Kinetics of Separating Multicomponent Mixtures by Nondispersive Solvent Extraction: Ni and Cd

Inmaculada Ortiz, Berta Galán, Fresnedo San Román, and Raquel Ibáñez
Dept. de Química, ESTIIyT, Universidad de Cantabria, 39005 Santander, Spain

A model for nonsteady metals separation using nondispersive solvent extraction presented explicitly accounts for selective separation of multicomponent solutions and concentration of separated components in a back-extraction phase. The separation process comprises extraction and back-extraction steps carried out in two different hollow-fiber modules, connected through the organic phase, together with three homogenization tanks. The model is based on a set of coupled differential equations describing mass balances of metallic solutes in the fluid phases. To be applied in its simplest form, it requires the knowledge of three characteristic parameters, two parameters related to the chemical reactions, and one mass-transport parameter. The latter describes the mass-transport rate through pores of the hollow-fiber membrane filled with the organic phase. The mathematical model was checked against the kinetic results of the separation of Cd/Ni mixtures working with high-concentration solutions and obtaining the characteristic parameters of this system.

Introduction

In the last decades, extensive studies on dispersion-free solvent extraction with the use of microporous membranes have been carried out (D'Elia et al., 1986; Yang and Cussler, 1986; Prasad and Sirkar, 1988, 1990; Wickramasinghe et al., 1992, and so on). This technique not only overcomes the limitations of conventional liquid extraction, such as flooding, close mixing, limitations on phase flow-rate variations, and the requirement of density difference, but also provides a large surface area of mass transfer per volume of contactor (Yeh and Hsu, 1998). Excellent reviews of the technology and its applications were presented by Ho and Sirkar in 1992, and more recently by Gabelman and Hwang (1999).

The efficient removal of toxic heavy metals like Cr(VI), Cd, Zn, Ni, and other contaminants like phenol from industrial wastewater (Cooney and Poufos, 1987; Basu et al., 1990; Yun et al., 1992, 1993; Alonso et al., 1994, 1997a,b; Yoshizuka et al., 1995; Ortiz et al., 1996, 1999; Breembroek et al., 1998), and the recovery of valuable solutes from aqueous phases, for example, citric acid, carboxylic acids, aminoacids, and L-phenylalanine (Basu and Sirkar, 1992; Escalante et al., 1998), are well-demonstrated applications of this technique.

From a practical point of view, it may be important not only to extract the solute but also to concentrate it (Basu et al., 1990). For this reason, simultaneous extraction and stripping of the solute has been developed using two hollow-fiber modules in series, one for the extraction and the other for the back-extraction processes. The modules are connected to each other by an organic extractant in a recirculating line. This configuration guarantees that saturation of the carrier does not occur, as it is continuously regenerated, and consequently the carrier concentration can be reduced maintaining the mass-transfer rate, and thus decreasing the associated operating costs of the process. Simultaneous membrane solvent extraction and back-extraction have been used for the removal and concentration of different solutes, for example, valeric acid (Rodriguez et al., 1997), sodium lactate (Coelhoso et al., 1997), Cu (Hu and Wiencek, 1998), and hexavalent chromium (Alonso et al., 1999).

The simultaneous or selective extraction of particular metals from metallic mixtures by nondispersive liquid−liquid extraction has also been widely studied. Raghuraman and Wiencek (1993) studied the separation of Cu, Ni, and Hg using two different extractants: LIX84 for Cu and D2HEPA for Ni. Yang et al. (1996) studied the separation of a mixture of Cr(VI) and Cu(II) using LIX84 and H_2SO_4 in the organic

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Correspondence concerning this article should be addressed to I. Ortiz.

and back-extraction phases, respectively, for the recovery of Cu, and TOA and NaOH for Cr. More recently, Ilias et al. (1999), and Lee et al. (1999) studied the separation of Zn and Cu.

For design purposes, analysis of the kinetics of the NDSX process on a laboratory scale is the first step required. The rate at which a component is transferred between two different phases depends on the mass-transfer coefficient, the interfacial area, and on the degree of departure of the components from its partitioning equilibrium. Evaluation of mass-transfer coefficients is very important, since they determine the rate at which equilibrium is approached, control the time required for a given separation, and therefore the size and cost of the equipment to be used.

In previous papers the authors studied the viability of the nondispersive solvent extraction technology to the separation of nickel and cadmium from highly concentrated solutions generated during the leaching step of the recycling process of Ni/Cd batteries (Galán et al., 1998) and the kinetics of the recovery of Cd by means of NDSX (Ortiz et al., 2001a). This article presents the mathematical model of the separation kinetics of multicomponent mixtures with the aid of nondispersive solvent extraction, analyzing the kinetic results of the separation of Cd and Ni as a case of study.

Experimental Setup

The case of study is the separation of nickel and cadmium from concentrated solutions that simulated those generated during the leaching step of the recycling process of Ni/Cd batteries. The aqueous feed solutions were prepared with $CdSO_4$ 8/3 H_2O and $NiSO_4$ $6H_2O$ (AR grade) in a concentration range of 0–0.2 M, 60% (v/v) D2EPHA; di(2-ethylhexyl) phosphoric acid (MERCK) was used as selective extractant; and kerosene (REPSOL S.A.) was used as the solvent. Tributyl phosphate (TBP), 10% v/v (MERCK), was added to the organic phase in order to avoid the segregation of a third phase (second organic). All the components of the organic phase were used as received without further purification. Finally, H_2SO_4 was used as the back-extraction (BEX) agent.

For the simultaneous extraction (EX) and back-extraction (BEX), two hollow-fiber modules in series were used, flowing the organic phase from the EX module to the BEX one. In the first module, extraction of solutes was accomplished by the organic phase that contacted the back-extraction solution in the second module, flowed to the homogenization tank of the organic phase, and reentered the extraction step. Aqueous phases flowed through the inner side of the microporous hollow-fiber membranes whose pores were filled with the organic extractant, and the organic extractant flowed concurrently in the shell side in both HF modules. Figure 1 depicts the experimental setup comprising two HF modules, three stirred tanks, and accessories.

The pH of both aqueous phases was kept constant during the runs by means of two pH controller systems (Metrohm 691-01). The feed phase pH was kept equal to 3.5 by the addition of a 9-M sodium hydroxide solution. The back-extraction solution pH was kept equal to 0.5 by the addition of 10 M of H_2SO_4 solution. The volume added to the aqueous phases was considered negligible compared to the total volumes of the tanks. The experiments were carried out at room temperature, $20 \pm 1°C$.

Pumping of both aqueous phases was achieved using PTFE diaphragm pumps capable of flows up to 0.8 L/min, and powered by a variable-speed DC motor, and the organic phase utilized a gear pump capable of flows up to 1 L/min. Three Teflon flowmeters were used to monitor the flow rates of the feed, stripping, and organic streams. The flowmeters were equipped with back-pressure control valves in order to maintain the appropriate differential pressure control of the aqueous–organic interface in both modules. Table 1 gives the characteristics of the modules used in this work that were purchased from Hoechst Celanese.

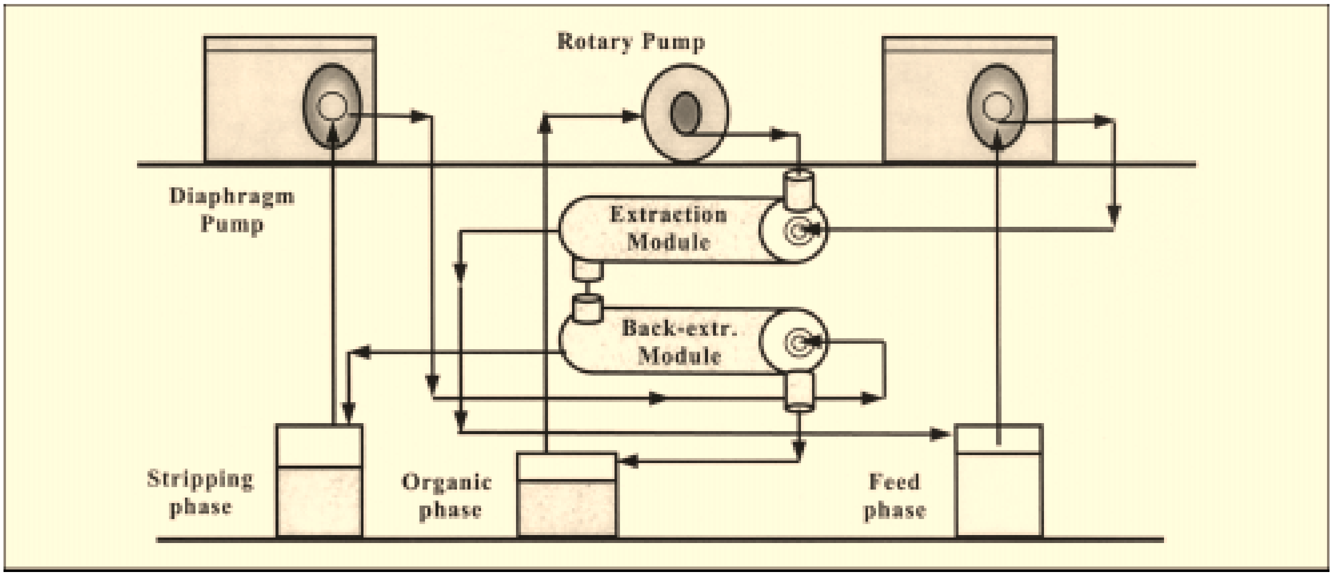

Figure 1. Experimental setup.

Table 1. Hollow-Fiber Membrane Module Characteristics

Characteristics of Modules	Values
Fiber	X-30/Polypropylene
Internal diameter	240 μm
Wall thickness	30 μm
Number of fibers	10,200
Nominal porosity	40%
Effective mass-transfer length	150 mm
Effective mass-transfer area	1.4 m^2

Table 2. Initial Conditions of the Experimental Runs

	Init. Conc. EX Phase $(mol/m^3)10^{-3}$		Init. Conc. ORG Phase $(mol/m^3)10^{-3}$		Init. Conc. BEX Phase $(mol/m^3)10^{-3}$		pH	
Exp.	Cd	Ni	Cd	Ni	Cd	Ni	EX	BEX
I	0.21	0.19	0.20	—	0.20	—	3.5	0.5
II	0.21	0.20	—	0.19	0.20	—	3.5	0.5
III	0.20	0.21	0.20	0.20	0.21	0.20	3.5	0.5
IV	0.20	0.21	0.194	0.20	0.21	—	3.5	0.5

The experiments were carefully planned in order to obtain the maximum information on the process, covering a wide range of variation of the concentration of the metals as shown in Table 2. In order to load the organic solution only the extraction module was used, that is, the BEX part of the experimental system was excluded in this process. An initial organic phase containing 1.7 M of D2EHPA was loaded with Cd and/or Ni according to the experimental schedule (Table 2). Cd loading was carried out by contacting the initial organic phase with an aqueous feed solution containing 0.2 M of $CdSO_4$ for 3 h until the concentration of Cd in the organic phase was about 0.2 M (Exps. I, III, IV). Ni loading was performed using an aqueous feed solution 0.2 M of $NiSO_4$ for 5 h until the concentration of Ni in the organic phase reached a value equal to 0.2 M (Exps. II, III, IV). When the organic phase was conveniently loaded, the BEX part of the experimental system was included, and the EX and BEX processes were carried out according to the schedule in Table 2.

Concentration change during a single pass was not large enough due to the small interfacial area in the module (1.4 m^2). In order to increase the change in the solute concentration, the extraction and back-extraction steps were carried out by recirculation of the aqueous and organic phases through the module and back into the aqueous and organic reservoirs, and solute concentration was measured as a function of time. Thus batch experiments were carried out.

The volume of the aqueous solutions in the stirred tanks was equal to 600 mL, and the volume of the organic solution was 1,200 mL. The kinetic experiments were carried out until the concentration of Cd in the aqueous phase decreased below 10% of the initial concentration value. The duration of the runs was between 1.5 and 3 h, depending on the initial conditions of the organic phase. The metallic content of the samples was analyzed in a Perkin-Elmer 1100 B Atomic Absorption Spectrometer.

Theoretical Background

The design of any process has to be supported by a proper understanding of the system behavior. In this system, the simultaneous extraction and back-extraction processes have been formerly described (Figure 1).

Chemical reactions between metallic solutes and organic extractant in the extraction process, and between complex organic species and the BEX agent were assumed to take place at the inside wall of the membrane where the aqueous−organic interface is located. The mass-transfer process of each solute from the initial phase to the receiving one is considered to take place through the following steps: diffusion through the aqueous feed layer, interfacial chemical reaction, diffusion through the hollow-fiber membrane, and diffusion through the organic-phase layer. The order of steps is reversed during the back-extraction process.

Mathematical modeling and determination of the characteristic parameters in order to predict the performance of membrane solvent extraction processes has been widely studied in the literature. The analysis of mass transfer in hollow-fiber modules has been carried out using two different approaches:

1. The velocity and concentration profiles are developed along the hollow fibers by means of the mass-conservation equation and the associated boundary conditions for the solute in the inner fluid. This analysis separates the effects of the operation variables, such as hydrodynamic conditions and the geometry of the system, from the mass-transfer properties of the system, described by diffusion coefficients in the aqueous and organic phases and membrane permeability. The solution of such equations usually involves numerical methods (Urtiaga and Irabien, 1993; Alonso and Pantelides, 1996; Qin and Cabral, 1997, 1998).

2. The mass flux of a solute can be related to a mass-transfer coefficient that gathers both mass transport properties and hydrodynamic conditions of the system (fluid flow and hydrodynamic characteristics of the membrane module). The total amount of a given solute transferred from the feed to the receiving phase can be assumed to be proportional to the concentration difference between both phases and to the interfacial area, defining the proportionality ratio by a mass-transfer coefficient. Several types of mass-transfer coefficients can be distinguished as a function of the definition of the concentration differences involved. When local concentration differences at a particular position of the membrane module are considered, the local mass-transfer coefficient is obtained, in contrast to the average mass-transfer coefficient (Cussler, 1997).

Studies on mass transfer through aqueous−organic interfaces immobilized at the pore mouths of a microporous membrane have shown that for a hollow-fiber device, the overall mass-transfer coefficient obtained can be related to the individual phase mass-transfer coefficients and the membrane resistance using simple film theory (Prasad and Sirkar, 1990). However, many authors considered that this separation-controlling, overall mass-transfer resistance was dominated by the resistance of the membrane. This is because the permeability of the membrane is low and because the membrane is thick (Wickramasinghe et al., 1992; Basu and Sirkar, 1992; Juang, 1993a; Coheloso et al., 1997; Escalante et al., 1998; Juang and Huang, 1999; among others). On the other hand, other authors reported for different systems and conditions that the kinetic control of the whole process could be shared between diffusion in the aqueous-phase boundary layer and the kinetics of the chemical reaction (Yoshizuka et al., 1992, 1995; Yun et al., 1993; Kubota et al., 1995; Mohammed et al., 1996; Kondo et al., 1997).

The principal assumptions underpinning the model developed in this work are (1) convective mass transfer dominates diffusive mass transfer in the fluid flowing inside the hollow fibers; (2) the resistance in the membrane dominates the overall mass-transport resistance, therefore the overall mass-transfer coefficient was set equal to the mass-transfer coefficient across the membrane; and (3) chemical reactions between ionic species are sufficiently fast to ignore the contribution of the chemical reaction rates. Thus, the reacting species are present in the equilibrium concentration at the interface everywhere (Juang, 1993b; Ortiz et al., 2001a). For systems working under nonsteady state, it is also necessary to describe the change in the solute concentration with time both in the modules and in the reservoir tanks. The reservoir tanks have been modeled as ideal stirred tanks.

In previous works, making use of the latter considerations, the authors managed to describe the dynamic response of the extraction and back-extraction processes of one solute, Cr(VI) (Ortiz et al., 1996; Alonso et al., 1997a, 1999), Cd (Alonso et al., 1997b; Ortiz et al., 1999, 2001a), and L-phenylalanine (Escalante et al., 1998). The description of the mass transport in those systems was obtained by simultaneously solving the differential equations describing the mass transport through the membrane modules and stirred tanks and estimating the characteristic parameters according to an optimization procedure. Two main parameters were needed in the description of the separation−concentration process of one solute, that is, the membrane mass-transport coefficient and the equilibrium parameter of the extraction interfacial reaction.

Next, we present the mathematical model for the separation−concentration process of two solutes, Ni and Cd by nondispersive solvent extraction with the cited assumptions; in order to avoid duplicate equations, the subscript i has been used, where $i=1$ represents cadmium and $i=2$ represents nickel.

Extraction module

The differential mass balances of the solutes in the feed and organic solutions in the extraction module are expressed through the following equations,

EX, Aqueous Solution

$$-\frac{1}{v_A}\frac{\partial C_{A_i}}{\partial t}=\frac{\partial C_{A_i}}{\partial z}+\frac{2\pi n_f r_f}{F_A}K_m\left(C_{OI_i}-C_{O_i}\right), \qquad (1)$$

with boundary conditions:

$$z=0 \qquad C_{A_i}=C_{\mathrm{out}_i} \qquad \text{(extraction tank)} \qquad (2)$$

$$t=0 \qquad C_{A_i}=C_{A_i,\,\mathrm{initial}}, \qquad i=1,2, \qquad (3)$$

where C_{OI_i} is the interfacial concentration of the metal in the organic phase that is related to the aqueous metal concentration through the chemical equilibrium equation.

Table 3. Variation of the Activity Coefficients of Cd $^{+2}$ and Ni $^{+2}$ with Concentration

Concentration (mol/L)	Activity coefficients, γ
0	1
0.05	0.6
0.1	0.18
0.15	0.15
0.2	0.1
0.25	0.08
0.3	0.07
0.4	0.07

Extraction:

$$\mathrm{Me_i}+n\overline{(\mathrm{HX})_m}\Leftrightarrow\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}}+n\mathrm{H}^+ \qquad (4)$$

$$K_{\mathrm{EX}}=\frac{\left(a_{\overline{[\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}}\right)\left(a_{(\mathrm{H}^+)}\right)^n}{\left(a_{[\mathrm{Me}_i]}\right)\left(a_{\overline{(\mathrm{HX})}_m}\right)^n} \qquad (5)$$

$$K_{\mathrm{EX}}=\frac{C_{\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}}}C^n_{\mathrm{H}^+}}{C_{\mathrm{Me}_i}C^{n}_{\overline{(\mathrm{HX})}_m}}\times\frac{\left\lfloor\gamma_{\overline{[\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}}\right\rfloor\left\lfloor\gamma_{(\mathrm{H}^+)}\right\rfloor^n}{\left[\gamma_{\mathrm{Me}_i}\right]\left[\gamma_{\overline{(\mathrm{HX})}_m}\right]^n}. \qquad (6)$$

In the first approach, in this work, it has been assumed that the ratio of the activity coefficients of the species in the organic phase keeps constant for the range of experimental conditions (Galán et al., 1994). In the aqueous phases the activity of the hydrogen ions, $a_{[(\mathrm{H}^+)]}$, remained constant in the extraction and back-extraction processes, since the pH values were kept constant during the experiments through the addition of sulphuric acid and sodium hydroxide, respectively, whereas the activity of the metallic solutes, $a_{[\mathrm{Me}_i]}$, varied during the experiment, since both the metal concentration and the activity coefficients changed significantly with operation conditions, as shown in Table 3. The corresponding values of the activity coefficient of the metal ions in aqueous solutions were calculated using the Debye-Hückel equation. Therefore Eqs. 5 and 6 can be expressed as follows:

$$K'_{\mathrm{EX}}=K_{\mathrm{EX}}\frac{\left\lfloor\gamma_{\overline{(\mathrm{HX})}_m}\right\rfloor^n}{\left[\gamma_{\overline{[(\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}}\right]}=\frac{C_{\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}}}C^n_{\mathrm{H}^+}}{C_{\mathrm{Me}_i}C^{n}_{\overline{(\mathrm{HX})}_m}}\times\frac{\left\lfloor\gamma_{(\mathrm{H}^+)}\right\rfloor^n}{\left[\gamma_{\mathrm{Me}_i}\right]}. \qquad (7)$$

Organic Solution

$$\frac{1}{v_O}\frac{\partial C_{O_i}}{\partial t}=-\frac{\partial C_{O_i}}{\partial z}+\frac{2\pi n_f r_f}{F_O}K_m\left(C_{OI_i}-C_{O_i}\right). \qquad (8)$$

Boundary conditions of the organic phase:

$$z=0 \qquad C_{O_i}=C_{\mathrm{out}_i} \qquad \text{(organic tank)} \qquad (9)$$

$$t=0 \qquad C_{O_i}=C_{O_i,\mathrm{initial}}, \qquad i=1,2. \qquad (10)$$

Back-extraction module

The extraction and back-extraction steps take place consecutively, being connected by the concentration of the metal−extractant complex species in the organic phase.

A description of the back-extraction process is carried out using equations similar to those used in the extraction process. The equilibrium of the interfacial reaction between the organic complex species and the back-extraction agent is applied in this case.

BEX Aqueous Solution

$$\frac{1}{\upsilon_S}\frac{\partial C_{S_i}}{\partial t} = -\frac{\partial C_{S_i}}{\partial z} + \frac{2\pi n_f r_f}{F_S} K_m \left(C_{O_i} - C_{OI_i} \right). \qquad (11)$$

Boundary conditions for the stripping aqueous phase:

$$z = 0 \qquad C_{S_i} = C_{\text{out}_i} \qquad \text{(stripping tank)} \qquad (12)$$

$$t = 0 \qquad C_{S_i} = C_{S_i,\text{initial}}, \qquad i = 1, 2. \qquad (13)$$

with the equilibrium back-extraction reactions,

$$\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}} + n\mathrm{H}^+ \Leftrightarrow \mathrm{Me}_i + n\overline{(\mathrm{HX})_m} \qquad (14)$$

$$K_{\mathrm{BEX}} = \frac{\left(a_{[\mathrm{Me}_i]}\right)\left(a_{[\overline{(\mathrm{HX})_m}]}\right)^n}{\left(a_{\overline{[\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}}\right)\left(a_{[(\mathrm{H}^+)]}\right)^n} \qquad (15)$$

and

$$K_{\mathrm{BEX}} = \frac{C_{\mathrm{Me}_i} C^n_{\overline{(\mathrm{HX})_m}}}{C_{\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}}} C^n_{\mathrm{H}^+}} \times \frac{\left[\gamma_{\mathrm{Me}_i}\right]\left\lfloor \gamma_{\overline{(\mathrm{HX})_m}} \right\rfloor^n}{\left[\gamma_{\overline{[\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}}\right]\left[\gamma_{(\mathrm{H}^+)}\right]^n}, \qquad (16)$$

which with similar assumptions to those made in the extraction reactions would transform into

$$K'_{\mathrm{BEX}} = K_{\mathrm{BEX}} \frac{\left\lfloor \gamma_{\overline{[\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}]}} \right\rfloor}{\left[\gamma_{(\overline{\mathrm{HX}})_m}\right]^n} = \frac{C_{\mathrm{Me}_i} C^n_{\overline{(\mathrm{HX})_m}}}{C_{\overline{\mathrm{Me}_i\mathrm{X}_n(\mathrm{HX})_{m-n}}} C^n_{\mathrm{H}^+}} \times \frac{\left[\gamma_{\mathrm{Me}_i}\right]}{\left[\gamma_{(\mathrm{H}^+)}\right]^n}. \qquad (17)$$

BEX Organic Solution

$$-\frac{1}{\upsilon_O}\frac{\partial C_{O_i}}{\partial t} = \frac{\partial C_{O_i}}{\partial z} + \frac{2\pi n_f r_f}{F_O} K_m \left(C_{O_i} - C_{OI_i} \right). \qquad (18)$$

Boundary conditions of the organic phase:

$$z = 0 \qquad C_{O_i} = C_{O_i} \qquad \text{(outlet extraction module)} \qquad (19)$$

$$t = 0 \qquad C_{O_i} = C_{O_i,\text{initial}}, \qquad i = 1,2. \qquad (20)$$

Stirred tanks

The dynamic response of the system is determined by simultaneously solving the differential equations 1 to 20 together with the modeling equations for the three vessels considered as ideal stirred tanks. It is assumed that the solute concentrations at the reservoir and at the module inlet for both phases are identical.

$$V\frac{dC_{\text{out}}}{dt} = F\left(C_{\text{in}_i} - C_{\text{out}_i}\right) \qquad (21)$$

$$t = 0 \qquad C_{\text{out}_i}(\text{organic tank}) = C_{O_i,\text{initial}} \qquad (22)$$

$$C_{\text{out}_i}(\text{extraction tank}) = C_{A_i,\text{initial}} \qquad (23)$$

$$C_{\text{out}_i}(\text{stripping tank}) = C_{S_i,\text{initial}}. \qquad (24)$$

Consequently, it is believed that the most basic model describes the separation of metallic mixtures using hollow-fiber membranes. It consists of a set of coupled differential equations corresponding to the mass balances of the metallic solutes in the extraction and back-extraction modules, a set of algebraic equations corresponding to the description of the chemical equilibrium reactions, and six total differential equations describing the mass balances in the stirred tanks. The use of the mathematical model would require the knowledge of the design parameters, that is, the membrane mass-transport coefficient and the parameters of the interfacial chemical equilibria.

Although this model has been outlined to determine the dynamic response of the separation of Ni and Cd, it can be generalized and applied to the determination of the response of different systems containing more than one solute.

Mass-Transport Modeling of Separating Ni/Cd Mixtures

An analysis of the viability of the separation of Ni/Cd mixtures from high-concentration solutions was reported previously (Galán et al., 1998). This work reports the analysis of the kinetic results obtained in a wide range of concentration values leading to the development of a kinetic model and to the determination of the characteristic parameters.

The experiments were carefully planned in order to obtain the maximum information on the process behavior. The initial concentrations of each metal in the aqueous, organic, and back-extraction solutions are shown in Table 2.

Extraction kinetics

Figure 2 shows a comparison of the kinetic extraction results of Cd and Ni. From the analysis of the results several considerations can be made: (1) the concentration of Ni in the aqueous feed phase remains almost unchanged, indicating that the extraction of Ni is negligible in the process, thus confirming the viability of the separation of Ni/Cd from highly concentrated solutions under the experimental conditions, $\mathrm{pH}_{\text{ext}} = 3.5$; (2) Cd concentration in the aqueous feed phase decreases below 10% of the initial value in 2 h, indicating that the extraction of Cd is achieved satisfactorily; (3) the variable that exerts the main influence on the extraction kinetics of Cd is the initial concentration of Cd in the organic phase. Figure 2 shows that when there is no Cd initially in the latter phase, (Exp. II), the extraction of the metal proceeded faster than when the organic phase was initially loaded with the metal (Exps. I, III, and IV).

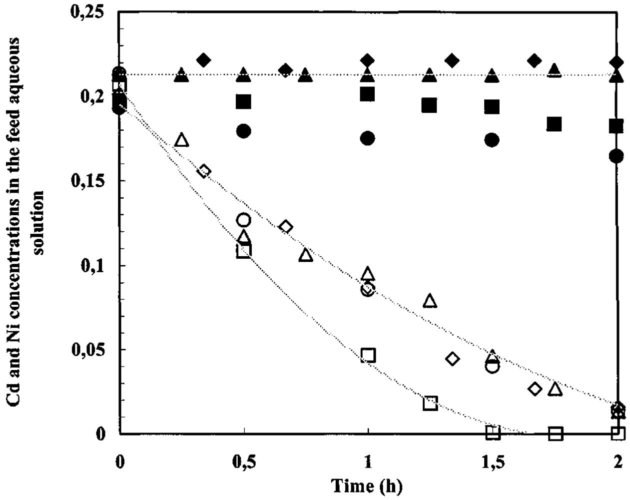

Figure 2. Experimental concentration of cadmium: I(○), II(□), III(◇), and IV(△), and experimental concentration of nickel in Exps. I(●), II(■), III(♦), and IV(▲) in the extraction phase.

Back-extraction kinetics

Figure 3 reports the kinetic results of the back-extraction of Cd. All the runs were performed starting from a BEX phase with an initial 0.2 M concentration of Cd. The initial concentration of metals in the organic phase ranged from 0 M to 0.2 M. It is clearly seen that the kinetic evolution of the Cd BEX concentration depended on the starting conditions of the organic phase that led to the simultaneous back-extraction of Cd and Ni.

Figure 4 depicts the Ni back-extraction kinetic results. When the organic phase did not contain Ni initially (Exp. I), no traces of the metal were detected in the BEX solution, since, as has been previously mentioned, Ni extraction was negligible under the operation conditions. A similar slope of the rest of the lines (Exps. II–IV), indicates that the rate of concentration of Ni was independent of the presence of Cd in the fluid phases.

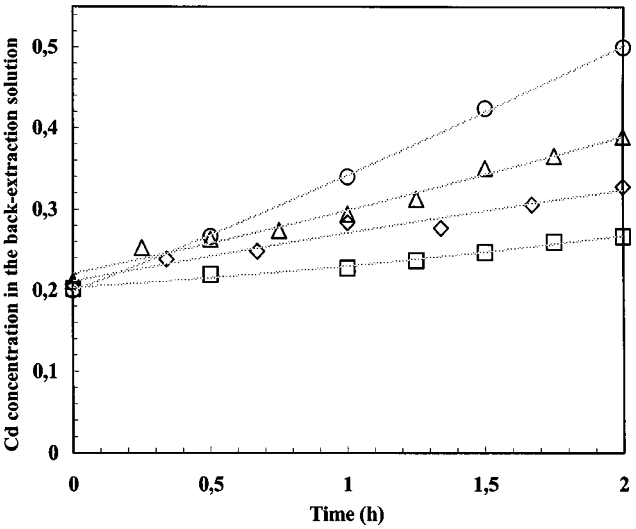

Figure 3. Experimental concentration of cadmium: I(○), II(□), III(♦), and IV(△) in the back-extraction phase.

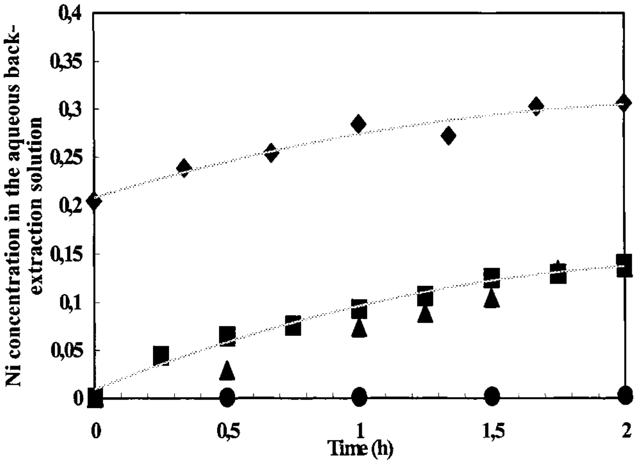

Figure 4. Experimental concentration of nickel: I(●), II(■), III(♦), and IV(▲) in the back-extraction phase.

Mathematical modeling

The mathematical model for the description of the separation kinetics of Cd and Ni in hollow-fiber modules under nonsteady-state conditions has been explained in detail in the previous section. The competition of both components in the complexation reaction with the organic carrier has been assumed to be the main difference in the permeation rates of the two components (separation process). This reaction depends on the individual equilibrium parameters rather than on the different diffusivity of the resulting complex species in the organic phase. Therefore, it was assumed the same value of the membrane mass-transport coefficient (K_m) for both metals, equal to 1.57×10^{-7} m/s, a value that had been calculated previously (Ortiz et al., 2000a).

Table 4 contains a comparison of the values of K_m of different nondispersive extraction systems of metallic solutes when hollow-fibers of similar characteristics were used. The higher values reported by Daiminger et al. (1996), $K_m = 5.11 \times 10^{-7}$ m/s and Yun et al. (1993), $K_m = 4.8 \times 10^{-7}$ m/s were calculated according to the following equation

$$K_m = \frac{D\epsilon}{\delta\tau} \tag{25}$$

after estimation of the corresponding diffusivity of the complex species through the organic membrane from well-known correlations. Since the value of the diffusivity coefficient depends on the concentrations of the species present in the organic membrane systems dealing with diluted aqueous solutions, again using lower concentrations of the organic extractant will lead to higher values of the diffusivities and therefore of the membrane mass-transport coefficients, as shown in Table 4.

Table 4. K_m Values in the Literature for Systems Containing Metals

Author	K_m (m/s)	System	Fibers
Daiminger et al. (1996)	5.11×10^{-7}	Cd ($< 8.0 \times 10^{-5}$ M) D2EPHA (0.05 M) + isododecane	Polypropylene $\epsilon = 40\%$ $\delta = 25\ \mu$m
Yun et al. (1993)	4.8×10^{-7}	Cu (7.8×10^{-3} M) LIX 84 (0.75 M) + *n*-heptane	Polypropylene $\epsilon = 30\%$ $\delta = 30\ \mu$m
Breembroek et al. (1998)	1.21×10^{-7}	Cd ($2-8 \times 10^{-3}$ M) Alamine 304 ($10^{-5} - 2 \times 10^{-4}$ M) + kerosene	Polypropylene $\epsilon = 28-40\%$ $\delta = 25\ \mu$m
Ortiz et al. (2000a)	1.57×10^{-7}	Cd (0.2–0.4 M) D2EPHA (1.76 M) + kerosene + TBP	Polypropylene $\epsilon = 40\%$ $\delta = 30\ \mu$m

The necessary consideration of equilibrium models of the chemical reactions in the overall mathematical model describing the separation kinetics of both metals involves considerable difficulty, since there is no agreement in the literature on the stoichiometry of the ion-exchange reactions of Cd and Ni with the organic carrier D2EHPA, neither in the value of the equilibrium parameters. The situation is even more complex when working with highly concentrated solutions, since D2EHPA has been reported to exist as a dimer in the organic phase and may form complex species with a metal acting as a dimer (Ferraro and Peppard, 1963; Biswass et al., 2000). The typical metal (Me^{2+}) complexation with n dimers, $\overline{(HX)_2}$, of D2EHPA could be described by the following equation, which also represents the back-extraction reaction:

$$Me^{2+} + n\overline{(HX)_2} \Leftrightarrow \overline{MeX_2(HX)_{2n-2}} + 2H^{+}. \qquad (26)$$

The equilibrium model and parameters of the Cd reaction with D2EHPA have been discussed in a previous work that reports a value of $n = 2$ and $K'_{EX(Cd)} = 1.82 \times 10^{-5}$ (Ortiz et al., 2001a). Since no reference to the equilibrium of systems with highly concentrated solutions had been found in the literature, some experimental runs were performed in a rotatory stirrer. The results approached predicted values with the calculated equilibrium constant.

In the case of Ni, the situation is even more complex, since the stoichiometric equations reported in the literature differ widely depending on the diluents used, on the aqueous-phase compositions, or on the extractant concentrations employed. Rao et al. (1986) and Juang (1993a) reported a stoichiometric coefficient of $n =$ 2 for the system Ni-D2EHPA; Matsuyama et al. (1987), and Golding and Barclay (1988), among others, mentioned a stoichiometric coefficient $n = 3$; Huang et al. (1989) reported two possibilities, $n = 2.5$ or $n = 3$. More recently Daiminger et al. (1996) supported a stoichiometry of 2.5. Besides, it is important to consider the fact that the reported experimental studies were carried out at considerably lower concentration values of both the metallic and organic components, thus neglecting the nonideal behavior of the liquid phases. Considering this situation and as a necessary step for the kinetic modeling of the separation of the Cd and Ni mixtures, a discrimination procedure of the equilibrium models corresponding to the back-extraction reactions was performed, starting with the models and parameters reported in the literature and considering the results previously reported for the extraction chemical reaction of Cd and D2EHPA (Ortiz et al., 2000b).

Under the experimental conditions, Ni was not extracted in the separation process, whereas both metals got concentrated in the BEX phase due to the initial loading of the organic phase.

In the multicomponent mixture the only unknown parameter under study was the equilibrium parameter of the back-extraction reaction releasing Ni to the aqueous BEX phase ($K'_{BEX(NiCd)}$).

Table 5 presents a summary of the equilibrium reactions that were proposed in order to describe the extraction of cadmium and the simultaneous back-extraction of cadmium and nickel.

The system of Eqs. 1 to 24 was integrated for all the reported equilibrium models using a commercial software pack-

Table 5. Extraction and Back-Extraction Reactions of Cd and Ni

Model	Extraction Reactions	Back-Extraction Reactions
A	$Cd^{+2} + 2(\overline{HX})_2 \Leftrightarrow \overline{CdX_2(HX)_2} + 2H^{+}$	$\overline{NiX_2(HX)_3} + 2H^{+} \Leftrightarrow Ni^{+2} + 2.5(\overline{HX})^2$ $\overline{CdX_2(HX)_2} + 2H^{+} \Leftrightarrow Cd^{+2} + 2(\overline{HX})_2$
B	$Cd^{+2} + \overline{NiX_2(HX)_3} \Leftrightarrow \overline{NiX_2CdX_2(HX)} + 2H^{+}$	$\overline{NiX_2CdX_2(HX)} + 2H^{+} \Leftrightarrow Cd^{+2} + \overline{NiX_2(HX)_3}$ $\overline{NiX_2(HX)_3} + 2H^{+} \Leftrightarrow Ni^{+2} + 2.5(\overline{HX})^2$
C	$Cd^{+2} + 2(\overline{HX})^2 \Leftrightarrow \overline{CdX_2(HX)_2} + 2H^{+}$	$\overline{CdX_2(HX)_2} + 2H^{+} \Leftrightarrow Cd^{+2} + 2(\overline{HX})_2$ $\overline{NiX_2CdX_2} + 2H^{+} \Leftrightarrow Cd^{+2} + \overline{NiX_2(HX)_2}$ $\overline{NiX_2CdX_2} + 2H^{+} \Leftrightarrow Ni^{+2} + \overline{CdX_2(HX)_2}$
D	$Cd^{+2} + 2(\overline{HX})_2 \Leftrightarrow \overline{CdX_2(HX)_2} + 2H^{+}$	$\overline{CdX_2(HX)_2} + 2H^{+} \Leftrightarrow Cd^{+2} + 2(\overline{HX})_2$ $\overline{NiX_2CdX_2} + 4H^{+} \Leftrightarrow Cd^{+2} + Ni^{+2} + 2(\overline{HX})_2$
E	$Cd^{+2} + 2(\overline{HX})_2 \Leftrightarrow \overline{CdX_2(HX)_2} + 2H^{+}$	$\overline{NiX_2CdX_2} + 4H^{+} \Leftrightarrow Cd^{+2} + Ni^{+2} + 2(\overline{HX})_2$

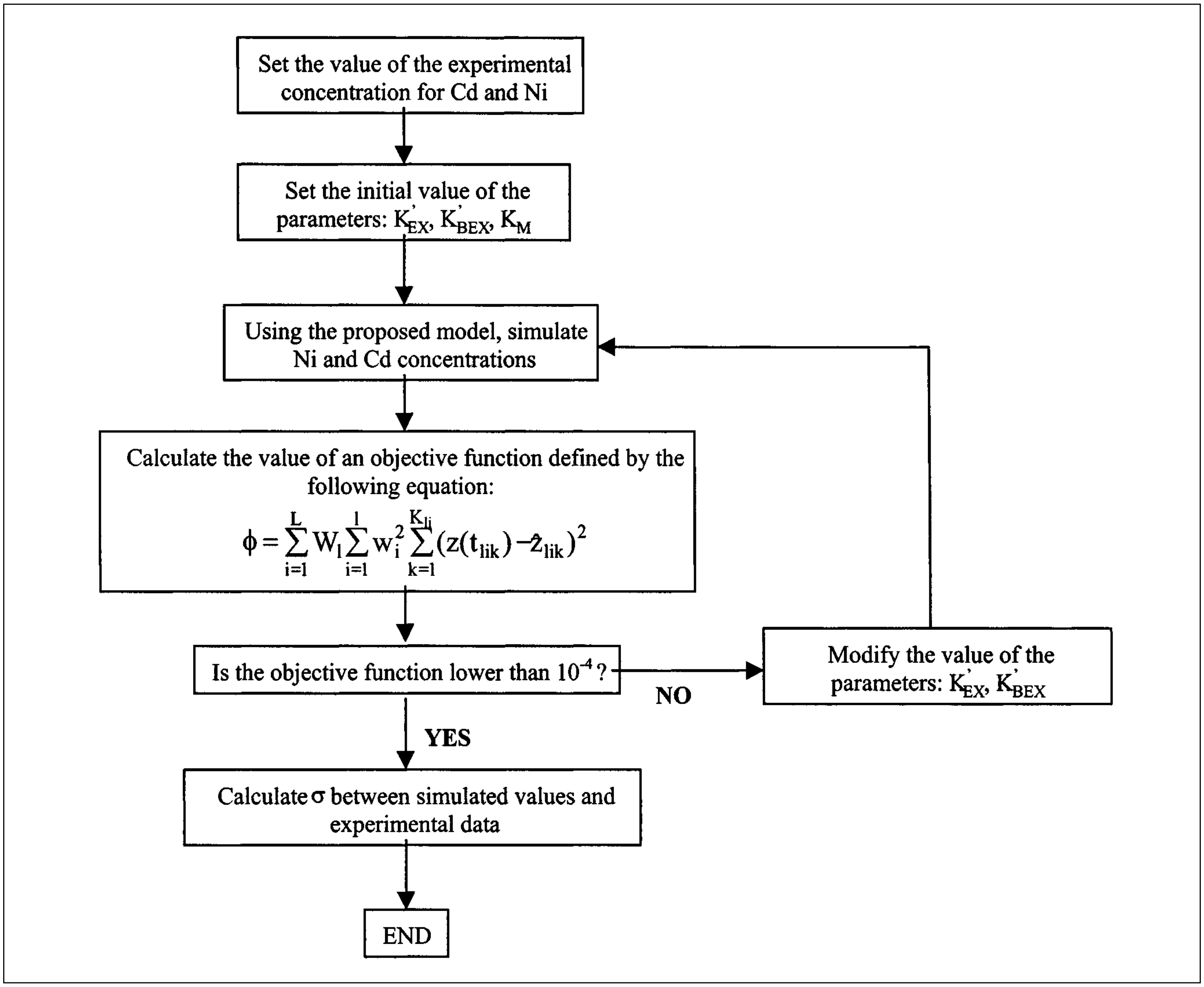

Figure 5. Flow diagram of the optimization procedure.

age called gPROMS (general PROces Modeling System). gPROMS is a general-purpose software applicable for modeling, simulation and optimization. gPROMS can be executed in connection with other tools such as gEST (general ESTimation), which is a package devoted to parameter estimation. Figure 5 shows the optimization procedure used in this work to estimate the optimum values of the parameters that could describe the kinetic behavior of the experimental data.

Table 6 shows the optimum value of the design parameters (K_m, K'_{EX}, K'_{BEX}) for both metals in each of the proposed equilibrium models together with the values of standard deviation, calculated according to the following equation:

$$\sigma=\sqrt{\frac{\Sigma\left[\left(C_{\exp}-C_{\mathrm{sim}}\right)/C_{\mathrm{sim}}\right]^2}{n-1}}\,. \tag{27}$$

Model E, which considers (1) the negligible extraction of nickel, (2) the formation of a mixed complex species in the organic phase between the extractant and both metals (Cd and Ni), during the initial loading of the organic phase, and (3) the existence of only one reaction responsible for the BEX process of Cd and Ni characterized by the corresponding equilibrium parameter, $K'_{\mathrm{BEX(NiCd)}}$, was selected as the best model since the standard deviation values were much lower ($<8\%$ in all cases) than the values obtained with the other models. A more detailed analysis of the differences among the equilibrium models is reported elsewhere (Ortiz et al., 2001b). Simulated data making use of the set of optimum values of the parameters, $K'_{\mathrm{EX(Cd)}}=1.82\times10^{-5}$, $K'_{\mathrm{BEX(NiCd)}}=8.8\times10^{-5}$ $\mathrm{m^3\cdot mol^{-1}}$, $K_m=1.57\times10^{-7}$ m/s, were calculated for all the experiments considered in this study. As a representative example, Figure 6 shows the comparison between experimental and simulated results corresponding to Exp. IV (see Table 2 for experimental conditions). Similar graphs were obtained for the rest of the experimental conditions.

Finally, parity graphs of the dimensionless results are shown in Figure 7 for EX and BEX of Exps. III and IV. Good

Table 6. Kinetic and Equilibrium Parameters and Standard Deviation Between Experimental and Simulated Data for the Proposed Models

			Exp. 3				Exp. 4			
			σ_{EX} (%)		σ_{BEX} (%)		σ_{EX} (%)		σ_{BEX} (%)	
Model	Known Parameters	Estimated Parameters	Cd	Ni	Cd	Ni	Cd	Ni	Cd	Ni
A	$K'_{EX(Cd)} = 1.82 \times 10^{-5}$ $K'_{BEX(Cd)} = 1/K'_{EX(Cd)}$ $K_m = 1.57 \times 10^{-7}$ m/s	$K'_{BEX(Ni)} = 0.6 \times 10^{1.5}$ $(mol/m^3)^{0.5}$	68	3.6	43	11.7	47	4.8	13.9	13.9
B	$K'_{BEX(Ni)} = 0.6$ $K_m = 1.57 \times 10^{-7}$ m/s	$K'_{BEX(Cd)} = 2 \times 10^{-8}$ (m^3/mol) $K'_{EX(Cd)} = 1/K'_{BEX(Cd)}$	18	3.6	47	18	19.8	4.8	34	16.4
C	$K'_{EX(Cd)} = 1.82 \times 10^{-5}$ $K'_{1\ BEX(Cd)} = 1/K'_{EX(Cd)}$	$K'_{BEX(Ni)} = 1.6 \times 10^{-4}$ (m^3/mol) $K'_{2BEX(Cd)} = K'_{BEX(Ni)}$ $K_m = 4.78 \times 10^{-8}$ m/s	26	3.6	24.3	17.2	27.2	4.8	4.9	7.9
D	$K_{EX(Cd)} = 1.82 \times 10^{-5}$ $K'_{BEX(Cd)} = 1/K'_{EX(Cd)}$ $K_m = 1.57 \times 10^{-7}$ m/s	$K'_{BEX(Ni\text{-}Cd)} = 6.87 \times 10^{-5}$ (m^3/mol)	4.3	2.8	12.2	10.6	6.4	4.8	12.8	10.4
E	$K'_{EX(Cd)} = 1.82 \times 10^{-5}$ $K_m = 1.57 \times 10^{-7}$	$K'_{BEX(Ni-Cd)} = 8.8 \times 10^{-5}$ (m^3/mol)	3.7	3.6	7	7.2	4.2	4.1	8.74	4.2

agreement between real and simulated data is observed, since in both processes more than 90% of the results of C_{sim} fall within the $C_{exp} \pm 10\%$ range.

Conclusions

This work reports the kinetic modeling of the separation of multicomponent metallic mixtures by nondispersive solvent extraction; the process also includes the back-extraction step for concentrating the separated metal and the regeneration of the organic phase. The kinetic model developed for systems under nonsteady state and based on the same fundamentals reported previously for the separation–concentration of one solute, consists of a set of coupled differential equations, solute mass balances of the fluid phases, that must be solved along with the equilibrium expressions of the chemical reactions between aqueous solutes and the organic extractant. Under the assumptions made in this work the model in its simplest form requires knowledge of three characteristic parameters, K_m, membrane mass-transport coefficient, and 2 equilibrium parameters representing the extraction and back-extraction reactions. The validity of the model has been checked against the kinetic results of the separation of Cd and Ni from high concentration solutions that simulated Ni/Cd batteries leaching solutions. After an analysis of the kinetic results obtained under conditions that favored the extraction of Cd against Ni ($pH_{ext} = 3.5$), and considering the parameters needed to describe the separation–concentration of Cd that was previously determined ($K'_{EX(Cd)} = 1.82 \times 10^{-5}$ and $K_m = 1.57 \times 10^{-7}$ m/s), the optimum value of the equilibrium parameter of the back-extraction reaction $K'_{BEX(NiCd)} = 8.8 \times 10^{-5}$ $m^3 \cdot mol^{-1}$ was obtained (model E in Table 5).

The potential of the model is high due to its simplicity. It also can be used to describe many separation systems.

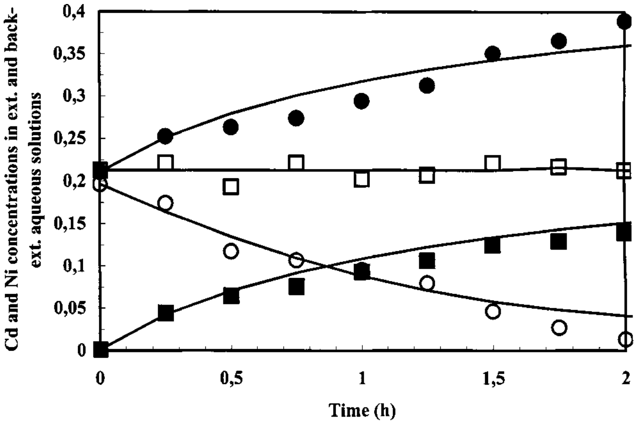

Figure 6. Experimental concentration of cadmium: (○) and nickel (□) in the extraction phase; cadmium (●) and nickel (■) in the back-extraction phase to Exp. IV.

(—) Simulated lines with $K'_{EX(cd)} = 1.82 \times 10^{-5}$, $K'_{BEX(NiCd)} = 8.8 \times 10^{-5}$ $m^3 \cdot mol^{-1}$, $K_m = 1.57 \times 10^{-7}$ m/s.

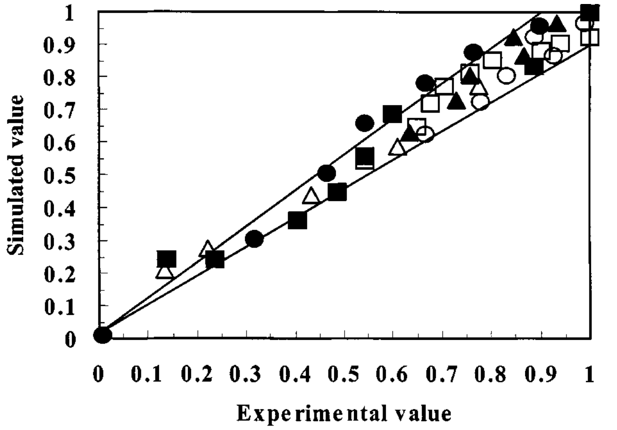

Figure 7. Parity graph.

Simulated solute concentration vs. experimental solute concentration. Cadmium in the extraction phase: Exp. III(△), Exp. IV(□). Cadmium in the back-extraction phase: Exp. III(▲), Exp. IV(■). Nickel in the back-extraction phase: Exp. III(○), Exp. IV(●).

Notation

a = activity, mol/m^3
C = solute concentration in the stirred tanks (feed, organic, and stripping), mol/m^3
C_{in} = inlet solute concentration to the stirred tanks (feed, organic, and stripping), mol/m^3
C_{out} = outlet solute concentration from the stirred tanks (feed, organic, and stripping), mol/m^3
C_{O_i} = solute concentration in the organic phase, mol/m^3
C_{OI} = interfacial solute concentration in the organic phase, mol/m^3
C_T = total carrier concentration, mol/m^3
F = flow rate of the fluid phases (feed, organic, and stripping), m^3/h
K_{EX} = extraction equilibrium constant defined in Eq. 5
K'_{EX} = extraction equilibrium constant defined in Eq. 7
K_{BEX} = back-extraction equilibrium constant defined in Eq. 15
K'_{BEX} = back-extraction equilibrium constant defined in Eq. 17
K_m = membrane mass-transfer coefficient in extraction and back-extraction modules, m/s
n_f = number of fibers
n = stoichiometric coefficient
r_f = inner radius of hollow fiber, m
t = time, h
V = tank volume (feed, organic, and stripping), m^3
v_A = linear velocity in the aqueous feed phase, m/h
v_S = linear velocity in the aqueous stripping phase, m/h
v_O = linear velocity in the organic phase, m/s
z = axial distance, m

Greek letters

γ = activity coefficient
σ = standard deviation

Subscripts

A = aqueous feed phase
i = metallic solute, cadmium or nickel
O = organic phase
S = back-extraction phase

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