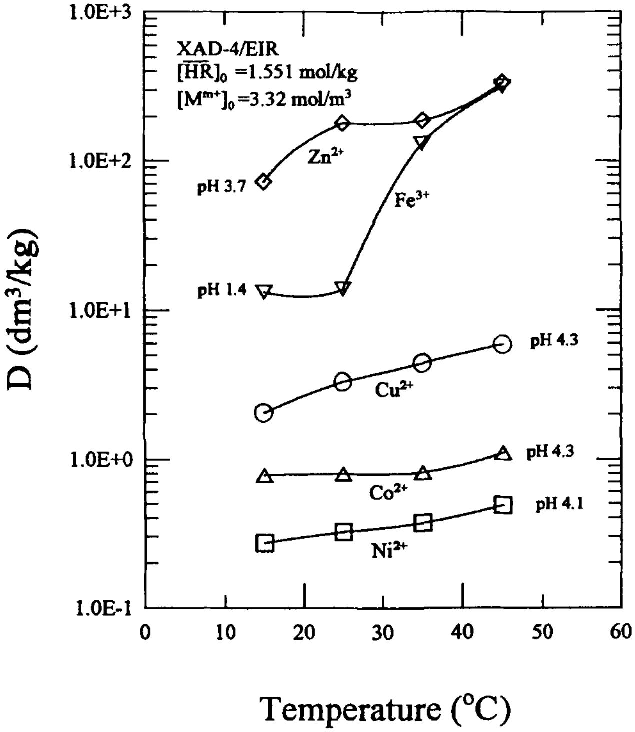

FIG. 6 Effect of temperature on the distribution ratio of metal ions in the XAD-4/EIR systems.

ture. Similar computer calculations were performed to treat the data obtained at different temperatures. The temperature corrections of K_d, K_2, and K_a were not taken into account here and those obtained at 298 K were used. This would be acceptable since the temperature range is rather narrow. Perhaps this action could slightly changes the value of K_{mn}; however, the complex formulations are not affected. The calculated results are also listed in Tables 2 and 3 for comparison in the XAD-2/EIR and XAD-4/EIR systems, respectively.

It is interesting to notice that the complex composition changes with temperature for most systems under the temperature ranges studied. Such observations have never been reported earlier. The explanation for these transitions is unavailable at this stage. It is likely to be concerned with such properties as the framework of the resins and the structure effects of metal–D2EHPA complexes. In the solvent extraction of Co(II) with

D2EHPA, Barnes et al. (39) indicated that a thermochromic reaction occurs in the organic phase at low Co(II) levels. They found that a pink octahedral Co(II) complex $CoR_2(HR)_2(H_2O)_2$ is observed at 298 K, and only the deep blue color of the tetrahedral Co(II) complex $CoR_2(HR)_2$ is seen on warming to about 323 K. In this respect an increase in the number of the solvated D2EHPA molecules (n) with temperature in the Co(II)- and Ni(II)-XAD-2/EIR systems (Table 2) can be explained by the exchange of water molecules presolvated in the complexes with free D2EHPA molecules. However, this is not the case in the Ni(II)-XAD-4/EIR system (Table 3). In addition, the value of n decreases by raising the temperature in the Ni(II)-, Cu(II)-, and Zn(II)-XAD-4/EIR systems. Further work is necessary to clarify these discrepancies.

The apparent enthalpy can be obtained by the van't Hoff equation:

$$d(\log K_{mn})/d(1/T) = -\Delta H/(2.303R) \tag{12}$$

Figure 7 shows the results. Other thermodynamic parameters, such as the

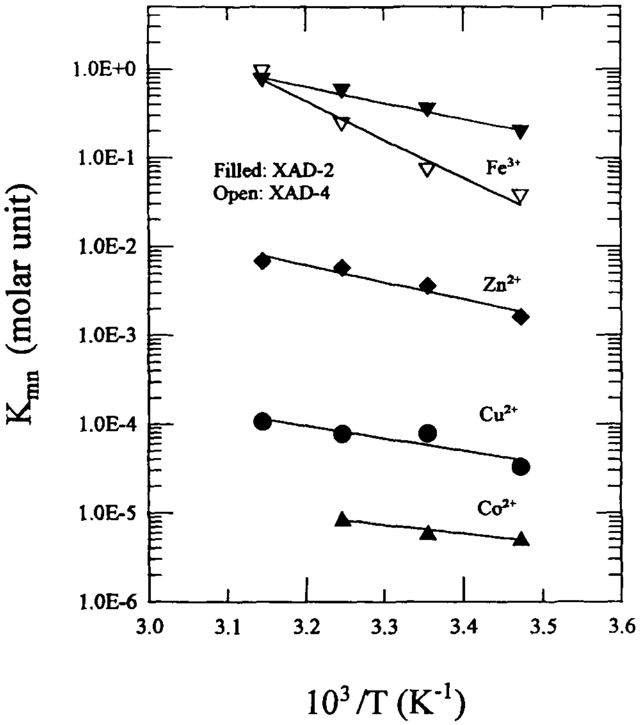

FIG. 7 Temperature dependence of the equilibrium constants K_{mn}.

TABLE 4
Apparent Thermodynamic Data for the Formation of Complex $\overline{MR_m(HR)_n}$ in the Temperature Range 288–318 K

Metal ions	XAD-2/EIR (m,n)	ΔH (kJ/mol)	ΔS (J/mol·K)	XAD-4/EIR (m,n)	ΔH (kJ/mol)	ΔS (J/mol·K)
Fe(III)	(3,0)	79.8	255.6 ± 3.6	(3,3)	190.3	613.4 ± 8.8
Co(II)	(2,0)	44.4	49.7 ± 2.0	(2,1)	59.1	93.3 ± 0.3
Ni(II)	(2,1)	81.8	170.3 ± 0.4	(2,3)	20.7	33.0 ± 0.2
Ni(II)	(2,4)	20.7	−38.6 ± 0.1	(2,4)	41.1	−39.4 ± 0.2
Cu(II)	(2,1)	62.8	127.8 ± 3.0	(2,3)	32.9	22.3 ± 0.2
Cu(II)				(2,4)	114.6	303.6 ± 0.7
Zn(II)	(2,0)	86.2	238.6 ± 4.1	(2,4)	81.2	244.2 ± 0.4

apparent free energy (ΔG) and the entropy (ΔS), can be calculated by Eqs. (13) and (14), respectively:

$$\Delta G = -RT \ln K_{mn} \tag{13}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{14}$$

Because the temperature range is rather narrow, it is assumed that the values of ΔH and ΔS are not functions of temperature. The calculated data are listed in Table 4. It should be noted that some results are presented in Table 4 for which no plot appears in Fig. 7. In these cases they were obtained at only two temperatures before a change in the composition of the complex was observed.

Critical comparison of the values of ΔH and/or ΔS is rather difficult between the two EIR systems or among the metal complexes because of their different complex compositions. Nevertheless, close agreement in the value of ΔS for the formation of the $\overline{NiR_2(HR)_4}$ complex in both XAD/EIR systems may be an indication that the present findings are acceptable.

CONCLUSIONS

The distribution equilibria of metal ions between sulfate solutions and Amberlite XAD-2 and XAD-4 macroporous resins containing D2EHPA have been investigated in the temperature range 288–318 K. The distribution of metal ions in the XAD-2/EIR system is larger compared to the XAD-4/EIR system under the same conditions, which is probably attributed to different pore structures of the two resins. Numerical analysis of the distribution data by the modified LETAGROP-DISTR program shows that the metal complexes form with a general composition of $\overline{MR_m(HR)_n}$ in the XAD-2/EIR and XAD-4/EIR systems, as listed in Tables 2 and 3. The values of ΔH and ΔS are listed in Table 4, which indicates that the formation of all metal complexes studied, except Ni(II), on both resins containing D2EHPA is favored by entropy change and unfavored by enthalpy change. The present results give a deep and systematic insight into the mechanism of sorption reactions between metal ions and organophosphorus extractant impregnated on macroporous polymeric supports.

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NOMENCLATURE

D	distribution ratio of metal ions between EIR and aqueous phase (dm^3/kg)
EIR	extractant-impregnated resin
ΔG	apparent Gibbs energy change for the sorption reaction (kJ/mol)
ΔH	apparent enthalpy change for the sorption reaction (kJ/mol)
HR	di(2-ethylhexyl)phosphoric acid (D2EHPA)
K_2	dimerization constant of D2EHPA in the resin phase (dm^3/kg)
K_a	dissociation constant of D2EHPA in the aqueous phase (mol/dm^3)
K_d	distribution ratio of D2EHPA between the resin and aqueous phase
K_{mn}	equilibrium constant defined in Eq. (5), $[(dm^3/mol)(mol/kg)^{1-m-n}]$
M	metal ions
n	number of free D2EHPA molecules involved in the complex
R	universal gas constant [J/(mol·K)]
ΔS	apparent entropy change for the sorption reaction [J/(mol·K)]
T	absolute temperature (K)
U	error square sum defined in Eq. (8)
V	volume of aqueous solution (dm^3)
W	mass of dry fresh resin (kg)
[ ]	concentration of species in the brackets (mol/kg or mol/dm^3)

Greek Letter

σ	standard deviation defined in Eq. (9)

Subscripts

min	minimum
t	total
0	initial

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