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Separation of Cobalt from a Nickel-Hydrometallurgical Effluent Using an Emulsion Liquid Membrane

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ABSTRACT

The mechanism of cobalt extraction by a tri-alkyl-amine hydrochloride (TAAHCl) was studied. Based on extraction solution chemistry, a mathematical expression was derived to identify metal transfer mechanisms. Both experimental results and theoretical consideration identified $CoCl_4^{2-}$ anions as the most favorable species for ion exchange with chloride anions in protonated TAAHCl. A new emulsion liquid membrane (ELM) system using TAAHCl as carriers was tested for

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the separation of cobalt from a nickel hydrometallurgical waste effluent. The effect of complex agent addition, carrier concentration, and acidity of the internal and external aqueous phases on cobalt extraction efficiency was investigated. Under optimum conditions, the enrichment of cobalt with a recovery rate of 99.8% was obtained by a one-stage process. The treated effluent contained mainly nickel, which is suitable for further nickel recovery, while the cobalt in the separated internal phase can be recovered as a value added by-product.

Key Words: Wastewater treatment; Tri-alkyl-amine hydrochloride; Cobalt; Nickel; Emulsion liquid membrane.

INTRODUCTION

A large volume of effluent or wastewater is generated in any hydrometallurgical operation. In general, the effluent contains a substantial amount of heavy metal ions. Taking a nickel hydrometallurgical process as an example, the effluent contains typically 6.0 g/dm^3 cobalt(II) and 4.0 g/dm^3 nickel(II) ions, along with a small amount of ferric(II), copper(II), lead (II), and chromium(II) ions. This kind of effluent cannot be discharged or recycled without proper treatment to remove these heavy metal ions. At this level of cobalt and nickel ions, there are some economic incentives to recover these metals while minimizing environmental consequences of discharging the waste effluent of hydrometallurgical operations. The separation of cobalt and nickel has been studied extensively and early studies have led to the development of many treatment technologies, including chemical precipitation,[1] ion exchange,[2] flotation,[3] and solvent extraction.[4–9] Although these technologies have been found to be satisfactory in treating industrial effluents containing a high level of metal ions, they have had rather limited applications to treating wastewater of a complex nature from hydrometallurgical processes. One common feature of the wastewater is extremely large volume at a metal ion concentration above the permitted level for safe discharge, but lower than the level suitable for direct recovery. Treating this kind of wastewater with the existing technologies incurs a high operating cost and inherits a low separation/removal efficiency.

Emulsion liquid membrane (ELM) technology, developed in 1968,[10] has been considered as an emerging separation and purification technology. In a typical ELM technology, extraction and stripping processes of desired species are combined into a single stage operation through a (water in oil) in water, i.e., W/O/W three-phase dispersion system. In this case, the extractant is contained in oil phase, which serves as a membrane and encapsulates the stripping aqueous phase. ELM technology has been examined extensively for potential applications to treating industrial effluents and wastewater.[11−17] The separation of cobalt from nickel by ELM technology, for example, has been reported in a number of cases.[18−21] The typical carriers contained in organic membranes vary from phosphoric acid to primary and quarterly amines. Although these carriers are effective for extracting/separating nonchloride bound metal ions, the separation efficiency of metal ions in a chloride-containing system was found to be unsatisfactory.[22] The low separation efficiency has been attributed to a weak binding between carriers and metal ions complexed with chlorides. To separate cobalt from nickel in a chloride-containing hydrometallurgical system, a more effective extractant needs to be used. In this study, TAAHCl was tested as a carrier for a synthetic industrial effluent from a nickel-hydrometallurgical process. The extraction behavior and mechanism of cobalt(II) by TAAHCl in hydrochloric acid solutions were first investigated. The basic knowledge was extended to construct an ELM with TAAHCl as carrier, which was tested to enrich cobalt(II) from the effluent of an electrolyte purification unit of nickel. Using this approach, the treated wastewater containing nickel could be recycled back to the electrolysis unit of nickel hydrometallurgy for further nickel recovery. This approach represents a modern concept of wastewater treatment that considers not only protection of environment, but also optimal utilization of natural resources. It has great social, economical, and environmental benefits.

EXPERIMENTAL

Reagents

Tri-alkyl-amine, $(CH_3\text{-}(CH_2)_{6-10}\text{-}CH_2)_3N$ was purchased from Guangzhou Chemical Reagent Company (China) and was used as mobile carriers. A polyamine with an average (number mean) molecular weight of 9150, designated as LMA, was synthesized in our laboratory and used as emulsifiers for water in oil (W/O) emulsion.[23] Commercial kerosene with a boiling point range of 200 to 400°C was treated with concentrated sulfuric acid (analytical grade) and neutralized with a $NaHCO_3$ solution before it was used as the organic phase of a membrane. A synthetic wastewater of similar chemical composition as in a nickel hydrometallurgy plant was prepared to contain 6.0 g/dm^3 cobalt(II) and 4.0 g/dm^3 nickel(II). Other chemicals were of reagent grade. Unless otherwise stated, all the solutions were prepared with deionized water and the experiments were performed at ambient temperature (ca. 25°C in Guangzhou).

Emulsion Preparation

The membrane phase was prepared by dissolving tri-alkyl-amine in the sulphonated kerosene. The resultant organic solution was treated with 3.0 mol/dm^3 hydrochloric acid solution, which converted tri-alkyl-amine to tri-alkyl-amine hydrochloride (TAAHCl). The surfactant LMA was then dissolved in the organic solution. A given volume of the prepared organic solution was transferred into a 250-mL polyethylene vial. Under the mild agitation, 1.0 mol/dm^3 hydrochloric acid solution was added into the vial. The mixture was then emulsified by a glass impeller rotating at 2000 rpm for 15 minutes, which resulted in a W/O emulsion of milky appearance.

Mass Transferring and Separation

The freshly prepared emulsion was dispersed in the synthetic feed solution at a given volume ratio. The mixture was agitated by a variable speed mixer equipped with a turbine-type Teflon impeller of 55-mm diameter and 15-mm width in a glass beaker of 100-mm inner diameter and 135-mm height. The mixing speed was fixed at 200 rpm. After mixing for a given period of time, a given volume of sample was taken and allowed to cream for 5 minutes. The separated external aqueous phase was then collected for chemical analysis.

De-emulsification

At the end of each experiment, the spent emulsion was phase-separated from the mixture by 5-minute creaming. To separate organic membrane phase from the internal aqueous phase, the separated (W/O) emulsion was demulsified by an EC-2 type electrostatic emulsion breaker, constructed in our laboratory. The recovered membrane phase was tested for re-emulsification, while the separated internal aqueous phase was collected for chemical analysis.

Liquid–Liquid Extraction

The screening of suitable experimental conditions for ELM study was accomplished by conventional liquid–liquid extraction experiments. In this case, 20 cm^3 of the organic phase containing different amount of TAAHCl without emulsifier addition was mixed with 20 cm^3 of the aqueous feed solutions. After shaking for 30 minutes at 25°C, the mixture was kept still for 5 to 10 minutes, during which, phase separation occurred. The aqueous phase was then collect for chemical analysis.

Analysis

The concentration of cobalt and nickel in aqueous phases was determined by EDTA complex titration and UV-visible spectrophotometer. In the volumetric EDTA titration for high concentration Co^{2+} and Ni^{2+} solutions, murexide was used as the indicator. At low Co^{2+} and Ni^{2+} concentrations, the accuracy of the volumetric EDTA titration was found unsatisfactory. In this case, a UV-visible spectroscopic method was used. It was found that the complex of Co^{2+} with 1-nitroso-2-naphthol exhibited a maximum absorbance at 317 nm. The complex of Ni^{2+} with diacetyldioxime showed a maximum absorbance at 465 nm. The concentrations of Co^{2+} and Ni^{2+} were, therefore, determined spectroscopically at these two wavelengths with 1-nitroso-2-naphthol and diacetyldioxime as the complex agents, respectively. The concentration of chloride ions, on the other hand, was determined by silver nitrate titration. The acidity was determined by acid–base titration. The analysis was duplicated for each sample and the experimental error was found to be within ±4%. The extraction/separation efficiency was evaluated using distribution coefficient (D) defined as:

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{1}$$

where $[M]_{org}$ and $[M]_{aq}$ are metal ion concentrations in organic and aqueous phases, respectively. The transfer ratio (T), on the other hand, can be calculated from metal ion concentrations in aqueous phase before (C_o) and after (C_t) contacting an EML for a given period of time t, using:

$$T = \frac{C_o - C_t}{C_o} \bullet 100\% \tag{2}$$

EXTRACTION CHEMISTRY OF COBALT

It is known that the type and concentration of carriers, properties of stripping phases and application conditions play a vital role in determining the success of ELM technology. It is often more complicated and time consuming to study these parameters using ELM technology directly. Use of a corresponding liquid–liquid extraction system could often serve as a good model system for studying the extraction fundamentals. In the current system, tri-alkyl-amine [TAA, $(CH_3\text{-}(CH_2)_{6-10}\text{-}CH_2)_3N$] is dissolved in kerosene and used as carriers/extractant for cobalt. By contacting TAA kerosene solution with 3.0 mol/dm^3 hydrochloric acid solution, TAA is converted to $(CH_3\text{-}(CH_2)_{6-10}\text{-}CH_2)_3NHCl$ (TAAHCl), which is considered to form complexes with many metal chloride complex anions.[24] The TAAHCl-metal chloride complexes are highly soluble in organic solvents, e.g., kerosene, but practically insoluble in water. Based on this characteristics, the metal ions that form complex anions with chloride ions in aqueous solutions are anticipated to be extracted by this kind of carrier. A suitable extraction system for a given set of metal ions can be designed to improve separation selectivity and efficiency. It is well established that Co^{2+}, Cu^{2+}, Fe^{2+}, and Zn^{2+} cations complex readily with chloride ions to form complex anions in aqueous solutions; while Ni^{2+} has little affinity with chloride ions. Therefore, the separation of cobalt(II) and other divalent metal ions from nickel(II) is favorable in hydrochloric acid solutions by solvent–solvent extraction using tri-alkyl-amine hydrochloride as an extractant. The extraction separation of these metal ions from aqueous phase to organic phase that contains TAAHCl has been reported[25] and simple ion-exchange of MCl_4^{2-} with Cl^- in TAAHCl has been proposed to be the extraction mechanism. However, metal ion complexation is a complex solution system, and a variety of complex species are present, with the distribution changing with aqueous solution chemistry, such as solution pH. It is, therefore, necessary to consider all possible equilibria of anionic species present in the system to have a more realistic representation of solvent–solvent or ELM extraction systems.

In an aqueous solution of our concern, cobalt undergoes various reactions as shown in Table 1. From these solution equibria, it is evident that both $CoCl_4^{2-}$ and $HCoCl_4^-$ can be extracted by anion exchange with Cl^- in TAAHCl. In the case of liquid–liquid extraction using TAAHCl as the extractant, the ion exchange reactions are summarized also in Table 1. Considering all the reactions described in Table 1, the distribution coefficient given by Eq. (1) can be written as:

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{[HCoCl_4^- TAAH^+] + [CoCl_4^- (TAAH^+)_2]}{[Co^{2+}] + [HCoCl_4^-] + [CoCl_4^{2-}] + [H_2CoCl_4]} \qquad (3)$$

Table 1. Pertained solution chemical reactions in aqueous and oil phases encountered in a cobalt liquid–liquid extraction system using TAAHCl as extractant.

Number	Reaction	K$_i$
1	$Co^{2+} + 4Cl^- = CoCl_4^{2-}$	$\frac{[CoCl_4^{2-}]}{[Co^{2+}][Cl^-]^4}$
2	$CoCl_4^{2-} + H^+ = HCoCl_4^-$	$\frac{[HCoCl_4^-]}{[CoCl_4^{2-}][H^+]}$
3	$HCoCl_4^- + H^+ = H_2CoCl_4^0$	$\frac{[H_2CoCl_4]}{[HCoCl_4^-][H^+]}$
4	$HCoCl_4^-(aq) + TAAHCl(o)$ $= HCoCl_4^- TAAH^+(o) + Cl^-(aq)$	$\frac{[HCoCl_4^- TAAH^+][Cl^-]}{[HCoCl_4^-][TAAHCl]}$
5	$CoCl_4^{2-}(aq) + 2TAAHCl(o)$ $= CoCl_4^{2-}(TAAH^+)_2(o) + 2Cl^-(aq)$	$\frac{[CoCl_4^{2-}(TAAH^+)_2][Cl^-]^2}{[CoCl_4^{2-}][TAAHCl]^2}$

Since cobalt complexes readily with chloride ions, the cobalt ions in chloride aqueous solutions are mainly in the complex form and $[Co^{2+}]_{aq}$ can be considered negligible. The extent of $CoCl_4^{2-}$ protonation to form neutral H_2CoCl_4 can also be considered insignificant unless extremely acidic aqueous solution is involved. By dropping out these two species in Eq. (3), one obtains:

$$D = \frac{[HCoCl_4^- TAAH^+] + [CoCl_4^{2-}(TAAH^+)_2]}{[HCoCl_4^-] + [CoCl_4^{2-}]} \tag{4}$$

Considering reactions (4) and (5) in Table 1, one obtains:

$$\frac{K_4}{K_5} = \frac{[HCoCl_4^- TAAH^+][CoCl_4^{2-}][TAAHCl]}{[HCoCl_4^-][CoCl_4^{2-}(TAAH^+)_2][Cl^-]} \tag{5}$$

For the convenience of discussion, let us define $n = \frac{[HCoCl_4^- TAAH^+]}{[CoCl_4^{2-}(TAAH^+)_2]}$. Substituting Eq. (5) and applying K$_2$ in Table 1 to the definition n result in:

$$n = \frac{K_2K_4[H^+][Cl^-]}{K_5[TAAHCl]} \tag{6}$$

Similarly, replacing relevant terms in Eq. (4) with K$_2$ and definition n, one obtains:

$$\begin{aligned} D &= \frac{1+n}{1+K_2[H^+]} \, \frac{CoCl_4^{2-}(TAAH^+)_2]}{[CoCl_4^{2-}]} \\ &= \frac{1+n}{1+K_2[H^+]} \, \frac{K_5[TAAHCl]^2}{[Cl^-]^2} \end{aligned} \tag{7}$$

At a given hydrochloride concentration, one can take partial differential with respect to [TAAHCl] after applying a normal logarithm to Eq. (7) which results in:

$$\frac{\partial \log D}{\partial \log[TAAHCl]} = 1 + \frac{1}{1+n} \tag{8}$$

From Eq. (8), a straight line is anticipated when plotting log D vs log[TAAHCl] and its slope is given by $1 + \frac{1}{1+n}$. By best fitting the experimental data to the double logarithm plot, the value of n can be obtained from the slope. Based on the definition of n, it is clear that n has to be greater than or equal to zero, which translates to a slope range between 1 and 2. It is interesting to note that any variations of n values with the experimental conditions of liquid–liquid extraction would provide a useful indication with respect to extraction mechanism, which is discussed as follows.

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

From the solution reactions given in Table 1, it is evident that the solution species distribution is highly dependent on hydrochloric acid concentration, which changes concentrations of both hydrogen and chloride ions. It is, therefore, anticipated that changing hydrochloric acid concentration would change liquid–liquid extraction performance. The distribution coefficients of cobalt and nickel in kerosene containing 1 mol/L TAAHCl obtained in liquid–liquid extraction tests are shown in Fig. 1. As shown in this figure, the nickel ion exhibited a negligible extraction by the organic phase over the HCl acid concentration range studied. At HCl acid concentration below 5 mol/L, cobalt also showed a negligible extraction into the organic phase. Increasing HCl acid concentration above 5 mol/L caused a drastic increase in cobalt extraction, reaching a maximum at HCl acid concentration of 7 mol/L. At HCl acid concentration above 7 mol/L, a further increase in HCl acid concentration resulted in a substantial decrease in the distribution coefficient. The similar dependence of distribution coefficient on HCl acid concentration was reported for other extraction systems using amine as extractants,[26] although its mechanism remains to be investigated. It is evident from Fig. 1 that cobalt can be selectively extracted into the organic phase by TAAHCl while keeping nickel in aqueous feed solutions. The difference in extractability between these two metal ions appears to be related to their ability to form chloride complexes in chloride aqueous solutions. It is well documented that

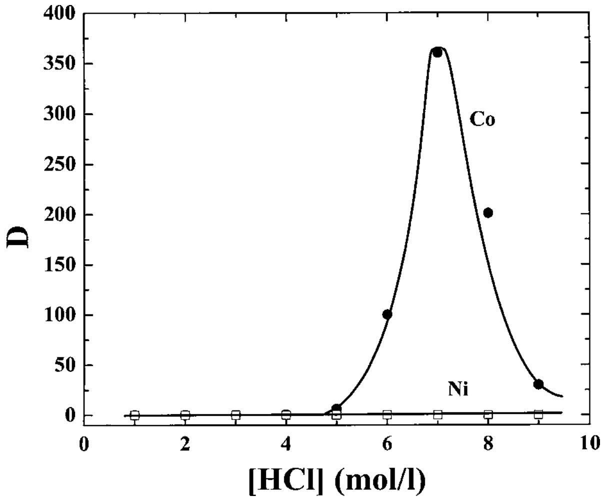

Figure 1. Extraction of cobalt(II) and nickel(II) from hydrochloric acid solutions of various acidity by 1 mol/L TAAHCl in kerosene.

cobalt complexes readily with chloride to form $CoCl_4^{2-}$ and/or $HCoCl_4^{-}$, while nickel showed only a marginal degree of complexation with chloride.[27] It is cobalt complex anions that are responsible for ion exchange with chloride in TAAHCl and, hence, extraction into the organic phase.

In constructing an emulsion liquid membrane, it is highly desirable to effectively transfer the extracted metal ions in organic phase into an inner aqueous phase. In Fig. 1, it is seen that cobalt showed a minimal extraction from aqueous phase to organic phase at aqueous HCl acid concentration below 5, suggesting a large distribution of cobalt in aqueous phase. This observation can be used as a possible avenue for stripping cobalt using aqueous solutions containing less than 5 mol/L HCl acids as the internal aqueous phase of ELM.

Although the ion exchange mechanism of $CoCl_4^{2-}$ with chloride ions in TAAHCl to form an oil-soluble $(TAAH^+)_2CoCl_4^{2-}$ compound has been considered as the extraction mechanism in ELM, this mechanism alone can not account for the observed HCl dependence of distribution coefficient shown in Fig. 1. To fully understand the observed decrease in D with increasing HCl acid concentration above 7 mole/L, the liquid–liquid extraction was performed as a function of TAAHCl concentration at a set of selected HCl acid concentrations. The results plotted with double logarithm scale in Fig. 2, showed an excellent linear correlation between distribution coefficient D and extractant concentration at a given HCl acid concentration. This observation

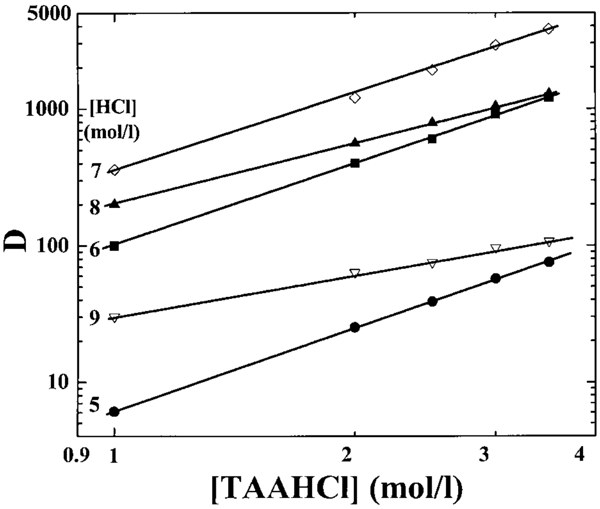

Figure 2. Extraction of cobalt(II) from hydrochloric acid solutions of various acidity by various TAAHCl concentrations in kerosene.

validates Eq. (8), derived from cobalt extraction chemistry. The slope $1 + \frac{1}{1+n}$ of the lines for a given HCl acid concentration can be found by linear regression and the results with corresponding n values are shown in Table 2. It is interesting to note that at relatively lower HCl acid concentration (<7 mol/L), n value was found to be almost zero. From the definition of n, a zero n value would suggest that the major ion-exchange species for cobalt extraction is $CoCl_4^{2-}(TAAH^+)_2$. At 7 mol/L HCl, TAAHCl showed the highest cobalt extraction with an n value being 1/9, indicating that 10% of the cobalt extracted was in $HCoCl_4^-TAAH^+$. Further increasing HCl acid concentration to 8 and 9 mol/L, the n value increased to 1 and infinite, respectively. At these acid concentrations, cobalt extraction becomes less

Table 2. Slope and corresponding n values obtained by double logarithm linear regression of cobalt distribution coefficient as a function of TAAHCl concentration at various HCl acid additions.

[HCl] (mol/L)	5	6	7	8	9
Slope	2.0	2.0	1.9	1.5	1.0
$n = \frac{[HCoCl_4^- TAAH^+]}{[CoCl_4^{2-}(TAAH^+)_2]}$	0	0	1/9	1	∞

effective, as shown in Fig. 2. These findings suggest that at extremely high HCl acid concentration, cobalt ions were in the form of $HCoCl_4^-$ and H_2CoCl_4, which were less favorable for ion exchange with chloride ions in TAAHCl. The current study demonstrates that in an aqueous solution of 7 mol/L HCl, where the transition of cobalt chloride complexes from $CoCl_4^{2-}$ to $HCoCl_4^-$ starts to occur and $CoCl_4^{2-}$ should be at its maximum, the ion exchange/extraction is the most favorable, confirming that $CoCl_4^{2-}$ is the most favorable species for ion-exchange with chloride in TAAHCl.

From the information contained in Figs. 1 and 2, an ELM can be constructed by using TAAHCl-containing kerosene as membrane phase while using low HCl acid aqueous solution as internal stripping phase and conducting cobalt separation in a feed effluent at conditions where the transition from $CoCl_4^{2-}$ to $HCoCl_4^-$ starts to occur.

Emulsion Liquid Membrane

From the previous extraction study, the parameters, such as TAAHCl concentration in membranes, volume ratio of membrane phase to internal stripping phase (R_{oi}) and external aqueous phase (R_{ew}), and hydrochloric acid concentration of external (i.e., feed effluent) and internal (stripping) aqueous phases, are anticipated to control the separation of cobalt from nickel in a waste effluent using an ELM system. In addition, the dispersion of emulsion also plays a significant role as it affects the interfacial mass transfer of extractable ions. The preliminary tests were performed to determine a suitable LMA concentration. It was found that an LMA concentration of above 2% by volume in organic phase resulted in a stable membrane. Based on the information derived from the liquid–liquid extraction study just described, an emulsion liquid membrane system was examined systematically at a fixed LMA concentration of 2% and the results are discussed as follows. It should be noted that in this study the initial cobalt concentration in the external aqueous phase was fixed at 6 g/L. Since nickel ion showed little transfer to the organic phase under the conditions studied, it will not be discussed further.

Effect of Carrier Concentration

The effect of carrier concentration on cobalt transfer ratio was studied using an ELM system with a R_{ew} of 1:10 and R_{oi} of 1:1 for a contact time of 20 minutes. The hydrochloric acid concentration in the external and internal aqueous phases was fixed at 7 and 1 mol/L, respectively. The results, in Fig. 3,

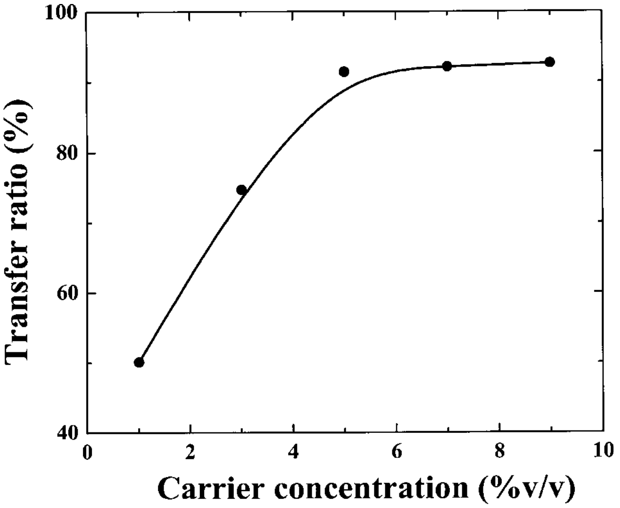

Figure 3. Effect of TAAHCl concentration on transfer ratio of cobalt(II). Experimental conditions are (1) membrane phase: 2% (V/V) LMA; (2) external aqueous phase: [HCl] = 7.0 mol/L and $[Co^{2+}] = 6.0$ g/L; and (3) internal aqueous phase: [HCl] = 1.0 mol/L; with $R_{oi} = 1{:}1$, $R_{ew} = 1{:}10$ and transport time = 20 min.

show that the cobalt transfer ratio increased with increasing TAAHCl concentration up to 5% by volume, after which, it leveled off at 92%. This observation is consistent with the principle of diffusion-controlled interfacial mass transfer. At the TAAHCl concentration above 5%, it appears that there are too many $CoCl_4^{2-}(TAAH^+)_2$ to be effectively transferred to the internal aqueous phase through the limited internal oil/water interface. In the subsequent tests, the TAAHCl concentration was fixed at its optimal value of 5% by volume.

Effect of Complexation

According to the ion exchange extraction mechanism of cobalt by TAAHCl, the metal ions to be extracted need to be in the form of complex anions with chloride ions in aqueous phase. Theoretical analysis showed that both $CoCl_4^{2-}$ and $HCoCl_4^-$ are ion exchangeable with TAAHCl as inferred experimentally (see Figs. 1 and 2), although the latter is less effective. The hydrochloric acid and chloride ion concentrations are, therefore, anticipated to affect cobalt transfer in an ELM system. This effect is studied by changing hydrochloric acid concentration in the external aqueous phase without and with chloride ion addition. The results, in Fig. 4, show that without the addition of sodium chloride, cobalt transfer ratio increased with increasing hydrochloric acid concentration up to 7 mol/L, above which, it experiences a slight drop. The formation of increasing amount of ion-exchangeable $CoCl_4^{2-}$ anions is responsible for the observed increase in cobalt transfer with increasing HCl acid concentration. The drop of cobalt transfer at HCl concentration above 7 mol/L may be attributed to the formation of less extractable $HCoCl_4^-$ anions and neutral H_2CoCl_4.

Although cobalt transfer in 7 mol/L HCl acid aqueous solution is more favorable, it is highly desirable to extract valuables by an ELM at a milder acidic condition as the ELM often becomes unstable in extremely high acidic aqueous solutions. In addition, operating at mild acidic condition could minimize potential corrosion of the process equipment. Since the most favorable species for ion exchange with TAAHCl is $CoCl_4^{2-}$, it is feasible to improve the cobalt transfer ratio in a milder acid solution by increasing complexation of cobalt with chloride addition. This hypothesis is confirmed by the results shown in Fig. 4. For example, addition of 1 mol/L sodium

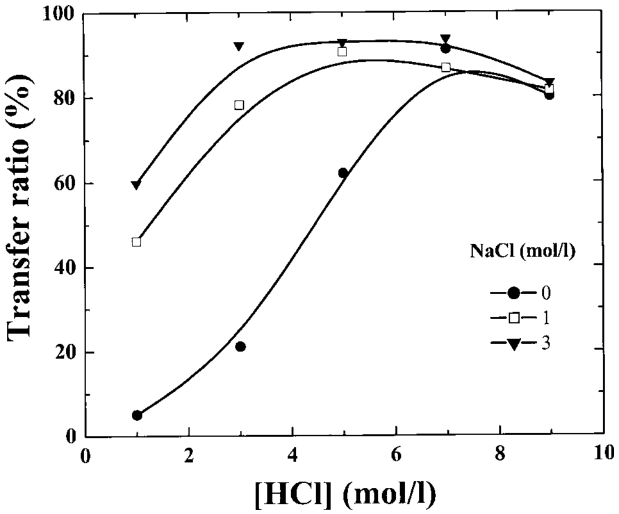

Figure 4. Effect of acidity and complex ion (Cl^-) on transfer ratio of cobalt(II). (1) membrane phase: 2% LMA and 5% TAAHCl (V/V); (2) external aqueous phase: $[Co^{2+}] = 6.0$ g/L; and (3) internal aqueous phase: $[HCl] = 1.0$ mol/L; with $R_{oi} = 1:1$, $R_{ew} = 1:10$ and transport time = 20 min.

chloride to an aqueous feed solution containing 1 mol/L HCl acid resulted in a significant increase in cobalt transfer ratio, from 5% to 48%. A further increase in sodium chloride addition to 3 mol/L showed only a marginal improvement. It is interesting to note that the cobalt transfer ratio converged to the case without sodium chloride addition at HCl acid concentration above 7. At such a high acid concentration, high concentration chloride ions from HCl acid masked the effect of further added chloride ions, suggesting that $CoCl_4^{2-}$ is the most favorable species for ion exchange with Cl^- in TAAHCl. From a balanced consideration of overall cobalt transfer ratio, recycle of the treated effluent and minimized corrosion of the process equipment, the suitable feed condition is selected at 4 mol/L hydrochloric acid concentration with 1 mol/L sodium chloride addition.

Effect of Acidity in Internal Solution Phase

To effectively recover cobalt using ELM technology, the stripping of extracted cobalt in the membrane phase into internal aqueous phase needs to be considered. Figure 1 showed that at low hydrochloric acid concentration, the extraction of cobalt to the membrane phase is negligible. This finding led us to construct an internal aqueous phase of low hydrochloric acid concentration. The effect of hydrochloric acid concentration of internal stripping phase on overall transfer ratio is examined. The results, in Fig. 5, show a significant increase in cobalt transfer ratio with increasing HCl acid concentration in the internal aqueous phase, reaching a maximum at 0.5 mol/L. Further increase in HCl acid concentration greater than 0.6 mol/L caused a significant drop in overall cobalt transfer ratio. This observation can be accounted for by considering striping reaction that can be expressed as a reverse process of reaction 5 in Table 1. At an HCl acid concentration in the internal striping phase lower than 0.5 mol/L, the effective Cl^- anion concentration appears to be insufficient to push reaction 5 in the stripping (left) direction effectively. Increasing chloride concentration at higher HCl acid concentration would increase the extend of stripping reaction as observed at HCl concentration below 0.5 mol/L. At an even higher HCl acid concentration above 0.7 mol/L, it appears that there are too many Cl^- anions in the internal aqueous phase that the stripped cobalt is mainly in the form of $CoCl_4^{2-}$. It is evident from reaction 5 (see Table 1) that the excess of $CoCl_4^{2-}$ in the internal aqueous phase is unfavorable for cobalt stripping, i.e., it favors extraction reaction 5. It is a delicate balance of Cl^- and $CoCl_4^{2-}$ in the internal aqueous phase that determines the overall cobalt transfer ratio in ELM. Although the chloride ion concentration in the internal aqueous phase can be

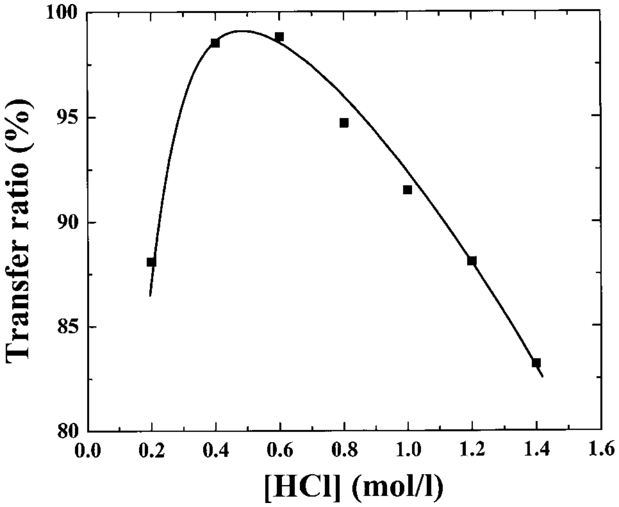

Figure 5. Effect of acidity in internal solution phase on transfer ratio of cobalt(II). Experimental conditions are (1) membrane phase: 2% LMA and 5% TAAHCl (V/V); and (2) external aqueous phase: [HCl] = 4.0 mol/L, [NaCl] = 1.0 mol/L and $[Co^{2+}]$ = 6.0 g/L; with R_{oi} = 1:1, R_{ew} = 1:10 and transport time = 20 min.

controlled by adding sodium chloride salt, the membranes formed without hydrochloric acid in the internal phase experienced a substantial swelling due to excessive osmotic pressure and was found unstable. The optimal HCl acid concentration in the internal aqueous phase was found to be at 0.5 mol/L.

Effect of R_{oi}

The volume ratio of oil to internal aqueous phases (R_{oi}) is another important parameter in ELM design. The effect of R_{oi} on the overall cobalt transfer ratio is shown in Fig. 6. For an internal aqueous phase of a fixed hydrochloric acid concentration at 0.5 mol/L, the cobalt transfer ratio was found to increase significantly with increasing R_{oi}, reaching a maximum of 98% at a R_{io} of 1. A further increase in R_{io} resulted in a gradual decrease in overall transfer ratio. It was found that a lower R_{oi} led to an unstable ELM, while a too high R_{oi} resulted in a membrane that was too thick to effectively transport the extracted cobalt through the membrane phase. The optimal R_{io} was therefore found to be at 1.

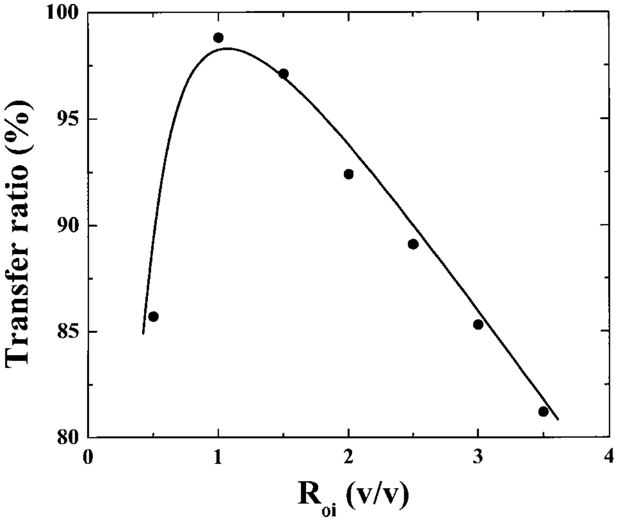

Figure 6. Effect of R_{oi} on transfer ratio of cobalt(II). Experimental conditions are (1) membrane phase: 2% LMA and 5% TAAHCl (V/V); (2) external aqueous phase: $[HCl] = 4.0\,mol/L$, $[NaCl] = 1.0\,mol/L$ and $[Co^{2+}] = 6.0\,g/L$ and (3) internal aqueous: $[HCl] = 0.5\,mol/L$; with $R_{ew} = 1{:}10$ and transport time = 20 min.

Effect of R_{ew}

The effect of volume ratio of emulsion phase to external feed solution on the overall cobalt transfer ratio and emulsion swelling ratio was also studied. The swelling ratio is defined as the percent increase in W/O emulsion volume before and after contact with feed solutions. In general, a high swelling ratio is undesirable as it would cause severe emulsion break during extraction. In addition, more feed solutions would be entrained in the separated emulsion phase for cobalt recovery from internal aqueous phases after breaking emulsions. The results, in Fig. 7, show that increasing R_{ew} increased the cobalt transfer ratio (solid symbols) at a short contact time, but converged when the contact time was longer than 25 minutes. From an economic consideration, it is highly desirable to perform metal extraction at the lowest R_{ew} with the shortest contact time and acceptable level of swelling. The swelling ratio (open symbols) was found to decrease with decreasing R_{ew}. At a higher R_{ew}, the swelling ratio also increased with increasing contact time, due possibly to the formation of smaller emulsion drops at prolonged agitation time. In this case, the emulsion droplets were found to be more stable. From Fig. 7,

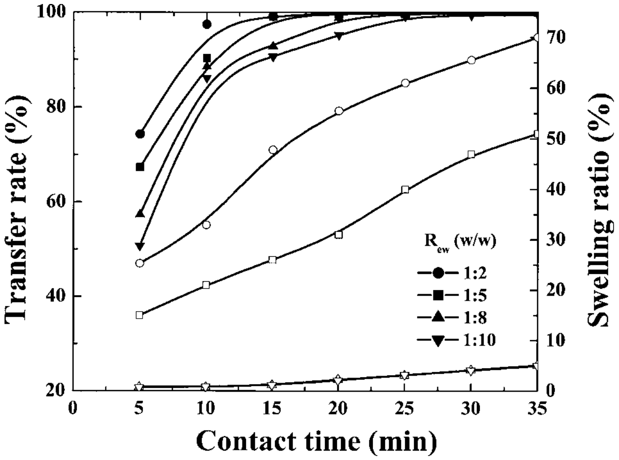

Figure 7. Effect of R_{ew} on transfer ratio of cobalt(II). Experimental conditions are (1)1 membrane phase: 2% LMA and 5% TAAHCl (V/V); (2) external aqueous phase: [HCl] = 4.0 mol/L, [NaCl] = 1.0 mol/L and $[Co^{2+}] = 6.0$ g/L and (3) internal aqueous: [HCl] = 0.5 mol/L; with $R_{oi} = 1{:}10$ and transport time = 20 min.

the optimal R_{ew} can be determined to be 1:8, at which, a contact time of 20 minutes is sufficient to achieve a transfer ratio of 99% with a minimal swelling ratio of 4%.

From the basic study just described, the cobalt transfer under various conditions can be summarized schematically as in Fig. 8. At hydrochloric acid concentration below 7 mol/L, cobalt ions are mostly complexed with chloride ions to form $CoCl_4^{2-}$ in feed solutions. The $CoCl_4^{2-}$ are effectively extracted into membrane phase by ion exchange with chloride ions in TAAHCl carriers, forming oil-soluble $CoCl_4^{2-}(TAAH)_2$. The diffusion of formed $CoCl_4^{2-}(TAAH)_2$ causes it to migrate to the interface of the membrane and internal aqueous stripping phases, where it is converted back to water-soluble $CoCl_4^{2-}$. With further increasing the hydrochloric acid concentration of feed solution above 7 mol/L, $CoCl_4^{2-}$ starts to be transferred to $HCoCl_4^-$, which is less effective for ion exchange with chloride ions on TAAHCl, resulting in less effective extraction of cobalt by the ELM. At extremely high HCl acid concentration greater than 9 mol/L, the cobalt extraction becomes further retarded by the formation of neutral H_2CoCl_4, which is ineffective for ion exchange.

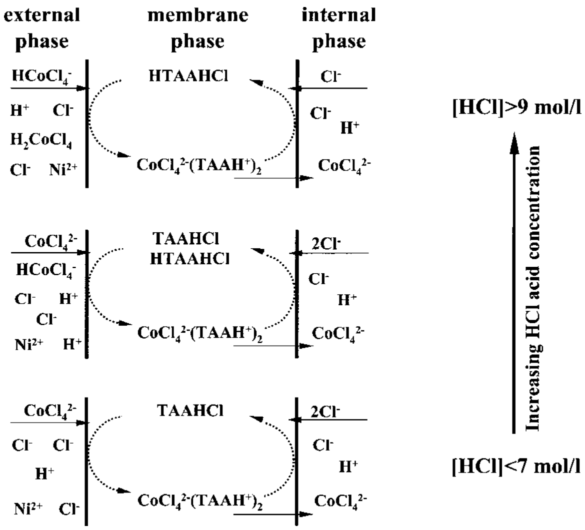

Figure 8. Schematic representation of cobalt transfer in an emulsion liquid membrane system at varying hydrochloric acid concentration.

Cobalt/Nickel Separation Using ELM

The liquid–liquid extraction tests performed in this study demonstrated separation of cobalt from nickel by using TAAHCl as extractants. Based on the fundamental study shown, an ELM system was designed to consist of an equal volume of internal aqueous phase containing 0.5 mol/L HCl acid and kerosene membrane phase containing 2% LMA and 5% TAAHCl, all by volume. The ELM system was applied to a synthetic feed sample containing 6 g/L Co(II) and 4 g/L Ni(II) containing 4 mol/L HCl acid and 1 mol/L NaCl. The contact time was fixed at 25 minutes. The separation results, in Table 3, show that after a one-stage separation, a cobalt transfer ratio as high as

Table 3. Separation results of a synthetic waste effluent using ELM technology.

Element	Initial concentration (g/L)	Residual concentration (g/L)	Transfer ratio (%)	Recovery (%)
Co(II)	6.0	0.024	99.6	99.3
Ni(II)	4.0	3.983	0.42	99.5

99.6% was achieved, corresponding to a cobalt recovery of 99%. The nickel transfer ratio, on the other hand, was kept minimal at 0.42%, with more than 99% nickel ions remaining in the external aqueous phase for further recovery by recycling the effluent back to nickel electrolysis and purification process. It is evident that high purity cobalt can be produced from the collected internal aqueous phase after breaking the emulsion. The small amount of nickel in the collected emulsion phase can be considered to be carried over by entrained external aqueous phase among the emulsion droplets.

In ELM technology, recycling of the oil phase needs to be considered to minimize the operating cost. In this study, a home-made emulsion breaker was used to break the collected emulsions and more than 99% of the added oil was recovered. The separated oil was used in the subsequent ELM tests. It was found that the organic phase experienced little degradation with cobalt recovery remaining at 97% after five cycles, without replenishment of carriers. This finding further confirms ion-exchange being the main extraction mechanism.

CONCLUSION

1. Extraction separation of cobalt(II) from nickel by protonated trialkyl-amine (TAAHCl) as carriers in emulsion liquid membrane (ELM) was studied. Cobalt was found to be transferred effectively into the internal aqueous phase, while nickel showed minimal transfer. Based on extraction solution chemistry, a mathematical expression was derived to identify metal transfer mechanisms. Both experimental results and theoretical consideration identified $CoCl_4^{2-}$ anions as the most favorable species for ion exchange with chloride anions in protonated TAAHCl.
2. A systematic study was conducted to reveal the role of aqueous acidity and sodium chloride addition in cobalt extraction. Under a hydrochloric acid concentration below 1 mol/L, cobalt showed minimal extraction, which can be considered as a candidate for stripping phase. Without the sodium chloride addition, the maximum cobalt extraction was found to be at a feed hydrochloric acid concentration of 7 mol/L, at which, the transition from $CoCl_4^{2-}$ to $HCoCl_4^-$ starts to occur. With 1 mol/L sodium chloride addition, the effective extraction HCl acid concentration can be reduced to 4 mol/L.
3. A new ELM system consisting of an equal volume of internal aqueous phase containing 0.5 mol/L HCl acid and kerosene

membrane phase containing 2% liquid polyamine surfactant and 5% TAAHCl, all by volume was constructed and applied to a synthetic nickel hydrometallurgical waste effluent. With a total 4 mol/L HCl acid and 1 mol/L NaCl concentration at 25-minutes contact time, a cobalt recovery of more than 99% with minimal nickel contamination (less than 0.4%) was achieved. The treated effluent containing less than 0.024% cobalt could be recycled for nickel recovery. The organic membrane phase showed minimal degradation, suitable for reuse without further replenishment.

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