

# Separation of Cobalt and Nickel Ions in Lithium Nitrate Solutions by Solvent Extraction and Liquid Membrane with HEHEHP Kerosene Solution

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The separation of cobalt(II) and nickel(II) ions in lithium nitrate solutions with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) dissolved in kerosene has been studied by solvent extraction and liquid membrane at  $25.0 \pm 0.1^\circ\text{C}$ . The distribution ratios of each metal increased with an increase in the HEHEHP concentration in the organic phase and the pH value in the aqueous solution. However, the distribution ratio was independent of the metal ion concentration at constant pH and HEHEHP concentration. The equilibrium constants of cobalt and nickel are found to be  $5.76 \times 10^{-6}$  and  $5.66 \times 10^{-7} \text{ m}^3 \text{ kmol}^{-1}$ , respectively. The permeabilities of cobalt(II) and nickel(II) are found to be dependent on the stirring rate, the pH value of the feed solutions, the metal ion concentrations in the feed solutions and on the carrier concentration in the supported liquid membrane. The experimental data also show that the separation factor increases on increasing the stirring rate, the pH value of the feed solution and the concentration of metal ions in the feed solution. However, the separation factor decreases with the concentration of HEHEHP in the organic phase.

The application of the solvent extraction process to metallurgical processing has increased over the last two decades, especially for the recovery of metals from dilute solutions. The separation of cobalt and nickel from aqueous solutions is difficult owing to the similar chemical nature of the two metals. Various solvent extraction reagents and processes have been proposed for the recovery and separation of cobalt and nickel ions in aqueous solution.<sup>1,2</sup>

The 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (abbreviated as HEHEHP or simply HA) is an organophosphorus acid extractant with the commercial trademark "PC-88A" for the Daihachi Chemical Industry Co., Ltd. and Nippon Mining, and patented as SME418 (or RD577) by the American Shell Chemical Co., Ltd. Recently, this reagent has been found to have a greater selectivity for cobalt over nickel than HDEHP, the well known extractant for cobalt–nickel separation.<sup>3–6</sup> It has also been studied for copper–zinc separation<sup>7</sup> and the separation of rare-earth elements.<sup>8</sup>

Liquid membranes containing extractants have been used for the concentration and separation of metal ions.<sup>9–13</sup> This simultaneous extraction and stripping operation is very attractive because metal ions can move from low- to high-concentration solutions.<sup>9,13</sup>

The potential advantages of supported liquid membranes (SLM) over traditional separation techniques are a lower

capital and operating cost, low energy and extractant consumption, high selectivity, high concentration factors and high fluxes relative to solid membranes. Because of these advantages, a supported liquid membrane contactor may be very useful for the recovery of metals such as copper,<sup>14–17</sup> cobalt,<sup>17–20</sup> nickel,<sup>17–20</sup> zinc,<sup>17,21</sup> uranium<sup>22,23</sup> and rare earths<sup>18,24</sup> from dilute solutions.

In this work, a systematic study of the extraction equilibrium of cobalt and nickel with HEHEHP was undertaken. Secondly, the permeation of cobalt and nickel through a supported liquid membrane containing HEHEHP as a carrier was studied. By combining the data for solvent extraction and supported liquid membrane experiments, it was possible to obtain values of the mass transfer coefficient of cobalt and nickel in the feed solution and of the metal–HEHEHP complexes in the supported liquid membrane. Finally, the separation factors of cobalt and nickel in this system were obtained. The nomenclature used is given at the end of the paper.

## Experimental

*Reagents and membranes.* The 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester used in this work was the product of the Daihachi Chemical Ind. Co., Ltd., Osaka, Japan, having a purity of 95%. It was further purified by precipitation as a copper complex from ether and an acetone solution, and was then dissolved in ether and a 4 kmol m<sup>-3</sup> sulfuric acid solution, following the procedure of Par-

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tridge and Jensen.<sup>25</sup> Kerosene used as a diluent was supplied by Union Chemical Works Ltd., Taiwan, Republic of China, and was washed twice with a 1/5 volume of 98% H<sub>2</sub>SO<sub>4</sub>, and then washed with distilled water until it reached neutral pH.<sup>26</sup> The other inorganic chemicals were supplied by Hayashi Pure Chemical Ind., Ltd., Osaka, Japan, and were of analytically pure reagent grade.

The porous membranes used were Durapore membranes made of poly(vinylidene difluoride) (PVDF), a product of the Millipore Co., U.S.A. These membranes are hydrophobic, with a mean pore size of 0.45 μm, a typical porosity of 70%, and a nominal mean thickness of 125 μm. The thickness of the membranes was measured, and only those with a thickness deviation of <5 μm were used in the experiments.

**Preparation of the supported liquid membrane.** The membrane solution was prepared by dissolving HEHEHP in kerosene saturated with the metal-free aqueous feed solution. A supported liquid membrane was prepared by putting Durapore membranes in an evacuated bottle for 5 min and then introducing the membrane solution into the bottle. The membrane was rapidly and completely impregnated with the membrane solution. After 10 min the vacuum was released.<sup>14</sup> The prepared liquid membranes were immersed in the membrane solution when not in use.

**Determination of equilibrium distribution ratio.** The distribution ratios of metal ions between the organic phase and the aqueous phase,  $D_M$ , were measured at 25.0 ± 0.1 °C by the following procedures.

Organic solutions of volume 20 ml containing 0.005–0.20 kmol m<sup>-3</sup> monomeric form of HEHEHP dissolved in kerosene, and equal volumes of aqueous solutions containing 1.0 kmol m<sup>-3</sup> (M<sup>2+</sup>, Li<sup>+</sup>)NO<sub>3</sub> were mixed in the glass flasks and shaken with a mechanical shaker for at least 30 min until equilibrium was attained. The concentrations of cobalt and nickel ions in the initial aqueous solutions ranged from 0.0017 to 0.034 kmol m<sup>-3</sup>. The two phases were separated after they had been allowed to settle for 4 h in a thermostat at 25.0 ± 0.1 °C.

After phase separation, the equilibrium hydrogen ion concentration of the aqueous solution was measured with a pH meter. The concentrations of cobalt and nickel ions were determined with an IL-551 atomic absorption spectrophotometer (Instrumentation Laboratory Inc., U.S.A.) at the wavelengths of 240.7 and 232.0 nm, respectively. The cobalt and nickel in the organic phases were stripped with 4 kmol m<sup>-3</sup> nitric acid, and the metal concentrations in the acidic solutions were analyzed with the atomic absorption spectrophotometer.

**Measurement of permeation rates.** The permeation experiments of metal ions through SLM were performed at 25 °C using apparatus similar to a diaphragm cell, as shown in Fig. 1. Chamber A (220 ml) of the cell was filled with metal nitrate feed solution, and chamber B (220 ml) with nitric

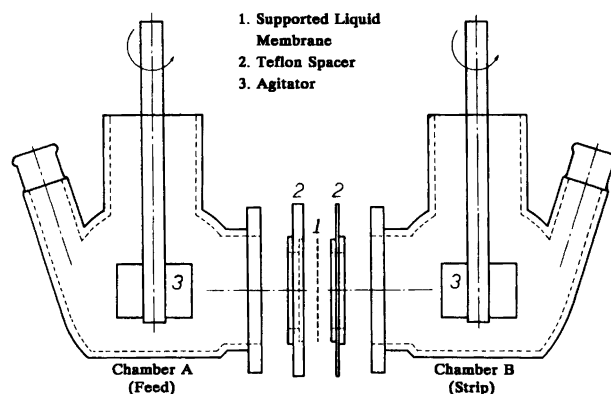


Fig. 1. Experimental apparatus of supported liquid membrane system.

acid stripping solution. A membrane impregnated with HEHEHP carrier was clamped between chambers A and B. The effective membrane area was 9.62 cm<sup>2</sup>. The pH values of the feed solution in chamber A were controlled with a pH meter (TOA HM-20S) and a pH stat (model HSM-10A, TOA Electronic Ltd., Japan) using LiOH solution. When a steady state was reached, 5 ml samples were taken from chamber B at preset intervals, and the same volume of fresh nitric acid stripping solution was added to maintain the original volume. The concentrations of cobalt and nickel were analyzed with the atomic absorption spectrophotometer, and corrections due to sample replacement were made.

## Results and discussion

**Liquid-liquid extraction.** Assuming that cobalt and nickel cations are extracted as an  $m$ -merized complex of composition  $(MA_2 \cdot n(HA)_2)_m$  into the slightly loaded organic phase, the extraction equilibria of Co(II) and Ni(II) with HEHEHP can be represented by the general eqns. (1) and (2), where  $K_{ex}$  is the stoichiometric equilibrium



$$K_{ex} = \frac{\overline{[(MA_2 \cdot n(HA)_2)_m]} [H^+]^{2m}}{[M^{2+}]^m [\overline{H_2A_2}]^{m(n+1)}} \quad (2)$$

constant,  $M$  is cobalt or nickel,  $\overline{H_2A_2}$  represents the dimeric form of HEHEHP in kerosene, and the bar indicates the species in the organic phase.

The distribution ratio of cobalt or nickel is given by eqn. (3). Combining eqns. (2) and (3), we can obtain the

$$D_M = \frac{\overline{[M(II)]}}{[M(II)]} = \frac{m \overline{[(MA_2 \cdot n(HA)_2)_m]}}{[M^{2+}]} \quad (3)$$

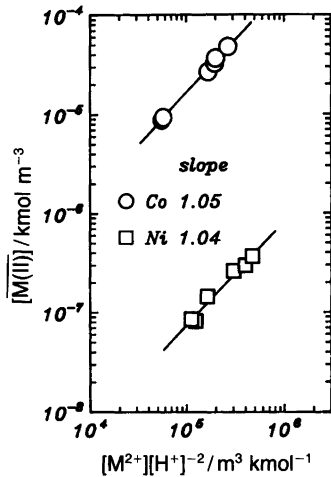


Fig. 2. Plots of  $\log \overline{[M(II)]}$  vs.  $\log [M^{2+}][H^+]^{-2}$  at equilibrium for cobalt and nickel at 25 °C. Aqueous phase:  $1.0 \text{ kmol m}^{-3}$   $(\text{Li,H})\text{NO}_3$ ,  $[\text{Co}^{2+}]_0 = [\text{Ni}^{2+}]_0 = 0.0017\text{--}0.034 \text{ kmol m}^{-3}$ . Organic phase:  $[\text{H}_2\text{A}_2] = 0.005 \text{ kmol m}^{-3}$ .

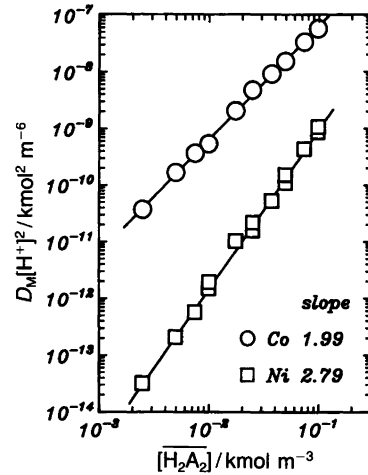


Fig. 3. Plots of  $\log D_M[H^+]^2$  vs.  $\log \overline{[\text{H}_2\text{A}_2]}$  at equilibrium for various HEHEHP concentrations in kerosene at 25 °C. Aqueous phase:  $1.0 \text{ kmol m}^{-3}$   $(\text{Li,H})\text{NO}_3$ ,  $[\text{Co}^{2+}]_0 = [\text{Ni}^{2+}]_0 = 0.017\text{--}0.034 \text{ kmol m}^{-3}$ . Organic phase:  $[\text{H}_2\text{A}_2] = 0.0025\text{--}0.1 \text{ kmol m}^{-3}$ .

concentration of metal-HEHEHP complex in the organic phase as eqn. (4), in which  $[\overline{\text{H}_2\text{A}_2}]^{m(n+1)}$  is approximately

$$\overline{[M(II)]} = \frac{mK_{\text{ex}} [M^{2+}]^m [\overline{\text{H}_2\text{A}_2}]^{m(n+1)}}{[H^+]^{2m}} \quad (4)$$

kept constant at constant concentrations of HEHEHP and low distribution ratios. Thus the slope of a plot of  $\log \overline{[M(II)]}$  vs.  $\log [M^{2+}][H^+]^{-2}$  gives the degree of aggregation of the metal-HEHEHP complex in the organic phase,  $m$ .

The experimental results are plotted in Fig. 2 for  $0.005 \text{ kmol m}^{-3}$   $[\overline{\text{H}_2\text{A}_2}]$  and  $1.0 \text{ kmol m}^{-3}$   $(\text{Li,H})\text{NO}_3$  at 25 °C. Fig. 2 indicates a linear relationship with unit slope ( $m = 1$ ) for both cobalt and nickel ions, i.e. there are no polymers formed in the complexes of Co-HEHEHP and Ni-HEHEHP. Thus, eqn. (4) can be simplified to eqn. (5),

$$D_M[H^+]^2 = K_{\text{ex}}[\overline{\text{H}_2\text{A}_2}]^{n+1} \quad (5)$$

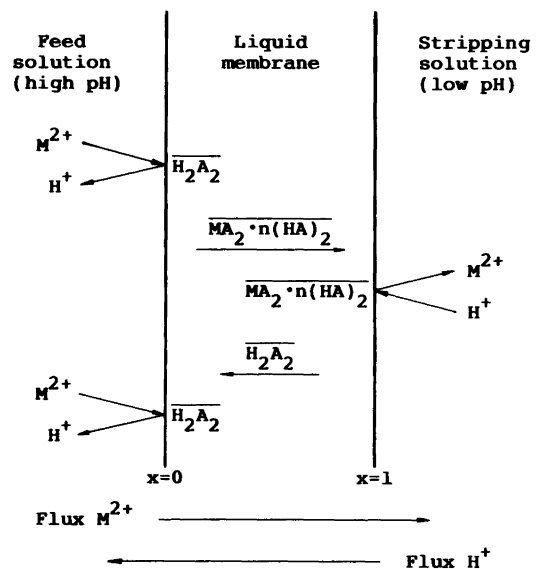
from which a plot of  $\log D_M[H^+]^2$  vs.  $\log \overline{[\text{H}_2\text{A}_2]}$  gives a straight line with a slope of  $n+1$ . The experimental results are shown in Fig. 3 for various HEHEHP concentrations and  $1.0 \text{ kmol m}^{-3}$   $(\text{Li,H})\text{NO}_3$  at 25 °C. For cobalt, a straight line of slope 1.99 is obtained, i.e.  $n=1$ , indicating that the composition is  $\overline{\text{CoA}_2 \cdot (\text{HA})_2}$ . For nickel, a straight line of slope 2.79 is obtained, i.e.  $n=2$ , indicating that the complex is  $\overline{\text{NiA}_2 \cdot 2(\text{HA})_2}$ .

Therefore, the extraction stoichiometries of cobalt ion and nickel ion with HEHEHP can be represented by reactions (6) and (7), respectively. Also, the extraction

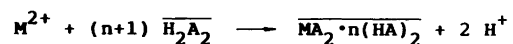


equilibrium constants of cobalt and nickel can be represented by reactions (8) and (9), respectively.

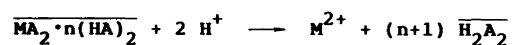
$$K_{\text{ex,Co}} = \frac{[\overline{\text{CoA}_2 \cdot (\text{HA})_2}][H^+]^2}{[\text{Co}^{2+}][\overline{\text{H}_2\text{A}_2}]^2} \quad (8)$$



Extraction ( $x=0$ ):



Stripping ( $x=1$ ):



( $n=1$ , for  $\text{M}=\text{Co}$ ;  $n=2$ , for  $\text{M}=\text{Ni}$ )

Fig. 4. Transport of metal ion through a supported liquid membrane containing HEHEHP as mobile carrier.

$$K_{\text{ex,Ni}} = \frac{[\text{NiA}_2 \cdot 2(\text{HA})_2][\text{H}^+]^2}{[\text{Ni}^{2+}][\text{H}_2\text{A}_2]^3} \quad (9)$$

To evaluate extraction equilibrium constants, the concentration of  $\text{H}_2\text{A}_2$  is obtained from eqns. (6) and (7) and is assumed equal to one-half the formal concentration, since alkyl phosphonic acids in aliphatic diluents exist as dimers.<sup>8</sup> From the experimental data, the extraction equilibrium constants for cobalt and nickel between HEHEHP dissolved in kerosene and  $1.0 \text{ kmol m}^{-3}$  (Li,H)NO<sub>3</sub> solution at 25°C are calculated to be  $K_{\text{ex,Co}} = 5.76 \times 10^{-6} \text{ m}^3 \text{ kmol}^{-1}$  and  $K_{\text{ex,Ni}} = 5.66 \times 10^{-7} \text{ m}^3 \text{ kmol}^{-1}$ , respectively.

From eqn. (5) we can obtain equations for the distribution ratios of cobalt and nickel between HEHEHP dissolved in kerosene and  $1.0 \text{ kmol m}^{-3}$  (Li,H)NO<sub>3</sub> solution at 25°C as eqns. (10) and (11), respectively.

$$\log D_{\text{Co}} = -5.24 + 2\text{pH} + 2 \log [\overline{\text{H}_2\text{A}_2}] \quad (10)$$

$$\log D_{\text{Ni}} = -6.25 + 2\text{pH} + 3 \log [\overline{\text{H}_2\text{A}_2}] \quad (11)$$

**Supported liquid membrane permeation.** The transport of cobalt and nickel through a supported liquid membrane containing HEHEHP as mobile carrier is illustrated in Fig. 4. The mechanism of mass transfer may be described with the following five consecutive steps. (1) Diffusion of metal ions in the feed solution through the aqueous film towards the interface  $x = 0$ . (2) Reaction of metal ions with the carrier at the interface  $x = 0$ , as well as complexation of the metal ion and dimeric HEHEHP. (3) Diffusion of the complex through the membrane towards the interface  $x = 1$ . (4) Reaction of the complex with the mineral acid at the interface  $x = 1$ , with the metal ions being stripped back into the stripping solution. This step regenerates the HEHEHP carrier, which then diffuses back to the interface  $x = 0$ . (5) Diffusion of metal ions at the interface  $x = 1$  towards the bulk stripping solution.

Such a process is called "counter-transport",<sup>18,21</sup> because it is able to transport the metal ion from a low-concentration solution to a higher concentration solution. The driving force of counter-transport is the concentration gradient of the hydrogen ion. In the above process, steps (1) and (5) are aqueous film diffusion resistance, steps (2) and (4) are boundary resistance or chemical reaction, while step (3) is membrane diffusion resistance.

The concentration profile of metal ions permeating through the supported liquid membrane is schematically shown in Fig. 5. It is assumed that linear concentration gradients exist throughout the system. The resistances of hydrogen ion diffusion in both aqueous solutions and of metal ions in the stripping solution are assumed to be negligible.<sup>13,16,18,19,21-23</sup>

At quasi-steady state and for a linear concentration gradient throughout the aqueous film and membrane, the permeation rates of the metal can be reduced to a simpli-

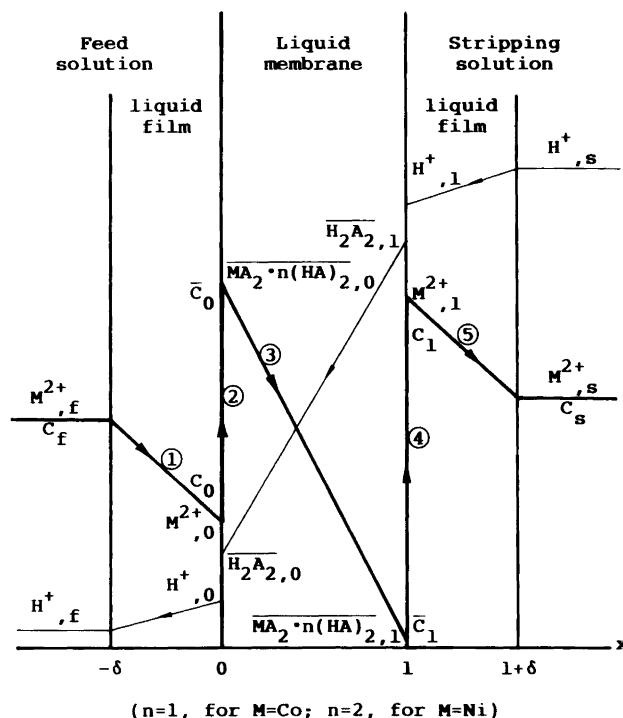


Fig. 5. Concentration profile of metal ion ( $\text{M}^{2+}$ ) permeating through liquid membrane containing HEHEHP as mobile carrier.

fied version of Fick's first diffusion law as eqns. (12) and (13), where  $k_a = D_a/\delta_a$  and  $\bar{k}_c = \bar{D}_c/\delta_m$ .  $D_a$ ,  $\delta_a$  and  $k_a$  are the

$$J_a = k_a \{ [\text{M(II)}]_f - [\text{M(II)}]_0 \} \quad (12)$$

$$\bar{J}_c = \bar{k}_c \{ [\overline{\text{M(II)}}]_0 - [\overline{\text{M(II)}}]_1 \} \quad (13)$$

diffusion coefficient, aqueous film thickness and mass transfer coefficient of metal in the aqueous solution.  $\bar{D}_c$ ,  $\delta_m$  and  $\bar{k}_c$  are the diffusion coefficient, membrane thickness and mass transfer coefficient of the metal-HEHEHP complex in the membrane.  $J_a$  is the mass flux of the metal species in the aqueous film,  $\bar{J}_c$  is the permeation rate of metal-HEHEHP complex through the membrane,  $[\text{M(II)}]$  is the concentration of metal in the aqueous solution,  $[\overline{\text{M(II)}}]$  is the concentration of metal-HEHEHP complex,  $\text{MA}_2 \cdot n(\text{HA})_2$ , in the membrane phase. The subscripts f, 0 and 1 refer to the positions shown in Fig. 5.

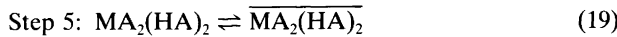
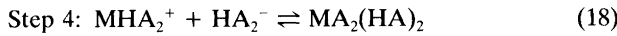
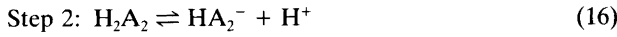
The concentration of metal-HEHEHP complex at the stripping side interface,  $[\overline{\text{M(II)}}]_1$ , is negligible compared to the feed solution side interface for the early stages of experiment.<sup>15,16,18-20</sup> Thus, eqn. (13) becomes eqn. (14).

$$\bar{J}_c = \bar{k}_c [\overline{\text{M(II)}}]_0 \quad (14)$$

Dreisinger *et al.*<sup>27</sup> studied the kinetics of cobalt and nickel extraction using HEHEHP dissolved in heptane. They presented a reaction model which involves (1) the partitioning of the extractant to the aqueous phase, (2) the

dissociation of the acidic extractant, (3) the addition of the first and second ligands in the aqueous phase and (4) the partitioning of the metal-extractant species into the organic phase.

The reaction mechanism could be listed as eqns. (15)–(19),



where step 3 is rate-determining step and  $k_R$  is rate constant.

Therefore, the formation rate of metal–HEHEHP complex at the interface ( $x = 0$ ) can be written as eqns. (20),

$$J_r = \frac{k_1[\text{M(II)}]_0[\overline{\text{H}_2\text{A}_2}]}{[\text{H}^+]} - \frac{k_{-1}[\overline{\text{M(II)}}]_0[\text{H}^+]}{[\text{H}_2\text{A}_2]^n} \quad (20)$$

where  $k_1$  and  $k_{-1}$  are the forward and backward rate constants of the interfacial reactions described in eqns (6) and (7).

When the quasi-steady state is reached, i.e.  $J = J_a = \bar{J}_c = J_r$ , the permeation rate of metal ion can be derived as eqn. (21). In the membrane transport process, the perme-

$$J = \frac{[\text{M(II)}]_f}{\frac{1}{k_a} + \frac{[\text{H}^+]}{k_1[\overline{\text{H}_2\text{A}_2}]} + \frac{[\text{H}^+]^2}{\bar{k}_c K_{\text{ex}}[\overline{\text{H}_2\text{A}_2}]^{n+1}}} \quad (21)$$

ability,  $P$ , is defined as eqn. (22). Substituting eqn. (21)

$$P = \frac{J}{[\text{M(II)}]_f} \quad (22)$$

into eqn. (22), the total resistance of permeation can be expressed as eqn. (23), where the three terms on the

$$\frac{1}{P} = \frac{1}{k_a} + \frac{[\text{H}^+]}{k_1[\overline{\text{H}_2\text{A}_2}]} + \frac{[\text{H}^+]^2}{\bar{k}_c K_{\text{ex}}[\overline{\text{H}_2\text{A}_2}]^{n+1}} \quad (23)$$

right-hand side represent the aqueous film resistance, interfacial chemical resistance and membrane diffusion resistance, respectively.

When the interfacial chemical reactions are very fast (local equilibrium), i.e.  $k_1[\overline{\text{H}_2\text{A}_2}]/[\text{H}^+] \gg k_a$  and  $k_1[\overline{\text{H}_2\text{A}_2}]/[\text{H}^+] \gg \bar{k}_c K_{\text{ex}}[\overline{\text{H}_2\text{A}_2}]^{n+1}/[\text{H}^+]^2$ , eqn. (23) can be further simplified to eqn. (24). The change of metal con-

$$P = \frac{k_a \bar{k}_c D_M}{k_a + \bar{k}_c D_M} \quad (24)$$

centration with time in the feed solution can be expressed as eqn. (25). Substituting eqn. (22) into eqn. (25), and then

$$-V \frac{d[\text{M(II)}]_f}{dt} = AJ \quad (25)$$

integrating eqn. (25), we obtain eqn. (26), where  $[\text{M(II)}]_f^0$

$$\ln \frac{[\text{M(II)}]_f}{[\text{M(II)}]_f^0} = -\frac{A}{V} Pt \quad (26)$$

and  $[\text{M(II)}]_f$  are the metal concentrations at time 0 and  $t$ , respectively,  $A$  is the effective area of liquid membrane and  $V$  is the volume of feed solution.

The membrane separation factor of cobalt and nickel in the supported liquid membrane is defined as the ratio of the permeation coefficients of cobalt and nickel [eqn. (27)].

$$\alpha_{\text{SLM}} = \frac{P_{\text{Co}}}{P_{\text{Ni}}} \quad (27)$$

Fig. 6 is a plot of  $\ln ([\text{M(II)}]_f/[\text{M(II)}]_f^0)$  vs.  $t$ . The straight lines have the slopes of  $-PA/V$ , where  $A = 9.62 \times 10^{-4} \text{ m}^2$  and  $V = 2.20 \times 10^{-4} \text{ m}^3$  in this experiment, and then the permeation coefficients are evaluated.

The influences of stirring rate of the aqueous feed solutions on the permeabilities of cobalt and nickel are shown in Fig. 7. The results indicate that the thickness of the aqueous boundary diffusion layers reaches its minimum value when the stirring rate is higher than 250 r.p.m. Also, the permeability of cobalt increases when the stirring rate is higher than 450 r.p.m. However, the system is unstable above this rate. Therefore, 300 r.p.m. is selected as the optimal operation condition in the majority of cases.

During counter-transport the pH value of the feed solution will decrease and causes the permeation rate to decrease. For the sake of keeping the permeation rate constant, a pH stat is applied to control the pH of the feed solution. The dependence of permeabilities on the acidity of the aqueous feed solution is shown in Fig. 8. It indicates that the permeation coefficients increase on increasing the pH of the aqueous feed solution. The permeation coefficient of the cobalt ion increases faster than that of the nickel ion with increasing solution pH. Therefore, the membrane separation factor increases with increasing pH, as can be seen from Fig. 8.

Fig. 9 shows the effect of carrier concentration in the supported liquid membrane on the permeabilities of cobalt and nickel. In general, the permeabilities increase as the carrier concentration increases. Since the permeation coefficient of the cobalt ion is greater than that of the nickel ion

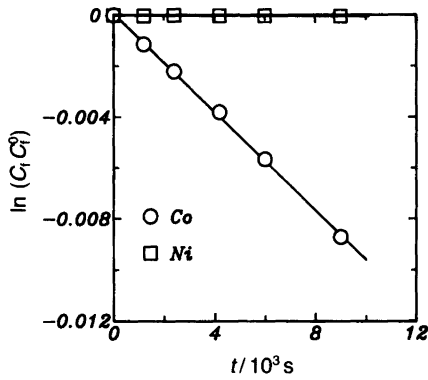


Fig. 6. Plots of  $\ln [M(II)]/[M(II)]_0$  vs. time. Feed:  $[Co^{2+}]_i = [Ni^{2+}]_i = 0.034 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.864 \text{ kmol m}^{-3}$ , pH 5.0, 300 r.p.m. SLM:  $[H_2A_2] = 0.05 \text{ kmol m}^{-3}$ . Strip: 0.1 N  $HNO_3$  + 0.9 M  $LiNO_3$ , 300 r.p.m.

at the same carrier concentration, the permeation coefficient of the nickel ion increases faster than that of the cobalt ion with increasing carrier concentration. Therefore, the membrane separation factors decrease with increasing carrier concentration, as shown in Fig. 10.

All experimental data of permeation coefficients shown in Figs. 8 and 9 are plotted as a function of the distribution ratio,  $D_M$ , in Fig. 11. The  $D_M$  values are calculated from eqns. (10) and (11). As can be seen from eqn. (24), two asymptotic straight lines of slopes 1 and 0 can be obtained for small and large  $D_M$  values, respectively, i.e. we have eqns. (28) and (29). From Fig. 11 and eqns. (28) and (29),

$$\log P = \log D_M + \log \bar{k}_c \quad \text{for small } D_M \quad (28)$$

$$\log P = \log k_a \quad \text{for large } D_M \quad (29)$$

the following mass transfer parameters are then evaluated:  $\bar{k}_{c,Co} = 3.00 \times 10^{-9} \text{ m s}^{-1}$ ,  $\bar{k}_{c,Ni} = 1.10 \times 10^{-9} \text{ m s}^{-1}$ ,  $k_{a,Co} = 1.75 \times 10^{-7} \text{ m s}^{-1}$  and  $k_{a,Ni} = 2.00 \times 10^{-7} \text{ m s}^{-1}$ .

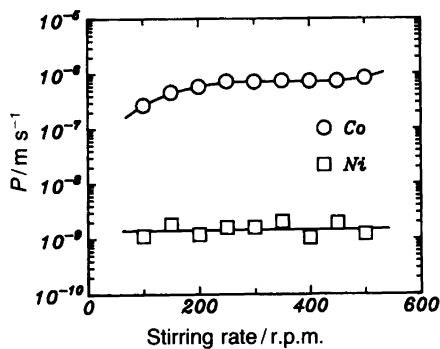


Fig. 7. Effect of stirring rate on permeation coefficient. Feed:  $[Co^{2+}]_i = [Ni^{2+}]_i = 0.034 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.864 \text{ kmol m}^{-3}$ , pH 5.0. SLM:  $[H_2A_2] = 0.05 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ .

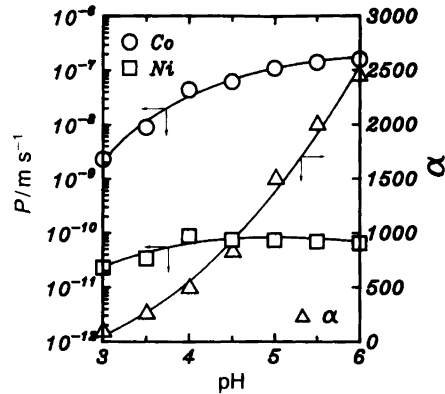


Fig. 8. Effect of hydrogen ion concentration in the aqueous feed solution on the permeation rate and separation factor. Feed:  $[Co^{2+}]_i = [Ni^{2+}]_i = 0.034 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.9864 \text{ kmol m}^{-3}$ , 300 r.p.m. SLM:  $[H_2A_2] = 0.05 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ , 300 r.p.m.

When the interfacial chemical reactions are slow, eqn. (23) cannot be simplified to eqn. (24). In this case, we can obtain  $k_a$ ,  $k_i$  and  $\bar{k}_c$  from eqn. (23) by computer calculation using an optimization technique. The results of such a computation are summarized in Table 1. The values of  $k_a$  and  $\bar{k}_c$  are nearly the same as those evaluated from Fig. 11. Since the membrane thickness is  $\delta_m = 1.25 \times 10^{-4} \text{ m}$ , the values of  $\bar{D}_{c,Co}$  and  $\bar{D}_{c,Ni}$  can be calculated from  $\bar{D}_c = \bar{k}_c \delta_m$ . The diffusion coefficients of cobalt and nickel in sulfate solutions can be obtained from the literature;<sup>27</sup> the aqueous film thickness,  $\delta_a$ , can be calculated from  $\delta_a = D_a/k_a$ .

Substituting the mass transfer coefficients given above into eqn. (23), the permeation coefficients of cobalt and nickel can be expressed as eqns. (30) and (31). Then,

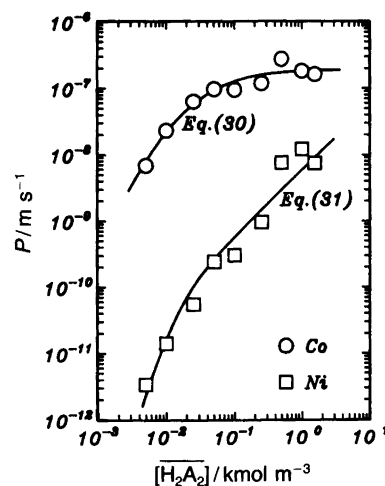


Fig. 9. Effect of the HEHEHP concentration in the membrane solution on the permeation rate. Feed:  $[Co^{2+}]_i = [Ni^{2+}]_i = 0.034 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.864 \text{ kmol m}^{-3}$ , pH 5.0, 300 r.p.m. SLM:  $[H_2A_2] = 0.005\text{--}1.55 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ , 300 r.p.m.

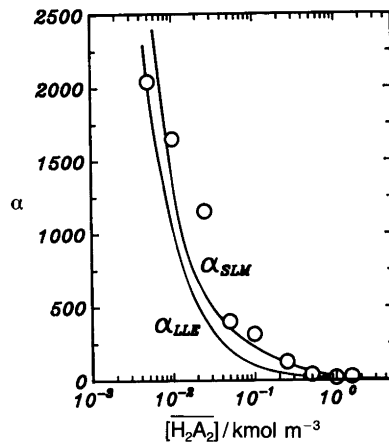


Fig. 10. Effect of the HEHEHP concentration in the membrane solution on the separation factor. Feed:  $[Co^{2+}]_f = [Ni^{2+}]_f = 0.034 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.864 \text{ kmol m}^{-3}$ , pH 5.0, 300 r.p.m. SLM:  $[H_2A_2] = 0.005\text{--}1.55 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ , 300 r.p.m.

$$P_{Co} = \frac{[\overline{H_2A_2}]^2}{2.19 \times 10^{10} [H^+] [\overline{H_2A_2}] + 2.08 \times 10^{13} [H^+]^2} (5.44 \times 10^6 [\overline{H_2A_2}]^2 + 2.19 \times 10^{10} [H^+] [\overline{H_2A_2}] + 2.08 \times 10^{13} [H^+]^2) \quad (30)$$

$$P_{Ni} = \frac{[\overline{H_2A_2}]^3}{1.72 \times 10^{13} [H^+] [\overline{H_2A_2}]^2 + 4.67 \times 10^{14} [H^+]^2} (3.04 \times 10^6 [\overline{H_2A_2}]^3 + 1.72 \times 10^{13} [H^+] [\overline{H_2A_2}]^2 + 4.67 \times 10^{14} [H^+]^2) \quad (31)$$

substituting eqns. (30) and (31) into eqn. (27), the membrane separation factor of cobalt and nickel can be expressed as eqn. (32).

$$\alpha_{SLM} = \frac{22.5}{[\overline{H_2A_2}]} \times \left( \frac{1 + 0.0368 [\overline{H_2A_2}]^2 [H^+]^{-1} + 6.50 \times 10^{-9} [\overline{H_2A_2}]^3 [H^+]^{-2}}{1 + 1.05 \times 10^{-3} [\overline{H_2A_2}] [H^+]^{-1} + 2.62 \times 10^{-7} [\overline{H_2A_2}]^2 [H^+]^{-2}} \right) \quad (32)$$

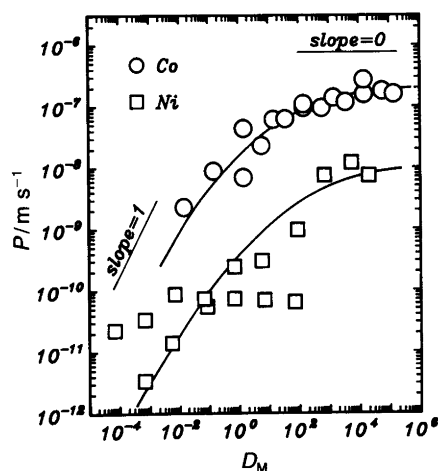


Fig. 11. Relationship between the permeability coefficients and distribution ratios.

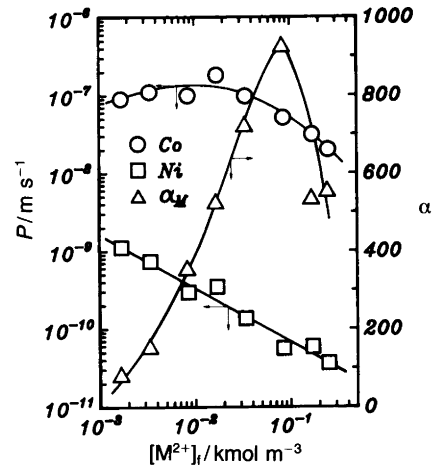


Fig. 12. Effect of the concentration of metal ions in the membrane solution on the permeation rate and separation factor. Feed:  $[Co^{2+}]_f = [Ni^{2+}]_f = 0.0017\text{--}0.25 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.9932\text{--}0 \text{ kmol m}^{-3}$ , pH 5.0, 300 r.p.m. SLM:  $[H_2A_2] = 0.05 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ , 300 r.p.m.

By defining the liquid-liquid extraction separation factor,  $\alpha_{LLE}$ , as the ratio of the distribution ratios of cobalt and nickel, and then introducing the eqns. (10) and (11), one obtains eqn. (33).

$$\alpha_{LLE} = \frac{D_{Co}}{D_{Ni}} = \frac{10.2}{[\overline{H_2A_2}]} \quad (33)$$

The effect of carrier concentration,  $[\overline{H_2A_2}]$ , on  $\alpha_{SLM}$  and  $\alpha_{LLE}$  calculated from eqns. (30) and (31) is also shown in Fig. 10. It can be seen that  $\alpha_{SLM}$  is better fitted than  $\alpha_{LLE}$ .

Fig. 12 shows the effect of metal ion concentration in the supported liquid membrane on the permeabilities of cobalt

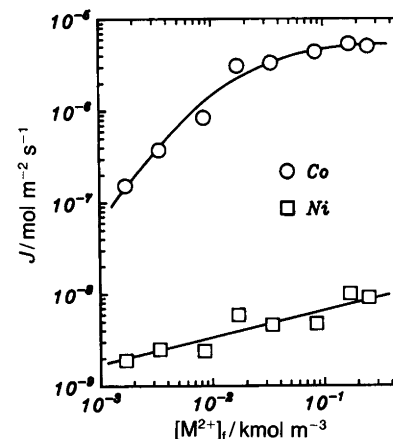


Fig. 13. Effect of the concentration of metal ions in the membrane solution on the flux rate. Feed:  $[Co^{2+}]_f = [Ni^{2+}]_f = 0.0017\text{--}0.25 \text{ kmol m}^{-3}$ ,  $[LiNO_3] = 0.9932\text{--}0 \text{ kmol m}^{-3}$ , pH 5.0, 300 r.p.m. SLM:  $[H_2A_2] = 0.05 \text{ kmol m}^{-3}$ . Strip: 1.0 N  $HNO_3$ , 300 r.p.m.

Table 1. Measured mass transfer and diffusion coefficients.

Coefficients	Cobalt(II)	Nickel(II)
$k_a/m\ s^{-1}$	$1.84 \times 10^{-7}$	$3.29 \times 10^{-7}$
$k_f/s^{-1}$	$4.57 \times 10^{-11}$	$5.82 \times 10^{-14}$
$\bar{k}_c/m\ s^{-1}$	$8.36 \times 10^{-9}$	$3.78 \times 10^{-9}$
$\bar{D}_c/m^2\ s^{-1}$	$1.05 \times 10^{-12}$	$4.73 \times 10^{-13}$
$D_a/m^2\ s^{-1\ a}$	$8.25 \times 10^{-10}$	$8.73 \times 10^{-10}$
$\delta_a/m$	$4.48 \times 10^{-3}$	$2.65 \times 10^{-3}$

<sup>a</sup>Taken from Ref. 27 in sulfate solution.

and nickel. It can be seen that the permeabilities decrease as the metal ion concentration increases. By curve fitting, we can obtain eqns. (34) and (35). Substituting these into

$$P'_{Co} = 1.19 \times 10^{-7} \exp(-7.42[Co^{2+}]_f) \quad (34)$$

$$P'_{Ni} = 1.42 \times 10^{-11} [Ni^{2+}]_f^{-0.687} \quad (35)$$

eqn. (27), the membrane separation factor can be expressed as eqn. (36).

$$\alpha_M = 8380 \frac{\exp(-7.42[Co^{2+}]_f)}{[Ni^{2+}]_f^{-0.687}} \quad (36)$$

The permeation coefficient of cobalt ion is greater than that of nickel ion at the same concentration of metal ions, and the permeation coefficient of the nickel ion decreases faster than that of the cobalt ion with increasing concentration of metal ions. Therefore, the membrane separation factors increase with increasing concentration of metal ions, as shown in Fig. 12. Fig. 13 indicates the effect of concentration of metal ions on the flux rate. It shows that the fluxes of cobalt and nickel increase with increasing concentration of metal ions.

## Conclusions

The distribution ratios of cobalt and nickel between lithium nitrate solutions and HEHEHP dissolved in kerosene have been studied at  $25.0 \pm 0.1$  °C. As a result, the distribution ratios of cobalt and nickel are dependent on the concentration of HEHEHP in kerosene and the pH value of the aqueous solution. However, the separation factor for liquid-liquid extraction,  $\alpha_{LLE}$ , is inversely proportional to the concentration of HEHEHP in kerosene, and independent of the pH value of the aqueous solution.

When supported liquid membranes are used to separate cobalt and nickel, a mass transfer model that takes into account aqueous film diffusion, interfacial chemical reaction and membrane diffusion has been derived to describe the permeation of metal ions. The permeabilities of cobalt and nickel increase as both the HEHEHP concentration and the pH value of the aqueous feed solution increase. The membrane separation factor,  $\alpha_{SLM}$ , depends on the

concentration of HEHEHP as well as on the pH value of the aqueous feed solution. Also, mass transfer parameters which describe the membrane transport process are obtained.

Alternatively, on increasing the metal ion concentration of the aqueous solution, the permeation coefficients of cobalt and nickel decrease. However, the membrane separation factor,  $\alpha_M$ , first increases and finally falls.

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## Nomenclature

- $A$ : area of liquid membrane, in  $m^2$   
 $D_M$ : distribution ratio of metal,  $M$   
 $D_a$ : diffusion coefficient of the metal in the aqueous feed solution, in  $m^2\ s^{-1}$   
 $\bar{D}_c$ : diffusion coefficient of the metal-HEHEHP complex in the supported liquid membrane, in  $m^2\ s^{-1}$   
 $J$ : mass flux of metal species, in  $kmol\ m^{-2}\ s^{-1}$   
 $K_{ex}$ : extraction equilibrium constant  
 $k_f, k_{-f}$ : interfacial reaction rate constants  
 $k_a$ : mass transfer coefficient in the aqueous film, in  $m\ s^{-1}$   
 $\bar{k}_c$ : mass transfer coefficient in the supported liquid membrane, in  $m\ s^{-1}$   
 $k_R$ : rate constant, in  $kmol\ m^{-3}\ s^{-1}$   
 $M(II)$ : cobalt or nickel species  
 $m, n$ : stoichiometric coefficients  
 $P$ : permeability, in  $m\ s^{-1}$   
 $t$ : reaction time, in  $s$   
 $V$ : volume of aqueous feed solution,  $m^3$   
 $[ ]$ : concentration of the species in brackets, in  $kmol\ m^{-3}$

## Greek letters

- $\alpha$ : separation factor  
 $\delta_a$ : film thickness in the aqueous feed solution, in  $m$   
 $\delta_m$ : thickness of supported liquid membrane, in  $m$

## Superscripts

- 0: initial concentration  
 $\bar{\quad}$ : property or concentration in the membrane or organic phase

## Subscripts

- $a$ : aqueous feed solution  
 $c$ : metal-HEHEHP complex  
 $f, 0, 1, s$ : indices corresponding to positions shown in Fig. 5  
 $LLE$ : liquid-liquid extraction  
 $M$ : metal ion  
 $SLM$ : supported liquid membrane



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