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Application of the Elovich Equation to the Kinetics of Metal Sorption with Solvent-Impregnated Resins

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The sorption rates of metal ions including Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) from sulfate solutions with macroporous resins containing bis(2-ethylhexyl)phosphoric acid (D2EHPA) were measured and compared in a batch stirred vessel. Experiments were carried out as a function of the pH and metal concentration in the aqueous phase, D2EHPA concentration in the resin phase, and temperature. The effect of impregnation methods of D2EHPA on the sorption rate was also investigated. It was shown that all sorption processes could be well described by the Elovich equation. For the examined systems there were similar trends of sorption rates with respect to the concentrations of metal ions and D2EHPA. With respect to the pH, however, three different trends were obtained depending on the magnitude of sorption rate. The apparent activation energy was obtained and used to discuss the rate-controlling mechanism.

Introduction

It was known that the use of solvent-impregnated resins (SIRs) as the polymeric sorbents offers another choice for the recovery and selective separation of metal ions from dilute solutions (Tavlaride et al., 1987; Warshawsky, 1981). This is attributed to the fact that the SIR sorption can bridge the gap between solvent extraction and resin ion-exchange processes. It combines 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 simplicity of equipment and operation characteristic of solid ion-exchange technology.

A large number of studies on the sorption and separation of metal ions with SIRs have been carried out. Acidic organophosphorus compounds were widely adopted as the impregnated extractants due to their chemical stabilities, extremely low aqueous solubilities, and high distribution ratios and selectivities of metals. They included bis(2-ethylhexyl)phosphoric acid (D2EHPA) (Akita and Takeuchi, 1992, 1993; Akita et al., 1994; Cortina et al., 1994a–c; Juang and Lin, 1995a,b), bis(2-ethylhexyl)dithiophosphoric acid (Jerabek et al., 1996; Strikovskiy et al., 1996), (2-ethylhexyl)-phosphoric acid mono(2-ethylhexyl) ester (Akita and Takeuchi, 1992, 1993), and bis(2,4,4-trimethylpentyl)-phosphinic acid (Cortina et al., 1992, 1993a,b). It was well recognized that the impregnated extractants can exhibit a strong affinity for the polymeric matrix but still behave as if in the liquid state (Cortina et al., 1993a, 1994a). The possible applications of the SIRs for recovering and separating metal ions from dilute solutions have been thus understood in both analytical and practical fields.

However, kinetic work for this purpose has been scarcely done compared to the equilibrium one. In the early studies on SIRs, it seemed that the rate-controlling step is film diffusion, rather than particle diffusion, e.g., the uptake of Cu(II) ions from dilute solution with LIX 64N impregnated on an expanded polyurethane foam (Hughes and Purdey, 1976). The same conclusion was

also made from the half-time measurements for the sorption of Cu(II) ions from sulfate solution by a polymeric pseudo crown ether containing a phenolic oxime (Warshawsky, 1981).

On the other hand, Gonzalez-Luque and Streat (1983) described the sorption of U(VI) from phosphoric acid solutions by Levextrel resins containing D2EHPA and tri-*n*-octylphosphine oxide using homogeneous diffusion and shrinking-core models. It was also found that the sorption of Cu(II) and Zn(II) by macroporous resins containing D2EHPA could be analyzed using modified shrinking-core model and mass-transfer equations based on Fick's law coupled with rate equations of complex formation (Juang and Lin, 1995a,b). In addition, Guan et al. (1991) used a particle diffusion model to describe the sorption of spiramycin from aqueous solutions on Amberlite XAD-4 resins loaded with amyl acetate. Although the above-mentioned models follow the sorption processes quite satisfactorily, the mathematical complexity of the models limits their use from a practical point of view. A simple but rather accurate model is highly desired.

The aim of this study is to measure and compare the rates of the sorption of Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions from sulfate solutions with D2EHPA-SIRs in a finite bath and to elucidate the sorption mechanism from temperature dependence of sorption rate. Experiments were performed as a function of the pH, metal concentration in the aqueous phase, and D2EHPA concentration in the resin phase. The effect of different impregnation methods of D2EHPA on the sorption kinetics of Zn(II) was also examined. A relatively simple model, the Elovich equation, was used to determine the sorption rate *via* initial-rate technique.

Experimental Section

Reagents and Macroporous Resin. The water used throughout the work was deionized by a Millipore Milli-Q water system. D2EHPA was the product of Merck Co. and was used as-received. It had a purity of approximately 98.5%. Metal sulfates, *n*-hexane (solvent), and other inorganic chemicals were also supplied by Merck Co. as analytical reagent grade, and all were used without further purification.

The Amberlite XAD-2 macroporous resin (styrene–divinylbenzene copolymer) was supplied from Merck Co.

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On a dry basis, it had a specific surface area of 350 m²/g, a porosity of 0.42, a mean pore diameter of 9 nm, and a pore volume of 0.69 cm³/g (Crook et al., 1975). The particle size of the resins was 0.3–0.9 mm (20–50 mesh). Prior to impregnation, these resins were washed with deionized water several times to remove Na₂CO₃ and NaCl, followed by acetone and *n*-hexane to remove organics, and then dried at 323 K in a vacuum for 2 h.

Preparation of the D2EHPA-SIRs and Solutions.

Four impregnation methods including the dry, wet, complex formation and the modifier addition (Warshawsky, 1981) were tested to investigate their effects on the sorption rates. The modifier poly(propylene glycol) with an average molar mass of 425 (Acros Organics, Belgium) was used here. Also, the dry procedure used in this work followed the modification of Juang and Chen (1996). That is, an aliquot of D2EHPA was diluted in a precalculated amount of *n*-hexane. The resulting hexane solution was then contacted with fresh resins until all the organic solution was absorbed by the resins. This step was finished within 12 h in a drying oven at 333 K. Finally, these resins were evaporated to remove the solvent at 323 K in a vacuum for 2 h. The concentration of D2EHPA held in the resin phase was measured by potentiometric titration with NaOH in ethanol of the amount of D2EHPA eluted from a packed column with hexane.

The aqueous phase contained 500 mol/m³ (Na,H,M)-SO₄, which means that the total sulfate concentration is kept constant. The aqueous pH was adjusted (1.6–6.0) by changing different fractions of H₂SO₄ and Na₂SO₄. 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 the dry fresh resin. The initial concentration of metal ions in the aqueous phase ranged between 1.53 and 18.2 mol/m³, and that of D2EHPA in the resin phase varied from 1.08 to 1.55 mol/kg.

Procedures. In each run, an aqueous phase containing metal ions (0.5 dm³) was first placed in the Pyrex glass vessel used previously (Juang and Lin, 1995a) and was mixed using a Cole-Parmer Servodyne agitator with six blades and a flat-bladed impeller. Since the loss of D2EHPA from the SIRs was experimentally found to be more serious at stirring speeds beyond 500 rpm, a speed of 300 rpm was selected. The D2EHPA-SIRs (5 g) were then poured into the vessel, and the timing was started at the end of the addition of the SIRs. The whole vessel was immersed in a thermostat (Haake Model K-F3, FRG).

At present time intervals, aqueous samples (2 cm³) were taken and the concentration of metal ions was measured using 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 (the error was generally within 5%).

Results and Discussion

Properties of the D2EHPA-SIRs. It was reported that the impregnation methods of hydrophobic impregnates like oximes play a dominant role in determining the sorption characteristics of impregnants, first and most of all, the rate of metal complexation (Warshawsky and Patchornik, 1976; Warshawsky, 1981). This is not the case here, as shown in Figure 1. The effect of the impregnation method of D2EHPA onto XAD-2 resin on

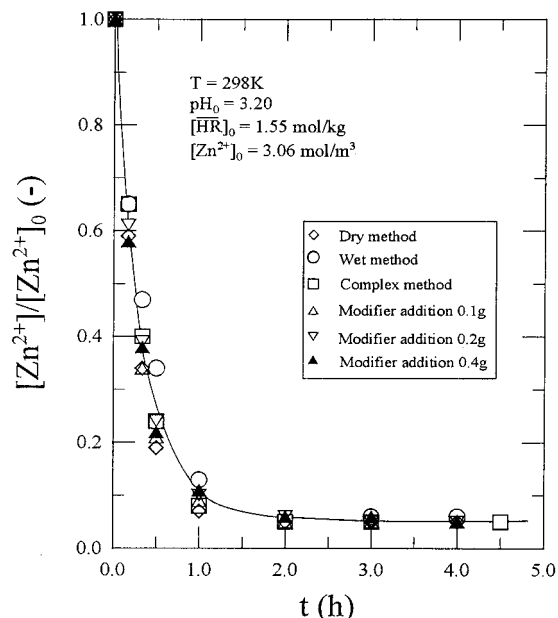


Figure 1. Effect of impregnation methods on the sorption rate of Zn(II) with D2EHPA-SIRs.

the sorption rates is negligibly small. This is probably connected with the structures of the metal–D2EHPA complexes (Warshawsky, 1981). The simplest, dry method is, hence, selected for further processing.

As indicated earlier (Juang and Lin, 1995a; Juang and Chen, 1996), the amount of D2EHPA transferred from the organic phase to the resin was more than 99.5% using the dry method. In this work, the concentration of D2EHPA analyzed by titration agrees well with that calculated from the changes in the weight of the resins before and after impregnations. Moreover, the resulting XAD-2/SIR becomes adhesive after drying when the D2EHPA concentration exceeds about 2.17 mol/kg. From the density of pure D2EHPA at 298 K (0.96 cm³/g), the above saturated concentration corresponds to 0.73 cm³ of D2EHPA adsorbed/g of fresh resin. Because the pore volume of XAD-2 is 0.693 cm³/g (Crook et al., 1975), this likely means that the impregnation of D2EHPA onto XAD-2 is mostly due to a combination of pore filling and surface adsorption (Jerabek et al., 1996).

Because the loss of D2EHPA from the SIRs could be neglected in the used glass vessel at the selected speed of 300 rpm (<4 wt %) when the concentration of D2EHPA in the resin phase is greater than 0.95 mol/kg (Juang and Lin, 1995a; Juang and Chen, 1996), the concentration of D2EHPA was kept higher than 1.08 mol/kg in this study.

Elovich Equation. In the reactions involving chemisorption of gases on solid surfaces without desorption of products, the rates may decrease with time due to an increase in surface coverage. One of the most useful models for studies of such activated chemisorption is the Elovich equation (Aharoni and Tompkins, 1970; Klusacek et al., 1989; Taylor and Thon, 1952):

$$dq/dt = a \exp(-\alpha q) \quad (1)$$

where q is the amount of solute adsorbed at time t , and α and a are constants during any one experiment. The constant a can be regarded as the initial rate since $dq/dt \rightarrow a$ as $q \rightarrow 0$.

The Elovich equation has been applied to study the adsorption of oxygen on coal and other carbonaceous

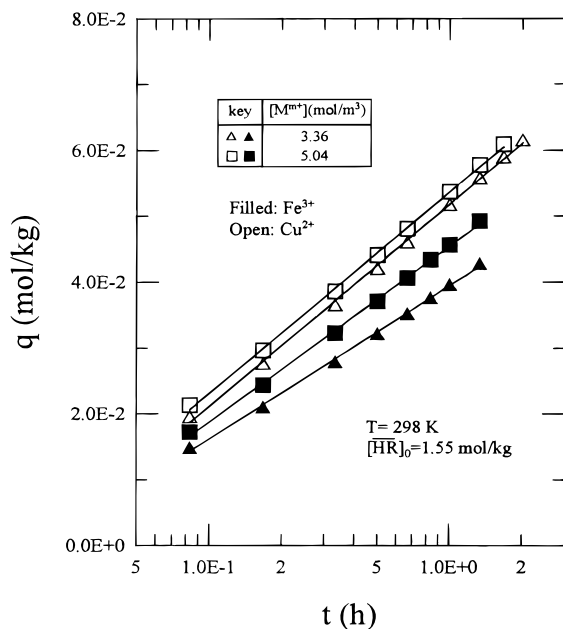


Figure 2. Typical kinetic results for the sorption of metal ions with D2EHPA-SIRs.

materials (Smith et al., 1988) and to analyze the reaction of hexane soot with $\text{NO}_2/\text{N}_2\text{O}_4$ (Akhter et al., 1984). This equation has also been extended and used on the interaction of phosphorus with sediment and soils (Chien and Clayton, 1980; House et al., 1995; Pavlatou and Polyzopoulos, 1988; Torrent, 1987).

Given that $q = 0$ at $t = 0$, the integrated form of eq 1 becomes

$$q = (1/\alpha) \ln(t + t_0) - (1/\alpha) \ln t_0 \quad (2)$$

where $t_0 = 1/\alpha a$. If $t \gg t_0$ (this will be justified later), eq 2 is simplified as

$$q = (1/\alpha) \ln(\alpha a) + (1/\alpha) \ln t \quad (3)$$

This is the case of Figure 2, which shows the variation of the amount of metals sorbed in the resin phase with contact time in the Fe(III) and Cu(II) systems. Acceptable linear relations are obtained for these semilogarithmic plots (correlation coefficient > 0.984).

From numerical analysis of the chemical model based on complex formation (Juang and Chen, 1996), the metal-D2EHPA complexes formed on the XAD-2/SIR have the compositions ZnR_2 , FeR_3 , $\text{CuR}_2(\text{HR})$, CoR_2 , and $\text{NiR}_2(\text{HR})$, respectively, at 298 K. The Elovich equation is therefore expected to be applicable for the present "activated" sorption systems.

In order to more accurately find kinetic parameters of the Elovich equation (a , α , and t_0), a further treatment is necessary. The testing of the Elovich equation is usually carried out by plotting q vs $\ln(t + t_0)$ and obtaining, by trial and error, t_0 such that q vs $\ln(t + t_0)$ becomes a straight line. The parameter α is obtained from the slope of that line, and then the initial sorption rate, a , can be calculated from t_0 and α (Akhter et al., 1984; Taylor and Thon, 1952).

In this work, the sorption rate at specific conditions is hence determined by this initial rate technique except that a computer program was alternatively written and used to obtain the best t_0 in each experiment. Another program was used to plot q vs $\ln(t + t_0)$ after choosing the best t_0 , and then α was obtained from the slope of

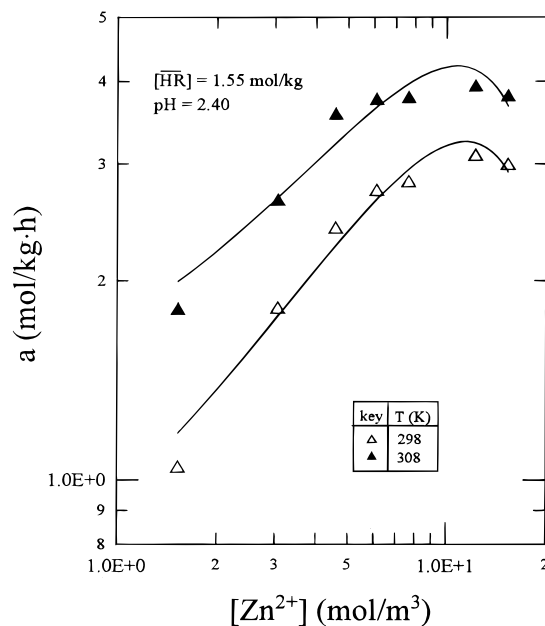


Figure 3. Effect of the concentration of Zn(II) in the aqueous phase on the sorption rate.

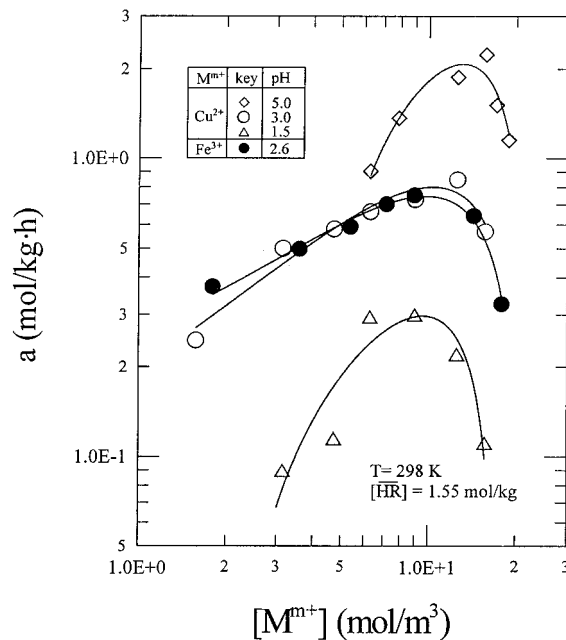


Figure 4. Effect of the concentration of Fe(III) and Cu(II) in the aqueous phase on the sorption rate.

the resulting line. Finally, the initial rate a was calculated from α and t_0 for each run. It should be noted that correlation coefficients of all lines obtained in this way are greater than 0.996.

Effect of Experimental Parameters on the Sorption Rates. Figures 3–6 show the effect of metal concentration in the aqueous phase on the sorption rate. There is a maximum for all systems investigated. As also seen in Figure 4, the location of metal concentration which shows the maximum rate shifts slightly with the pH. The influence of D2EHPA concentration in the resin phase on the sorption rate is shown in Figures 7 and 8. The same trends are obtained under the ranges studied; i.e., the sorption rate linearly increases with D2EHPA concentration in these log-log plots.

On the other hand, the effect of aqueous pH on the sorption rates is illustrated in Figures 9–13. Although the sorption rates normally decrease by reducing the

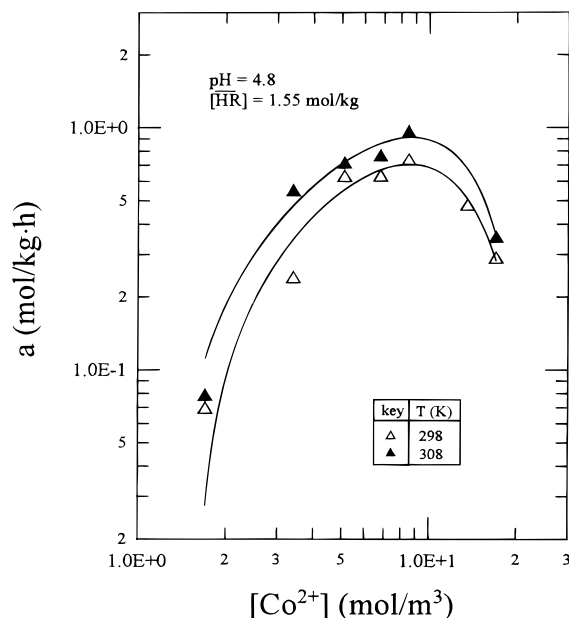


Figure 5. Effect of the concentration of Co(II) in the aqueous phase on the sorption rate.

pH, three different trends are observed. At $[M^{m+}] = 1.53\text{--}1.79\text{ mol/m}^3$, pH = 2.8, and $[\text{HR}] = 1.55\text{ mol/kg}$, for example, the values of a are obtained to be 5.52, 0.512, 0.238, 0.054, and 0.029 mol/(kg·h) in the case of Zn(II), Fe(III), Cu(II), Co(II), and Ni(II), respectively, at 298 K. Evidently, the differences in sorption rates are about 1 order of magnitude among these three groups (Zn(II), Fe(III)/Cu(II), Co(II)/Ni(II)).

On the basis of the experimental data shown in Figures 3–13, three types of rate equations can be obtained by the curve-fitting method. They have the form

$$a = k[M^{m+}](p[M^{m+}] + 1 + n[M^{m+}]^{-1})[\overline{\text{HR}}]^s \times \exp\left(\frac{b[\text{H}^+]^d}{1 + c[\text{H}^+]^e}\right) \quad (4)$$

in the Zn(II) system,

$$a = k[M^{m+}](p[M^{m+}] + 1 + n[M^{m+}]^{-1})[\overline{\text{HR}}]^s \times \left(\frac{b[\text{H}^+]^d}{1 + c[\text{H}^+]^e}\right) \quad (5)$$

in the Fe(III) and Cu(II) systems, and

$$a = k[M^{m+}](p[M^{m+}] + 1 + n[M^{m+}]^{-1})[\overline{\text{HR}}]^s[\text{H}^+]^d \quad (6)$$

in the Co(II) and Ni(II) systems.

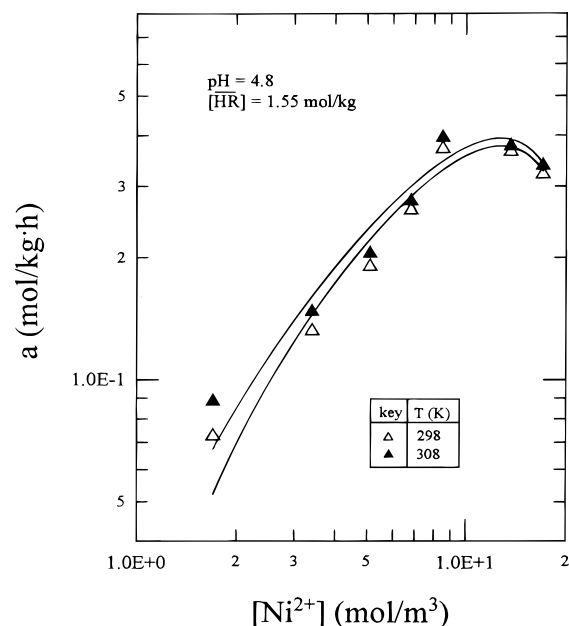


Figure 6. Effect of the concentration of Ni(II) in the aqueous phase on the sorption rate.

The rate constants k and other parameters obtained at 298 K are listed in Table 1. In addition, the normalized deviations between the calculated and measured rates, Δa , defined in eq 7, are also given in Table 1.

$$\Delta a = \left\{ \sum_i [(a_i^{\text{calc}} - a_i^{\text{expt}})/a_i^{\text{expt}}]^2 / (N - 1) \right\}^{1/2} \quad (7)$$

where N is the number of data points. Evidently, the fitting is acceptably good ($\Delta a < 9.6\%$). It is noted that eqs 4–6 are purely experimental findings, and hence the eight parameters have no closely physical or chemical meaning.

Possible Mechanism of SIR Sorption. Following the work of Boyd and Soldano (1953), the magnitude of activation energy can be used to indicate the mechanism of an ion-exchange process. In general, the process is classified to be film-diffusion-controlled when $E_a < 4$ kcal/mol, particle-diffusion-controlled when $E_a = 5\text{--}9$ kcal/mol, and chemical-reaction-controlled when $E_a > 12$ kcal/mol. In practice, Swami and Dreisinger (1995) measured the rates of Zn(II) removal by the OC1026 resin (Bayer Chemical Co.) impregnated with D2EHPA. They obtained the same conclusions on the mechanism from standard ion-exchange kinetic models (Helfferich, 1962) and the above activation energy treatment. Although it is not well supported to determine the controlling steps from activation energy, the simplicity makes it easy to have a general insight into the present complicated sorption systems.

Table 1. Parameters in Eqs 4–6 Calculated for the Sorption of Metal Ions with D2EHPA-SIRs at 298 K and Their Normalized Deviations

parameter	eq 4 Zn(II)	eq 5		eq 6	
		Fe(III)	Cu(II)	Co(II)	Ni(II)
k	0.15	194	253	17.0	3.5
b	3.31	6.2×10^{-3}	6.0×10^{-4}		
c	5.36×10^7	1.0×10^{-2}	1.1×10^{-3}		
d	0.16	−1.0	−1.0	−0.16	−0.15
e	2.61	−1.0	−1.0		
n	1.62	1.25×10^{-3}	1.12×10^{-3}	-1.13×10^{-3}	-8.2×10^{-4}
p	−0.05	−51.1	−48.5	−50.6	−39.3
s	3.20	2.67	1.18	2.30	3.20
Δa (%)	9.6	7.6	3.0	8.9	5.6

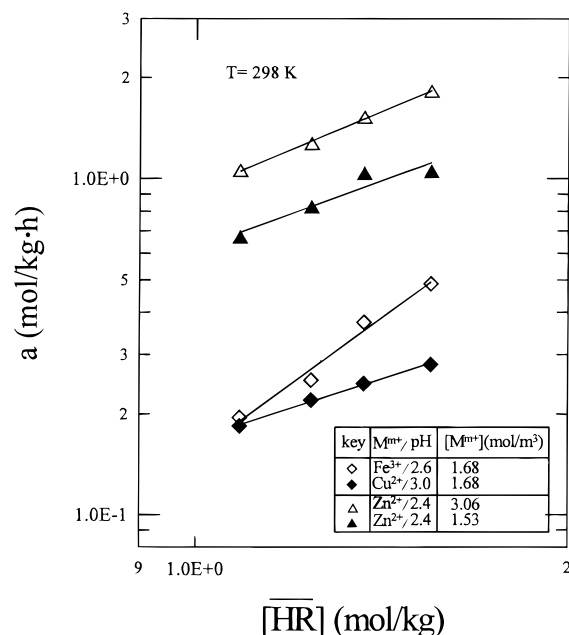


Figure 7. Effect of D2EHPA concentration in the resin phase on the sorption rate.

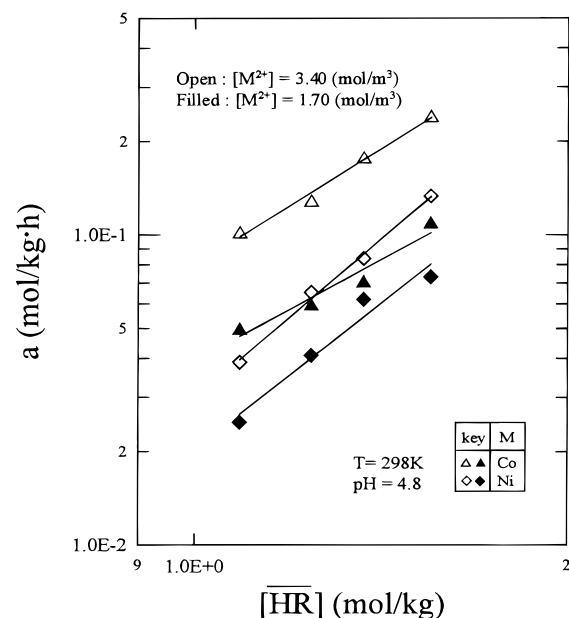


Figure 8. Effect of D2EHPA concentration in the resin phase on the sorption rate.

The apparent activation energy for the sorption of metal ions E_a can be calculated from the temperature dependence of the sorption rate. In this work, the plots of $\log a$ vs $1/T$ based on the data shown in Figures 9–13 give acceptably linear relations (correlation coefficient larger than 0.920 and, mostly, 0.980). Figure 14 gives an example. Table 2 lists the values of E_a calculated and the possible rate-controlling steps at $[M^{m+}] = 1.53$ –1.79 mol/m³ and $[\overline{\text{HR}}] = 1.55$ mol/kg. It is a general trend that E_a increases with the pH, indicating that the rate-controlling step changes as pH changes. The differences in the mechanism probably imply that the nature and structures of the metal–D2EHPA complexes play an important role in the sorption mechanism.

In the kinetic studies of SIR sorption, the concentration effects of metal ions and the extractant on the mechanism were scarcely discussed. In our opinion, the previous findings in the mechanism of metal transport

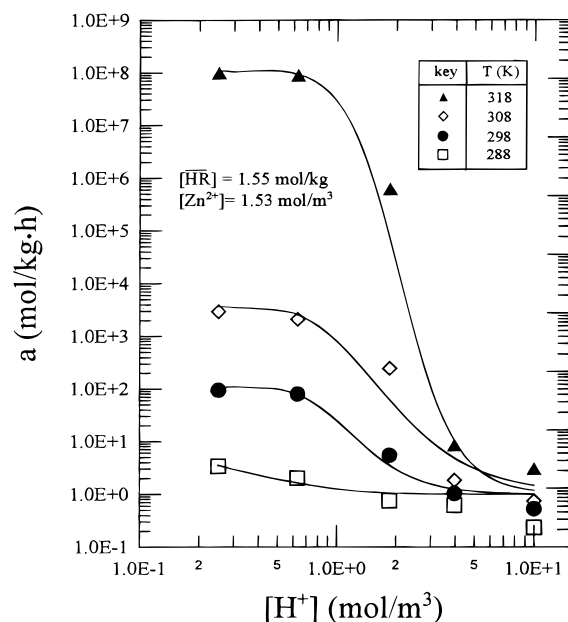


Figure 9. Effect of aqueous pH on the sorption rate of Zn(II) at different temperatures.

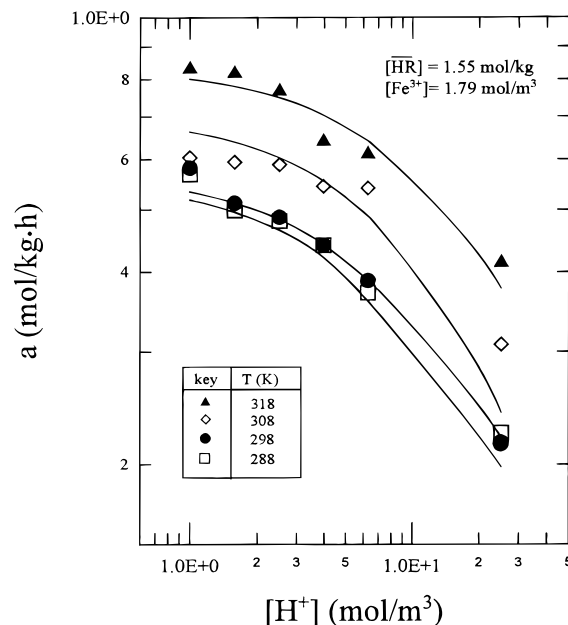


Figure 10. Effect of aqueous pH on the sorption rate of Fe(III) at different temperatures.

Table 2. Apparent Activation Energy Obtained in the Temperature Range 288–318 K and the Possible Rate-Controlling Steps^a

metal ion	pH	E_a (kcal/mol)	rate-controlling step(s)
Zn(II)	2.0–3.6	62.4–418	chemical reaction
Fe(III)	1.6–3.0	2.9–3.7	film diffusion
Cu(II)	2.0–3.6	8.8–10.5	chemical reaction and particle diffusion
Co(II)	3.6–6.0	3.8–4.6	film and particle diffusion
Ni(II)	3.6–6.0	3.5–8.4	film and particle diffusion

^a $[M^{m+}] = 1.53$ –1.79 mol/m³, $[\overline{\text{HR}}] = 1.55$ mol/kg.

through a supported liquid membrane containing acidic organophosphorus extractants like D2EHPA as mobile carriers could be collated in some aspect. The major difference between the two processes is that liquid membranes combine the forward and backextraction steps in one unit, allowing metal ions continuously to

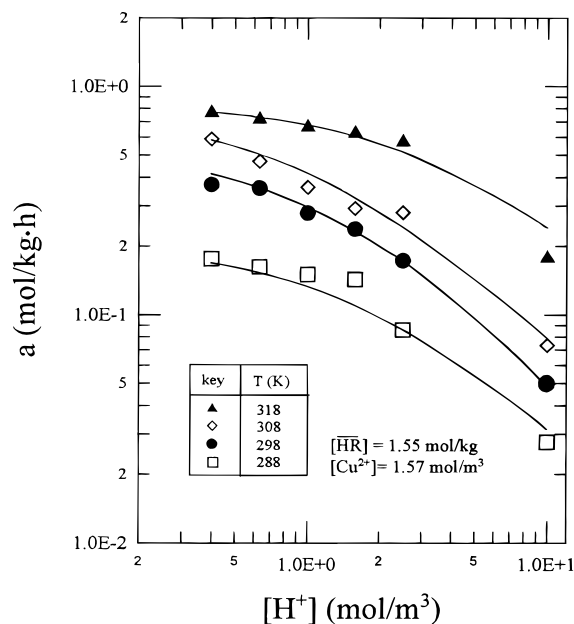


Figure 11. Effect of aqueous pH on the sorption rate of Cu(II) at different temperatures.

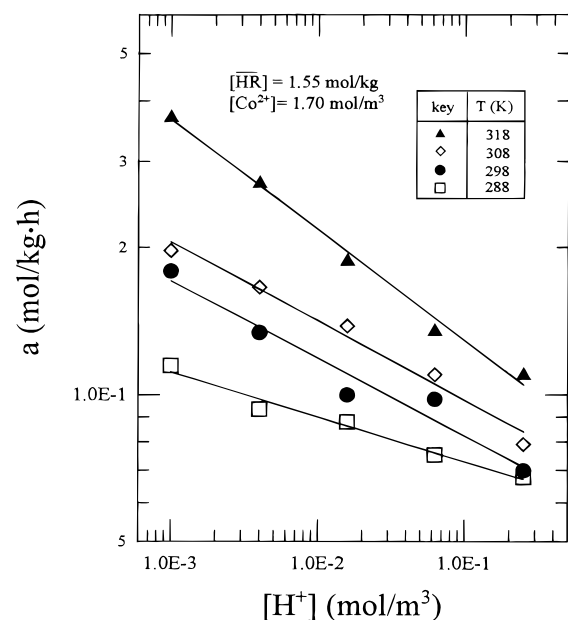


Figure 12. Effect of aqueous pH on the sorption rate of Co(II) at different temperatures.

pass through the membrane. Also, the membrane diffusion in the liquid membranes corresponds to the particle diffusion in the SIR systems.

It has been reported that the contribution of membrane diffusion to the overall liquid membrane process is more pronounced when the feed $[M^{m+}]$ increases or $[\overline{HR}]$ decreases. Conversely, the roles of aqueous film diffusion and interfacial chemical reaction become significant when the feed $[M^{m+}]$ decreases or $[\overline{HR}]$ increases (Juang and Lee, 1996; Juang and Lo, 1994). Therefore, a decrease in the sorption rate when $[\overline{HR}]$ decreases from 1.55 to 1.08 mol/kg, as shown in Figures 7 and 8, probably implies that the role of particle diffusion becomes gradually important.

It follows from Figures 3–6 that the sorption rate increases with $[M^{m+}]$ but then decreases when $[M^{m+}]$ is raised up to about 10 mol/m³. As shown in Figure 4, a shift in the maximum rate toward higher $[Cu^{2+}]$ with

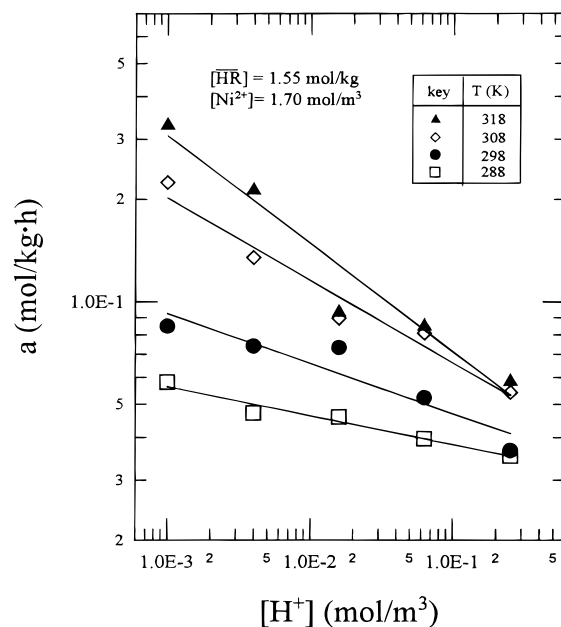


Figure 13. Effect of aqueous pH on the sorption rate of Ni(II) at different temperatures.

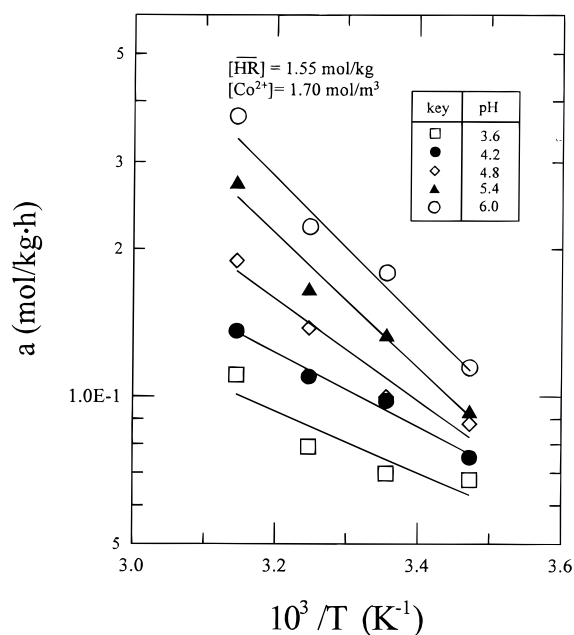


Figure 14. Determination of the apparent activation energy for the sorption of Co(II).

pH may be due to an increase in the number of effective sites for equilibrium sorption as the pH rises (Juang and Chen, 1996). In the rising region of the sorption rate (at low $[M^{m+}]$), chemical reaction (and/or film diffusion) would be rate-controlling. On the other hand, in the falling region (at high $[M^{m+}]$) the contribution of particle diffusion to the overall process becomes dominant. The drop in sorption rate at $[M^{m+}] > 10$ mol/m³ could be the result of a great decrease in diffusivities of the metal–D2EHPA complexes due to an increase in the concentration of the complexes and hence in the viscosity of the “liquid” D2EHPA within the SIR pores.

The present results are different from those obtained earlier. For example, Hughes and Purdey (1976) stated that the sorption of Cu(II) from dilute solutions (1.5 mol/m³) using expanded polyurethane foams containing 3.2 g/g of LIX 64N is film-diffusion-controlled. Warshawsky (1981) also indicated film diffusion to be rate-controlling

for the sorption of Cu(II) (10–240 mol/m³) from sulfate solutions (pH 4) by a polymeric pseudo crown ether containing an oxime (1 mol/kg) based on half-time measurements. In comparison with the present results, such discrepancies may be attributed to different experimental conditions and different inner structures of polymer supports which have a significant but complex effect on the rate behavior (Warshawsky and Berkovitz, 1979).

On the other hand, Swami and Dreisinger (1995) found that the rate data for the sorption of Zn(II) from dilute solutions (0.18 mol/m³) at pH 3 with the resin OC1026 obey the Fickian film diffusion model for the first 15 min, after which the mechanism appears to shift to the particle diffusion model. It was also found that homogeneous particle diffusion based on Fick's law and the ash-layer diffusion model fit the kinetic data for the sorption of U(VI) from phosphoric acid solutions (0.042–0.78 mol/m³) with Levextrel resins containing D2EHPA (Gonzalez-Luque and Streat, 1983).

Comments on the Values of α , t_0 , and a . Under the ranges given in Figures 3–6, for example, α and t_0 obtained at 298 K by the above numerical calculation are in the ranges 19.7–74.5 kg/mol and 0.013–0.017 h in the Zn(II) system, 52.7–107 kg/mol and 0.015–0.029 h in the Fe(III) system, 85.4–199 kg/mol and 0.013–0.02 h in the Cu(II) system, 120–1165 kg/mol and 0.006–0.018 h in the Co(II) system, and 141–1064 kg/mol and 0.003–0.016 h in the Ni(II) system. Two important points are noted from these results. First, the assumption that $t \gg t_0$ made in eq 3 is reasonably justified in this study. Second, α obtained in each sorption system is considerably different under similar conditions. Also, the higher the sorption rate, the smaller the value of α (because t_0 is roughly identical). The present findings about α are opposite to those obtained in the conventional activated chemisorption systems (Aharmoni and Tompkins, 1970; Smith et al., 1988), which revealed that α is related to the number of sites available for adsorption. Satisfactory evidence and a physical meaning of α cannot be given for this system. These behaviors are likely due to the complicated nature of the sorption reactions, whose degree greatly depends on $[M^{n+}]$, $[H^+]$, and $[HR]$ (Juang and Chen, 1996).

As demonstrated above, the sorption rate decreases in the order Zn(II) \gg Fe(III) $>$ Cu(II) \gg Co(II) $>$ Ni(II) under comparable conditions. In liquid–liquid extraction of metal ions with D2EHPA, however, the rate decreases in the order Zn(II) $>$ Cu(II) $>$ Co(II) $>$ Ni(II) $>$ Fe(III) (Dreisinger and Cooper, 1989; Matsuyama et al., 1990). The discrepancies in the order of Fe(III) may be a result of different compositions of its D2EHPA complex, which has a form of $\overline{FeR_3}$ in the XAD-2/SIR system (Juang and Chen, 1996) and $\overline{FeR_3(HR)_3}$ in the solvent extraction (Matsuyama et al., 1990). It is expected that the formation of the octahedral complex $\overline{FeR_3(HR)_3}$, which has a greater steric hindrance compared to $\overline{FeR_3}$, retards mass-transfer rate in the solvent extraction. On the other hand, the differences in the local environment (resin vs nonpolar solvent) could also explain the differences in the different metal–D2EHPA complexes. In fact, the extraction of Fe(III) from aqueous solution with D2EHPA in benzene is controlled by chemical reaction of complex formation occurring at the organic–aqueous interface (Matsuyama et al., 1990), whereas that of Cu(II) and Co(II) with

D2EHPA (Dreisinger and Cooper, 1989) or other acidic organophosphorus extractants like (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl) ester (Miyake et al., 1990) in benzene is controlled by diffusion of the complexes in the organic stagnant layer.

Conclusions

Batch kinetics of the sorption of metal ions from sulfate solutions with D2EHPA-impregnated Amberlite XAD-2 macroporous resins were studied in the temperature range 288–318 K. It was shown that the impregnation process of D2EHPA onto XAD-2 resins had a negligible effect on the sorption rate. Also, the kinetic data could be well described by the Elovich equation (correlation coefficient > 0.996). Under comparable conditions, the sorption rate decreased in the order Zn(II) \gg Fe(III) $>$ Cu(II) \gg Co(II) $>$ Ni(II). Three types of rate equations (eqs 4–6) were obtained for groups of Zn(II), Fe(III), and Cu(II) and Co(II) and Ni(II), respectively, depending on the magnitude of the sorption rates (differentiating by nearly 1 order each). The sorption mechanisms in the present SIR systems were discussed in Table 2 according to the values of activation energy. Under the ranges studied, particle diffusion played a dominant role in the rate phenomena at higher metal concentrations (> 10 mol/m³).

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Nomenclature

a = initial rate of sorption, mol/kg·h
 HR = bis(2-ethylhexyl)phosphoric acid (D2EHPA)
 k = rate constant defined in eqs 4–6
 m = valence of metal ions
 q = amount of metals sorbed at time t , mol/kg
 SIR = solvent-impregnated resin
 t = time, h
 T = absolute temperature, K
 $[]$ = concentration of species in the brackets, mol/kg or mol/m³

Greek Letter

α = constant characteristic of the process, kg/mol

Subscript

0 = initial (total)

Superscript

overbar = resin phase

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