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NOTE

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Abstract

A comparative study was conducted on the adsorptions of cobalt(II) and nickel(II) from aqueous ammonium nitrate solutions on a Levextrel resin containing acidic organophosphinate extractant, Cyanex 272, as an active component and on chelating resins containing phosphorus-based acidic functional groups. It was found that the Levextrel resin has much higher selectivity for cobalt(II) over nickel(II) then the chelating resins. The origins of the low selectivity of the chelating resins are qualitatively discussed.

INTRODUCTION

One of the most interesting features in the hydrometallurgy of cobalt and nickel has been the growth of commercial application of the solvent extraction technique for the separation of these metals. Two new cobalt/nickel extraction separation processes using acidic organophosphorus compounds as extractants have been developed and commercialized in South Africa and Japan (*1*).

Di-2-ethylhexylphosphoric acid (D2EHPA) has been employed as the selective extractant for cobalt over nickel by Matthey Rustenburg Refining Ltd. (MRR) in South Africa while Daihachi's PC-88A, 2-ethylhexyl 2-ethylhexylphosphonic acid, has been employed by Nippon Mining Co. in Japan. Recently, American Cyanamid Co. has developed a novel commercial extractant for cobalt/nickel separation, Cyanex 272, the active species of which is di(2,4,4′-trimethylpentyl) phosphinic acid. It provides a much higher separation factor of cobalt from nickel than D2EHPA and PC-88A.

In comparison with solvent extraction, the separation process using chelating resins has various advantages: applicability to the treatment of very dilute solutions, ease of liquid/solid phase separation associated with lack of serious problems such as crud formations and solvent losses into the aqueous phase frequently encountered in solvent extraction, ease of handling and simplicity of equipment by operating with packed columns, and so on. On the other hand, it also has various drawbacks: low selectivities, slow adsorption rates, low loading capacities of metals, and so on.

Solvent-impregnated resins and Levextrel resins bridge the gap between these two separation processes (*2–4*). These are resins containing metal extractants within their polymer matrixes and can be treated in the same manner with ion-exchange and chelating resins. The former resins are prepared by loading or soaking prefabricated polystylene resins with a liquid extractant together with diluents or wetting agents which may aid as modifiers. The extractant is fixed by adsorption according to the pore structure of the resin. On the other hand, the latter resins are macroporous styrene/divinylbenzene copolymers containing an extractant which has been added directly to the mixture of monomers during bead polymerization. The extractant is also retained in the resin structure in this case by adsorption rather than by chemical bonding.

In the present work the authors investigated the adsorption of nickel(II) and cobalt(II) in aqueous ammonium nitrate solutions on Levextrel resin containing about 150 kg/m^3 of Cyanex 272 as the active component, Levextrel 807 '84 Type Cyanex 272 (abbreviated Levextrel 807 '84 hereafter). We also investigated the adsorption on two new types of macroreticular chelating resins containing phosphorus-based acidic functional groups analogous to acidic organophosphorus extractants as shown in Fig. 1: RSP, a phosphinic acid cation-exchanger, and RCSP, a

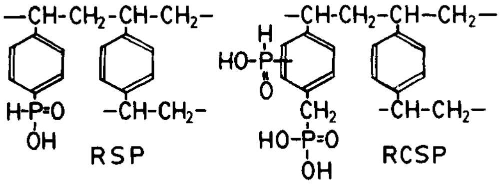

FIG. 1. Structures of RSP and RCSP resins. The amount of phosphinic acid groups is very small.

phosphonic acid cation-exchanger. These chelating resins were recently developed by Egawa et al. (5) for the purpose of recovering uranium from seawater.

The total ion-exchange capacities of Levextrel 807 '84, RSP, and RCSP are 1.17, 4.69, and 6.85 meq/g dry resin, respectively.

EXPERIMENTAL

All resins were dried in vacuum at room temperature to constant weight. All experiments were carried out batchwise.

In the adsorptions on RSP and RCSP, about 0.5 g of the resin was shaken with 0.03 dm^3 aqueous ammonium nitrate solution containing a small amount of nickel(II) or cobalt(II) in a glass-stoppered flask immersed in a water-bath incubator maintained at 303 K. Levextrel 807 '84 was shaken in a separating funnel using a Iwaki's type V-DN mechanical shaker installed in a thermostated air-bath maintained at 303 K since the specific gravity of this resin is less than 1; consequently, the resin particles were not dipped into the aqueous phase.

The initial metal concentrations were around 4.5×10^{-3} mol/dm^3. Aqueous solutions were prepared by dissolving reagent grade metal nitrates into 1 mol/dm^3 aqueous ammonium nitrate solution. pH ranged from 0.5 to 9 in the adsorptions on RSP and RCSP while it ranged from 3 to 9 in those on Levextrel 807 '84 by the addition of a small amount of nitric acid or ammonia. Equilibrium was attained within 4 h for all resins in the preliminary experiment.

After equilibration, the metal concentration in the aqueous phase was determined by titration with EDTA using the ammonium salt of purpuric acid diluted with potassium sulfate (MX reagent) as an indicator.

The amount of metal adsorbed on the resin, q, was calculated from the concentrations before and after equilibrium. The distribution ratio of metal, D, was calculated according to

$$D = (q/W)/(C_e/1000) \qquad (1)$$

where W and C_e denote the weight of the resin and the metal concentration in the aqueous phase at equilibrium, respectively.

RESULTS AND DISCUSSION

Figures 2, 3, and 4 illustrate the relation between the distribution ratio of cobalt(II) and nickel(II) and pH in the adsorptions on RSP, RCSP, and Levextrel 807 '84, respectively.

In all cases the adsorption of cobalt(II) takes place at a lower pH than that of nickel(II) as observed in solvent extraction with acidic organophosphorus compounds: organophosphoric, -phosphonic, and -phosphinic acids. This order is in agreement with the adsorption observed on the commercial phosphonic acid cation exchanger, Duolite C-63, by Persoz and Rosset (*6*).

The adsorptions on RSP and RCSP are almost analogous to each other as seen from Figs. 2 and 3, while that on Levextrel 807 '84 is quite different (Figs. 2, 3, and 4). In the adsorptions on RSP and RCSP, the distribution ratio of nickel(II) increases with increasing pH at low pH and, after passing through a maximum, decreases with increasing pH at high pH, while that of cobalt(II) continues to increase monotonously over the

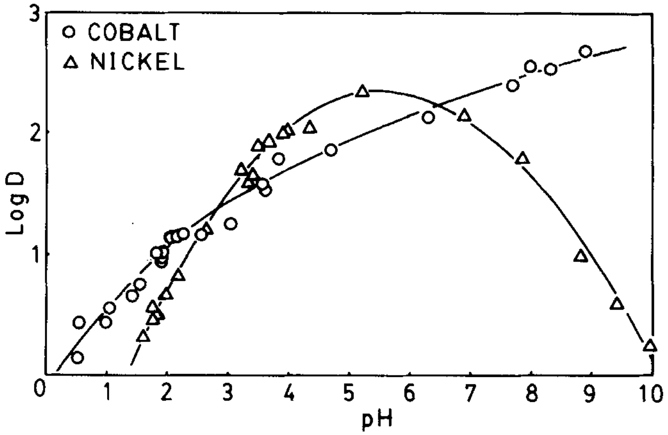

FIG. 2. Relation between the distribution ratios of cobalt(II) and nickel(II) and pH in the adsorption on RSP resin.

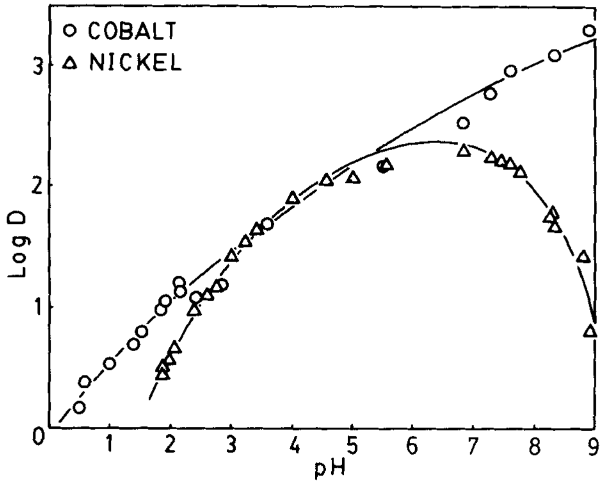

FIG. 3. Relation between the distribution ratio of cobalt(II) and nickel(II) and pH in the adsorption on RCSP resin.

whole pH. On the other hand, in the adsorption on Levextrel 807 '84, the distribution ratios of both metals increase with increasing pH at low pH and, after passing through a maximum, they decrease with increasing pH at high pH.

As seen from Figs. 2 and 3, the two curves representing the adsorptions of nickel(II) and cobalt(II) are close to each other at low pH, which suggests that RSP and RCSP resins provide only poor separation of these metals. In Fig. 4, however, the two curves have satisfactory separation, which suggests that Levextrel 807 '84 has excellent selectivity for cobalt(II) over nickel(II).

The shapes of the convex curves in Fig. 4 appear to be substantially different from those in Figs. 2 and 3. In Fig. 4 the plots lie on straight lines with slopes of 2 at low pH and on slopes of about −1 at high pH for the adsorption of cobalt(II) and of nickel(II).

Danesi et al. (*7*) reported that nickel(II) and cobalt(II) are extracted with various acidic organophosphorus reagents according to the following stoichiometric relation:

$$M^{2+} + (m + n)\overline{(HX)_2} \rightleftharpoons \overline{M(HX_2)_m \cdot 2n(HX)} + 2H^+, \qquad K_e \quad (2)$$

where $m = 2$ and $n = 0$ for cobalt(II), while $m = 2$ and $n = 1$ for nickel(II), and $\overline{(HX)_2}$ denotes the dimeric species of the acidic organophosphorus reagents.

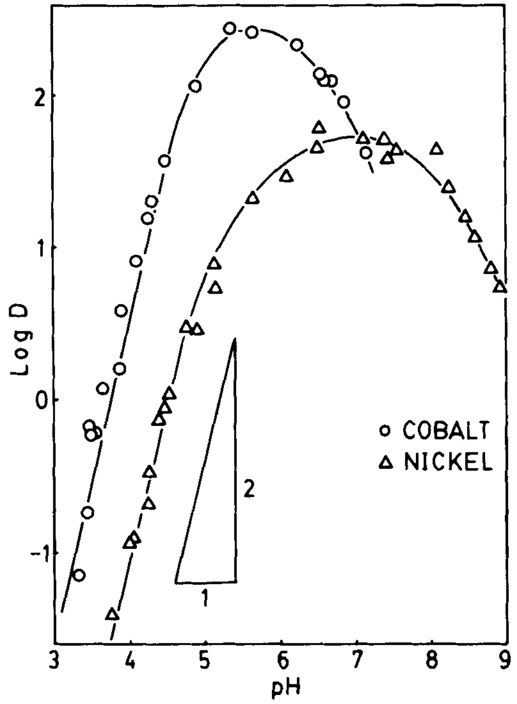

FIG. 4. Relation between the distribution ratio of cobalt(II) and nickel(II) and pH in the adsorption on Levextrel 807 '84 resin.

Provided that the extracting reagents can behave within the Levextrel resin in the same manner as in the organic solutions, the distribution ratio is expressed by Eq. (3) from the equilibrium relation of the extraction reaction described by Eq. (2):

$$D = \frac{1000}{W} \frac{K_e[M^{2+}][\overline{(HX)_2}]}{[H^+]^2 C_e} \tag{3}$$

In the aqueous solutions containing ammonia, the divalent metal ions giving rise to complexes with ammonia exist not only as free aqua-ions but also as ammine complexes:

$$M^{2+} + iNH_3 \rightleftharpoons M(NH_3)_i^{2+}, \qquad \beta_i \tag{4}$$

Consequently, the concentration of the free aqua-ion, $[M^{2+}]$, which participates in the extraction reaction is described by the total metal concentration in the aqueous phase, C_e, and the free ammonia concentration:

$$[\mathrm{M}^{2+}] = C_e \Big/ \left(1 + \sum_{i=1}^{6} \beta_i [\mathrm{NH}_3]^i\right) \tag{5}$$

Under the present experimental conditions, the concentrations of high ammine complexes, $\mathrm{M(NH_3)}_i^{2+}$ (i = 5 and 6), can be neglected compared with those of lower ammine complexes, $\mathrm{M(NH_3)}_i^{2+}$ (i = 0–4). Further, the concentration of free ammonia is correlated to that of hydrogen ion by Eq. (7) through the dissociation equilibrium of ammonium ion described by Eq. (6):

$$\mathrm{NH_4^+} \rightleftharpoons \mathrm{NH_3} + \mathrm{H^+}, \qquad K_A \tag{6}$$

$$[\mathrm{NH_3}] = K_A[\mathrm{NH_4^+}]/[\mathrm{H^+}] \tag{7}$$

Combination of Eqs. (5) and (7) gives Eq. (8) as the ultimate expression of $[\mathrm{M}^{2+}]$:

$$[\mathrm{M}^{2+}] = C_e \Big/ \left(1 + \sum_{i=1}^{4} \beta_i (K_A[\mathrm{NH_4^+}]/[\mathrm{H^+}])^i\right) \tag{8}$$

where $[\mathrm{NH_4^+}]$ = 1 mol/dm^3 in the present experiment.

Equations (3) and (8) are combined to give the ultimate expression for the relation between the distribution ratio and hydrogen ion concentration:

$$D = \frac{1000}{W} \frac{K_e[\overline{(\mathrm{HX})_2}]}{\left(1 + \sum_{i=1}^{4} \beta_i (K_A[\mathrm{NH_4^+}]/[\mathrm{H^+}])^i\right)[\mathrm{H^+}]^2} \tag{9}$$

At low pH the majority of the metal ions exist at free aqua-ions, and the distribution ratio is approximately expressed by

$$D \simeq \frac{1000}{W} \frac{K_e[\overline{(\mathrm{HX})_2}]}{[\mathrm{H^+}]^2} \tag{10}$$

Equation (10) can qualitatively interpret the linear relation with a slope of 2 as observed at low pH in Fig. 4. On the other hand, at high pH, Eq. (9) is approximated by

$$D \simeq \frac{1000}{W} \frac{K_e[\overline{(\mathrm{HX})_2}]}{\beta_j(K_A[\mathrm{NH}_4^+])^j[\mathrm{H}^+]^{2-j}} \tag{11}$$

where $j > 2$.

Equation (11) can also qualitatively interpret decreases of the distribution ratios with increasing pH as observed at high pH in Fig. 4.

However, it is apparent from Figs. 2 and 3 that, in adsorption on RSP or on RCSP resins or of nickel(II) or of cobalt(II), the plots appear to be lying on straight lines with slopes of less than 2 at low pH. These facts suggest that the charges of the metal ions (= +2) adsorbed on these resins are not only neutralized by the acidic functional groups of the chelating resins but are partly neutralized by the counteranions in the aqueous phase and, in addition, these metal ions are coordinated by several molecules of water and ammonia as schematically shown in Fig. 5. This is inferred to be due to the fact that the functional groups fixed to the polymer chains cannot always come to the favorable positions to form complexes that are electrically neutralized and coordinately saturated. This is reflected in the low selectivities of the chelating resins and in the differences of the distribution curves between chelating resins and Levextrel resins as observed in Figs. 2, 3, and 4. In the adsorptions on Levextrel resins or solvent-impregnated resins, metal ions are electrically neutralized and coordinately saturated by the molecules of the extracting reagent which can unrestrictedly move through the spaces between the reticulation within a polymer bead. Consequently, the excellent selectivity of solvent extraction reagents is maintained in these resins.

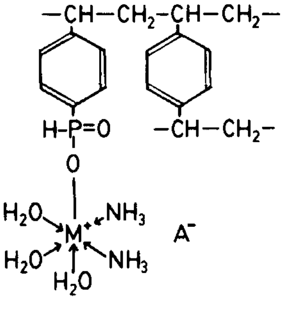

FIG. 5. Probable structure of the metal complex with RSP resin.

SYMBOLS

C_e	equilibrium metal concentration in the aqueous phase (mol/dm^3)
D	distribution ratio (cm^3/g)
K_A	dissociation constant of ammonium ion (mol/dm^3)
K_e	equilibrium constant of the reaction described by Eq. (2) ((mol/dm^3)$^{2-m-n}$)
q	amount of metal adsorbed on the resin (mol)
W	weight of resin (g)
β_i	stability constant of ith ammine complex ((mol/dm^3)$^{-i}$)
[ ]	concentration (mol/dm^3)
overline	organic phase

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