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THE EQUILIBRIUM CHARACTERISTICS OF  
AQUEOUS COBALT AND NICKEL MIXTURES WITH  
THE EXTRACTANT  
BIS-(2-ETHYLHEXYL)-PHOSPHONIC ACID

A THESIS  
SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING  
AND THE SCHOOL OF GRADUATE STUDIES  
OF THE UNIVERSITY OF OTTAWA  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
MASTER OF APPLIED SCIENCE

By  
Christopher J. Wells  
February 1991



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# Abstract

The technique of liquid-liquid extraction of metallic ions from aqueous solutions has attracted considerable attention over the years as a serious alternate strategy to the traditional pyro-metallurgical extraction techniques. The technique was first used during the 1940's to process radioactive isotopes and has since been used to recover and purify a variety of semi-precious and commodity metals. In this work, binary solutions of cobalt and nickel in aqueous ammonium sulfate solutions were extracted using a simple shake-out technique at 25 °C with a mixed organic phase consisting of the extractant bis-(2-ethylhexyl)phosphonic acid (PC-SSA), the modifier tributyl phosphate, and the diluent Esso Varsol DX3641 in a ratio of 20:5:75 respectively. The volumetric ratio between the two phases was maintained at a value of 1.0.

It was found that the optimum pH for the separation of cobalt and nickel from aqueous sulfate solutions, based upon equilibrium studies, was a pH of 5.0, and that the separation of the ions at that pH was a complex function of the proportion of cobalt and nickel in the equilibrium phases. In fact there exists an operating region over which the two phases exist in equilibrium, bounded by the individual component isotherms and the solubility curve for the mixed nickel-ammonium and cobalt-ammonium double salts. The maximum metal loading of the organic phase, based on the population of dimer extractant complexes was approximately 73 % at the optimum pH. Above this organic phase loading, a rapid rise in the viscosity of the organic phase was observed, indicating that a polymerization of the extractant-metal complex was occurring. This observation was in agreement with conclusions drawn by other investigators.

Two methods, used to describe the equilibrium extraction of two or more metal

ions from an aqueous solution using organic extractants were compared: namely, the Delta-Y method proposed by Iannou et al., and the Pseudo-Gamma approach proposed by Barclay. Each of these methods account for the non-ideal interactions between mixture components. Of the methods tested, Barclay's Pseudo-Gamma relationship was found to be simpler, and correlated the data very well. Simple expressions for the Pseudo-Gamma correction factor as a function of the component solvent free mole fraction were obtained for PC-SSA, Cyanex 272 and D2EHPA. Although an indefinite limit exists for the method as the solvent free mole fraction of a component approaches zero, an analogy to Henry's Law is able to overcome the problem.

# Nomenclature

A	Amperes.
AAS	Atomic Absorption Spectrophotometer.
A/O	Aqueous Phase to Organic Phase volume ratio
$C_{org}$	Molar Organic Phase Metal concentration.
$C_{aq}$	Molar Aqueous Phase Metal concentration.
Cyanex 272	American Cyanamic trade name for di-(2,4,4-trimethylpentyl)phosphinic acid.
D	Distribution Coefficient equal to the ratio of the organic phase concentration to the aqueous phase concentration of a solute.
D <sub>2</sub> EHPA	Di-(2-ethylhexyl)phosphoric Acid
gpm	Gallons(US)/Minute.

g	Grams.
K	Equilibrium Constant.
L	Liter
m	Meter
mol	Moles
M	Molar Concentration (moles/Litre).
N	Newton, a unit of force. = $\frac{kg \cdot m}{s^2}$
PC-SSA	Diahachi Chemical trade name for bis-(2-ethylhexyl)phosphonic acid
ppm	concentration in parts per million parts
RD-557	Shell Chemical trade name for bis-(2-ethylhexyl)phosphonic acid
SME-418	Shell Chemical trade name for bis-(2-ethylhexyl)phosphonic acid
TBP	Tributyl Phosphate
TM	Trade Mark

- v/v volume fraction of a substance usually used in concert with a concentration given in percentages.
- w/w weight fraction of a substance usually used in concert with a concentration given in percentages.
- y or Y 1. Concentration of solute in moles solute/kg adsorbant. used in the Langmuir and Freundlich Adsorption Isotherms.  
2. Molar Concentration of solute in the Organic Phase.
- Y<sup>\*</sup> Pure or single component Equilibrium Molar Concentration of solute in the Organic Phase, .
- x or X 1. Mole Fraction of solute in the bulk phase. used in the Langmuir and Freundlich Adsorption Isotherms.  
2. Molar Concentration of solute in the aqueous phase
- df degrees of freedom in a model, difference between the number of known and required information.
- SSR Sum of Squared Residuals, a statistical measure of the scatter in a data sample when compared to a predicted value.
- MSR Mean Squared Residual, equal to the sum of Squared residuals divided by the number of degrees of freedom, SSR/df
- Ratio of the n<sup>th</sup> to n<sup>th</sup> + 1 aggregate from aggregation model by Brisk and McManamey

- $\gamma_{s,i}$  The pseudo gamma function for solute  $i$
- $\beta$  Separation constant equal to the ratio of the Distribution coefficients of two solutes.
- $\theta_i$  Mathematical parameter

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# Chapter 1

## Literature Review

### 1.1 Phosphorus Based Extractants and Processes

#### 1.1.1 Phosphoric Acid Extractants and Extraction Processes

Phosphorus-based extractants, after the chelating extractants, have enjoyed the most success as selective extractants for metal ions from aqueous solutions. Used primarily for the extraction of metal ions from acidic sulphate or nitrate solutions, the advantages of the phosphorus-based extractants include chemical stability, good loading and stripping characteristics, low aqueous solubility, reasonably fast kinetic behavior, versatility and availability. The first of the phosphorus-based extractants to be successfully exploited was di-(2-ethylhexyl)-phosphoric acid, (D<sub>2</sub>EHPA ). This reagent had been used during the early 1960's as a selective extractant for uranium and the rare earth metals, but it has been as an extractant of cobalt that D<sub>2</sub>EHPA has enjoyed the most success [45, p. 90].

Cobalt and nickel in chloride leach liquors have been processed using amine extractants with excellent separation and loading characteristics, however highly concentrated chloride solutions are extremely corrosive. High capital and operating costs therefore have forced engineers to search for a less expensive method for cobalt-nickel separation. Carboxylic acids have been used in alkaline solutions to separate cobalt and nickel, but the high solubility of the carboxylic acids can lead to high

operating costs. [45, p. 114]. and potential water pollution problems.

Sulfuric acid leach liquors are not very corrosive, and can be easily handled with equipment made of stainless steel and fiberglass reinforced plastic. Unfortunately cobalt and nickel in sulphate solutions exhibit similar physical and chemical behaviors which make it difficult to separate the two metals.

Ritcey and Ashbrook, first patented a continuous process for the separation of cobalt from sulphate leach liquors, using  $D_2EHPA$  in kerosene [49]. The process, resulted from the requirement to treat cobalt ores and concentrates containing Ni, As, Cu, Bi, and Fe in order to recover cobalt and nickel as high purity products [47]. Following leaching and solid-liquid separation, Cu was removed by cementation. Solvent extraction with a chelating extractant can also be used. Iron was removed by oxidation and precipitation with sodium hydroxide, and the filtrate pH was adjusted to about 5.0. The cobalt and nickel solution was sent to a solvent extraction circuit and contacted with 20% (v/v)  $D_2EHPA$  in an aliphatic diluent also containing 5% (v/v) tributyl phosphate (TBP) as a modifier. The extractant phase was previously pre-equilibrated with ammonia to maintain the system at a pH range of 5.0 to 5.5 during extraction. A pulsed column 40 ft. high and 22 inches in diameter was used to extract the cobalt from the aqueous phase at a temperature of 60 °C. The organic phase was continuous with a phase ratio of 1 (A/O ratio) and a feed rate of 7 gpm. The loaded organic phase was scrubbed with a concentrated aqueous cobalt (40 g/L) solution to remove co-extracted nickel, in a second 40 ft high pulsed column (22 inch dia.) at a pH of 5.5, and an A/O ratio of 1:2. The scrub raffinate was returned to the extraction circuit. Stripping was done in a single mixer settler with an aqueous acid. Depending on the Co/Ni ratio of the feed solution, and the amount of scrubbing used, final cobalt to nickel ratios of 1000:1 could readily be achieved [47]. Similar processes were later developed by Matthey-Rustenburg Mining of South Africa, and Nippon Mining of Japan for the recovery of cobalt from leach liquors [46,11,19].

The recovery and separation of cobalt and nickel from process residues, scrap metal, and spent catalyst using  $D_2EHPA$  has also been demonstrated. Notable processes include INCO's pressure carbonyl process residue treatment plant and

the Pyrites Co. metal recovery plant [46.10].

In the INCO process, cobalt and nickel are separated using a 30% (v/v) solution of D<sub>2</sub>EHPA in aliphatic diluent and 5% (v/v) TBP [46]. The feed for the process is derived from the pressure leaching of the cobalt-rich residue from the nickel carbonylation plant with sulfuric acid. It is pretreated to remove iron, copper, calcium and magnesium. Adjusted to a pH of 5.0 and heated to 65 °C, the aqueous phase is contacted in the extraction column with the organic phase at a phase ratio of 3:1 (A/O=3.0), and an aqueous flowrate of 60 gpm. Extraction is performed in a 66 foot high, 6 foot diameter Mixco<sup>TM</sup> column, with a continuous aqueous phase. The solvent is pre-equilibrated with NaOH to allow the final pH of the aqueous phase to be approximately 5.0. About 95% of the cobalt can be recovered from the extraction stage. After scrubbing with a mild sulfuric acid scrub solution, in three mixer-settlers, a 500:1 Co/Ni ratio can be achieved. The cobalt product is precipitated with (Na)<sub>2</sub>CO<sub>3</sub> after stripping the organic phase in a 35 foot high, 3.5 foot diameter Mixco column with sulfuric acid. The nickel raffinate from the extraction column, after precipitation, is recycled to the carbonylation plant. The scrub raffinate, after precipitation, is recycled to the leaching circuit.

The Pyrite Company Inc., no longer in operation, used the solvent extraction process as a pretreatment step for their feedstock before recovering cobalt and nickel by precipitation as the hydroxide or carbonate [10,18]. The feedstock was essentially a nickel-bearing pyrite cinder from a sulfuric acid plant, and residues such as spent catalysts, and leach pit sludge. Copper was removed by electrowinning, and iron removed by chlorine oxidation and neutralization. Calcium and magnesium were removed from the feedstock by precipitation with HF. The leach liquor, after treatment, was contacted with 12% (v/v) D<sub>2</sub>EHPA in Shell 140 with 3% (v/v) isodecanol as a modifier. Five mixer-settlers were used to extract cobalt into the organic phase, at an A/O ratio of 1.0 at 50 °C, with a pH of 4.1-5.95. Three mixer-settlers were used to remove co-extracted zinc by scrubbing the organic phase with a concentrated cobalt solution. After stripping the organic was pre-equilibrated with 8% caustic to maintain the extraction pH of 5.0. Co-extracted iron was removed by chelating with a 3% sugar solution during the pretreatment stage. Poor phase

disengagement required a 3% aqueous NaCl wash to remove any residual sugar from the organic phase.

A great deal of research has been done using D<sub>2</sub>EHPA and this is well reviewed by Ritcey and Ashbrook [45,46]. A more general perspective of the refining of cobalt and nickel is given by the monographs by Boldt and Pehlke [7,37].

### 1.1.2 Phosphonic Acid Extractants

Despite the use of D<sub>2</sub>EHPA on an industrial scale, this extractant is a relatively inefficient one characterized by a low cobalt-nickel separation factor. The separation factor is the ratio of the distribution coefficients of the individual metals. A distribution coefficient is defined as the ratios of phase concentrations of a metal. As a result multistage contacting equipment operating at high temperatures, 60-80 °C, is necessary to achieve high purity products [45,46,47,19]. As the cost of production of cobalt and nickel in sulphate media has increased, and as the quality of cobalt and nickel ores has decreased, alternative extractants have been proposed [45,46,19].

Amongst the most attractive of these alternatives are the phosphonic acid esters and the phosphinic acid derivatives. The phosphonic acid esters and the phosphinic acid derivatives are the oxidation products of the alkyl phosphines.

Little data, however, can be found in the literature concerning the behavior of the phosphonic acid esters, or phosphinic acids, in solvent extraction processes. This is especially true for multicomponent extraction processes. Early studies compared the extraction of actinides and lanthanides with phosphonic and phosphinic acids.[39,38]

Fujimoto et al. patented a liquid-liquid extraction process using a number of phosphonic acid esters to separate cobalt from aqueous cobalt-nickel mixtures.[22] Most of their work however concentrated on the behavior of 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester, (EHPA). This ester is marketed by Chugai Chemical Co., in Japan, and Diahachi Chemicals in the United States, under the trade-name PC-SSA<sup>TM</sup>. Shell Chemicals marketed this extractant under the tradenames SME 418<sup>TM</sup> and RD 577<sup>TM</sup>, but Shell has now withdrawn from this market.[45] Since small differences may exist between the manufacturing methods for PC-SSA.

SME 418, and RD 577, minor differences in the behavior between the products would not be surprising, even though the active agent in the extraction is the same in all three cases. For this reason, experimental observations will be quoted with respect to the actual product used.

It has been known for some time that the phosphorus-based extractants tend to self-associate when in solution with organic diluents. As Marcus and Kertes point out, unlike most acidic extractants, organophosphorus extractants have a tendency toward association into dimers, and larger aggregates [33, p. 521]. These observations were later verified by Cox et al. for EHPA in particular citecox.

Fujimoto et al. compared the extraction capability of EHPA to that of  $D_2EHPA$  [21,22]. Each extractant was dissolved in kerosene to give a concentration of 20% by volume. The extractants were converted to their ammonium salts using varying amounts of ammonium hydroxide. The extractions were carried out at 50 °C at an A/O ratio of 1. The aqueous phase was a mixture of cobalt and nickel at an initial total concentration of 10 g/L. They found the EHPA to be much more selective for cobalt over nickel than  $D_2EHPA$ . Fujimoto et al. also found that the viscosity of the organic phase increased as the concentration of the cobalt-extractant complex increased. They also noted that the temperature and nature of the metal salts had little effect on the loading characteristics.

In a countercurrent extraction test using two mixer-settlers at an A/O ratio of 1 with 13–15 g/L cobalt and nickel, recoveries of 99% and purities of 99% could be demonstrated with EHPA. Virtually 100% of the cobalt and nickel could be stripped from a loaded organic phase with 1.N sulfuric acid, after 3 stages with an A/O ratio of 0.5.

Scrubbing with a 13 g/L cobalt scrub solution was found to be an effective method if removing residual Ni in the loaded organic phase, reducing the nickel concentration by a factor of 10. They also found that TBP, at a concentration of 2.5–5% (v/v), had no effect on the extraction of cobalt and nickel. However isodecanol was shown to have a mildly deleterious effect on metal recovery and Co-Ni separation.

Motoba and Itoh patented a process for improving the final purity of cobalt

from a solvent extraction circuit using a alkyl ester of a phosphonic acid as the extractant. They pointed out that even though alkyl phosphonic esters, such as EHPA, were selective extractants for cobalt from aqueous mixtures of metal ions, it was impossible to completely exclude other metal ions such as Cu, and Zn from the loaded organic phase. While Fujimoto et al. had proposed a scrubbing circuit to alleviate this problem, Motoba and Itoh proposed a selective stripping circuit [35,21]. Using a two stage stripping circuit, cobalt can be selectively removed by controlling the pH of the first stripping stage to a pH of 1.5 to 3.5. Following removal of the cobalt from the organic phase, contacting with fresh strip solution at a pH of less than 1.0 will remove the copper and zinc impurities. The preferred stripping temperature was 60 °C.

Ogata et al. indicated that in a counter-current solvent extraction process in which EHPA was the extractant, if the first extraction stage had its pH controlled to a value not exceeding pH=5.0, the cobalt could be extracted into the organic phase without the observed rise in organic phase viscosity. The second and further extraction stages could be carried out at a pH between 5.5 and 7.0 [36].

Nippon Mining patented a process similar to Ritcey and Ashbrook's for the extraction of cobalt from cobalt-nickel solutions. The difference between Ritcey and Ashbrook's D<sub>2</sub>EHPA process and Nippon Mining's lay in the replacement of D<sub>2</sub>EHPA by the extractant PC-88A. In fact Nippon Mining actually started their process using D<sub>2</sub>EHPA but later switched to PC-88A [19,46,16,11].

After iron, zinc and copper removal from the aqueous feed, the cobalt is extracted with the ammonium salt of the mono ester at a pH=6.0 at 60 °C. The loaded solvent is scrubbed with a bleed from the stripping raffinate. Nippon Mining reported that the phosphonic ester performed better than D<sub>2</sub>EHPA [11].

Metallurgie Hoboken-Overpelt, (MHO), tested PC-88A on a solution with a Ni/Co ratio of 15.[11] In order to avoid contamination of the nickel raffinate from the extraction circuit with sodium or ammonium, and yet maintain the pH of the extraction stages within the desired range, the organic phase was pre-equilibrated with an aqueous nickel solution to transform the extractant into its nickel salt. Tests used 15% (v/v) PC-88A, containing 5% (v/v) TBP in Escaid 110, with three

continuous extraction stages at 40 °C and an A/O ratio of 1.7:1. The aqueous feed contained 75 g/L Ni with a Ni/Co ratio of 15:1. The loaded organic phase contained 8.8 g/L Co with a Co/Ni ratio of 10:1.

Using a three stage mild acid scrub, at 40 °C, with an A/O ratio of 13:1, they increased the ratio of cobalt to nickel from 10:1 to 1.140:1. Stripping in a two stage circuit with 131 g/L HCl and an O/A ratio of 16:1 resulted in the aqueous strip raffinate having a Co/Ni ratio of 1.600:1.

MHO noted however that calcium and magnesium presented a problem in the solvent extraction circuit because they co-extracted with cobalt. Final Co/Ca and Co/Mg ratios were 55 and 58 respectively. The co-extraction of calcium could be avoided by the pre-extraction of the feed solution with D<sub>2</sub>EHPA, which is necessary for zinc removal, but magnesium would still present a problem. If sulfuric acid had been used for the stripping solution instead of hydrochloric acid, gypsum would have precipitated in the stripping circuit.

It should be noted however that using HCl as the stripping agent also has its drawbacks. Even at this relatively low concentration of HCl, high grade stainless steels or glass lined equipment would be required.

In 1983, Flett et al. reported on a small study of the behavior of SME 418 and some principle process variables with aqueous mixtures of cobalt and nickel [20]. They found for small initial concentrations of cobalt and nickel as sulphates (0.025 M. each) with 0.1M. SME 418 in the diluent MSB 210, at 25 °C, the separation factor,  $\beta_{Co/Ni}$ , increased linearly from 100 to 1000, with the equilibrium pH, over the pH range of 3.5 to 4.5. The separation factor is the ratio of the distribution ratios for the individual metal ions at equilibrium. Similar studies with D<sub>2</sub>EHPA showed no such dependency, nor was this behavior expected from the single metal extraction isotherms [20].

They also showed that SME 418 was a consistently better extractant than D<sub>2</sub>EHPA over the temperature range of 0–70 °C at an equilibrium pH of 4.0. These results, the separation of cobalt and nickel increasing with increasing temperature, were as expected. Flett et al. also showed that an increase in the aromatic content of the diluent tended to increase the cobalt/nickel separation factor for SME 418.

but at the expense of cobalt loading, while the addition of isodecanol to the system as a phase modifier tended to decrease the cobalt /nickel separation by increasing the amount of nickel hydrate extracted.

In 1982, Preston reported on a comparative study between D<sub>2</sub>EHPA, Shell RD 577 and Cyanex CNX<sup>TM</sup> [40]. Nickel and cobalt extraction isotherms, as a function of pH were found, using 0.1M RD 577 as the dimer, in xylene and aqueous phases having initial concentrations of 0.1M metal nitrate in 1.0M ammonium nitrate.

For RD 577 at 20 °C the pH<sub>0.5</sub> for Co and Ni were found to be 3.9 and 5.12 respectively. At 50 °C they were found to be 3.55 and 5.04 respectively. It is apparent that the change in behavior of the metal extractions as a function of temperature is primarily due to the increased extraction of cobalt.

Similar experiments on D<sub>2</sub>EHPA indicated its pH<sub>0.5</sub> for Co to be 3.68 at 20 °C and 3.32 at 50 °C For nickel the pH<sub>0.5</sub> were found to be 4.11 and 4.10 at 20 °C and 50 °C respectively.

Although each extractant improved its separation as the temperature of the system increased, it is apparent that the difference in the separation for RD 577 between 20 °C and 50 °C is more than that for D<sub>2</sub>EHPA. It is interesting to note that the improved cobalt-nickel separations obtained at 50 °C were due almost entirely to the shifts observed in the cobalt extraction isotherms. The phosphinic acid extractant Cyanex CNX showed an even greater Co/Ni separation than either RD 577 or D<sub>2</sub>EHPA, but these results will be discussed later.

Preston found that the distribution of cobalt was unaffected by the nature of the extractant. However, nickel extraction was demonstrably reduced through the series phosphoric > phosphonic > phosphinic. This was largely due to shifts in the nickel extraction curves.

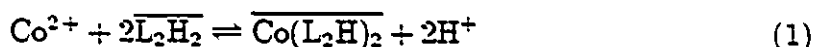
He also showed that as the concentration of the extractant increased in the organic phase, at 20 °C, the metal extraction isotherms shifted to lower pH values, and the Co/Ni separation decreased.

Changing the diluent from xylene to heptane at 20 °C with 0.5 M extractant, as the dimer, was found to decrease the separation of the cobalt/nickel extraction

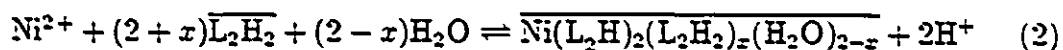
isotherms. However, at the same time the metal loading of the organic phase was found to increase.

Although a pH shift for a nitrate to sulphate ion change was greater than for a similar change from nitrate to chloride, at the same ionic strength, the nature of the anion in solution had no effect upon the Co/Ni separation. However, Preston did note that at an initial ionic strength of 6M ammonium sulphate, the nickel ammonium double salt precipitated [40].

Preston also determined that the cobalt-RD 577 complexation could be described by the stoichiometry:



Nickel could be described by the equation:



where  $x = 0, 1, 2$  depending upon the availability of the free extractant  $\text{L}_2\text{H}_2$ . The overbars indicate organic phase species. In keeping with these observations the Co-RD 577 coordination was found to display tetrahedral characteristics for all concentrations of the extractant, while the nickel complex was shown to have a basic octahedral geometry, with varying amounts of absorbed water. Preston showed that high concentrations of additives, (0.5M TBP or isodecanol), did tend to decrease the cobalt-nickel separation for all of the extractants he examined (0.5M extractant, 1.0M metal nitrate, 1.0M ammonium nitrate).

However whereas TBP reduced the difference in  $\text{pH}_{0.5}$  between cobalt and nickel with  $\text{D}_2\text{EHPA}$  by 42% (0.43–0.25), with RD 577 the difference was only reduced by 19% (1.22–0.99).

In a further publication, Preston compared the behavior of PC-SSA, and Cyanex 272<sup>TM</sup> to that of  $\text{D}_2\text{EHPA}$  [41]. Cyanex 272 is reported to be bis-(2,2,4-trimethylpentyl)-phosphinic acid. He showed that an increase in Co/Ni selectivity for the phosphorus-based extractants was of the order  $\text{D}_2\text{EHPA} < \text{PC-SSA} < \text{Cyanex 272}$ , by showing the changes in  $\text{pH}_{0.5}$  for cobalt and nickel at 20 °C and

50 °C . He showed that the nickel pure component isotherm shifted more than the cobalt pure component isotherm as one went from D<sub>2</sub>EHPA to Cyanex 272, and it was this behavior which accounted for the increased cobalt selectivity displayed by PC-SSA and Cyanex 272. These experiments were performed with 40 g/L ammonium sulphate and 3 g/L metal sulphate in the initial aqueous phase. Preston indicated that the optimum pH for the extraction of cobalt, consistent with a low coextraction of nickel was 5.0 at 20 °C for 0.45M PC-SSA, as the dimer, in xylene. Similar considerations showed that for Cyanex 272 a pH of 5.25-5.5 would give optimum performance. Construction of a McCabe-Theile diagram for the extraction of cobalt with PC-SSA, indicated that at pH =5.0, three extraction stages would be required to produce a raffinate containing less than 10 ppm cobalt at an A/O ratio of 2:1. Similar results were found for Cyanex 272.

Batch countercurrent experiments were carried out under the conditions described above, with 3 g/L cobalt and nickel as sulphate in 40 g/L ammonium sulphate. An A/O ratio of 2:1 was maintained with 0.45M PC-SSA, as the dimer, at 20 °C . These tests indicated that after three extraction stages, the nickel rich raffinate contained 10 ppm cobalt (0.32% of the metal), while the cobalt rich organic phase contained 11 ppm nickel (0.18% of the metal). The extraction stages were maintained at a pH of 5.0

He also showed that when the fresh organic phase initially contacted the cobalt-lean aqueous phase, high levels of nickel were taken into the organic phase. However, as the organic phase progressed to the remaining stages in which the concentration of cobalt in the aqueous phase increased, the coextracted nickel was gradually displaced by cobalt. This effect was characteristic of all the extractants Preston studied.

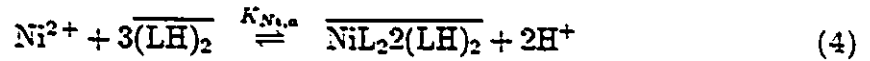
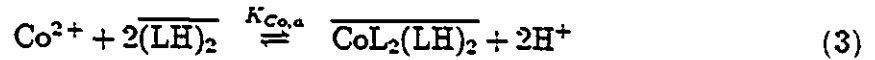
Batch countercurrent tests were also carried out under similar conditions using Cyanex 272 and an equilibrium pH of 5.25. The final concentration of cobalt in the raffinate after three extraction stages was 7 ppm or 0.24% while the final concentration of nickel in the organic phase was 7 ppm or 0.11% .

Preston concluded that unlike D<sub>2</sub>EHPA extraction circuits, operation at ambient temperatures seemed to be feasible for Cyanex 272 and PC-88A.

In 1983 Komasaawa et al. published a study of the stoichiometric relationship between cobalt and nickel cations and the extractant PC-SSA, and compared their results to D<sub>2</sub>EHPA [28].

PC-SSA was purified by precipitation with copper from ethyl ether solution before being diluted in either distilled xylene or n-heptane. The aqueous metal nitrate solutions were prepared by dissolving the metal nitrate in distilled water, and adding 0.5 M (Na, H)NO<sub>3</sub>. The concentration of the extractant in the organic phase was kept within the range of 0.003–0.6 mol./L. of the dimer, but the usual concentration range was 0.01–0.10 mol./L.

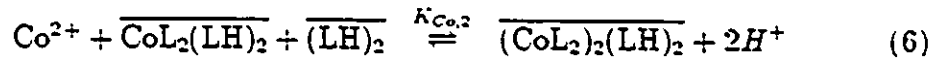
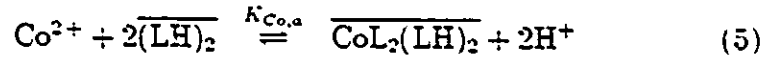
At low loading of the organic phase, ( $[\overline{M}]/[(\overline{LE})_2]_{feed} < 0.002$ ), Komasaawa et al. found that the overall extraction equilibria could be described by the equations:



These equations are identical to those found for the D<sub>2</sub>EHPA systems and similar to those proposed by Preston [45,40]. For the cobalt extraction process the equilibrium constants were found to be  $7.53 \times 10^{-7}$  and  $3.4 \times 10^{-6}$  at 25 °C, in xylene and n-heptane respectively. For the nickel extraction process, the equilibrium constants were similarly found to be  $1.5 \times 10^{-11}$  m<sup>3</sup>/mol and  $2.4 \times 10^{-10}$  m<sup>3</sup>/mol respectively. For D<sub>2</sub>EHPA under the same conditions they found for cobalt the extraction equilibrium constant, or coefficient was  $4.5 \times 10^{-6}$  in toluene and  $4 \times 10^{-5}$  in n-heptane. For nickel and D<sub>2</sub>EHPA the constants were  $1.5 \times 10^{-9}$  m<sup>3</sup>/mol and  $4.5 \times 10^{-8}$  m<sup>3</sup>/mol respectively.

They found however, that these extraction constants were only valid at very low loadings. Cobalt loading ratios above 0.08, indicated that the apparent equilibrium constants were in fact a function of the organic phase loading [28]. Similar behavior was shown for the nickel extraction equilibrium constant at loadings above 0.008. The changes in the apparent equilibrium constant at higher loading may be due to the number of free extractant molecules in the metal-extractant complex decreasing below the value assumed in the equilibrium expression. The reduction in the number

of free extractant molecules in the metal-extractant complex is most easily explained by the assumption of the formation of successively larger aggregated species in the organic phase. This assumption is qualitatively supported by the observation of a sharp rise in the organic phase viscosity, which has been noted by others [16,21,36,32]. For cobalt, the typical steps are:



$$\vdots$$


If one assumes, as Baes et al. did for uranium extraction with  $\text{D}_2\text{EHPA}$ , that the value of  $K_{\text{Co},n}$ , the equilibrium constant for the  $n^{\text{th}}$  reaction, is constant and independent of  $n$ , (i.e.  $K_{\text{Co},2} = K_{\text{Co},n}$ ), then the ratio of concentrations of successively larger aggregates,  $\gamma$ , is constant [2]. Brisk and McManamey also used this analysis for the extraction of cobalt with  $\text{D}_2\text{EHPA}$  [9]. This assumption allows the total organic concentration of cobalt to be expressed as a simple function of the smallest subunit,  $\text{CoL}_2(\text{LH})_2$ :

$$[\overline{\text{Co}}]_t = \overline{[\text{CoL}_2(\text{LH})_2]}(1 - \gamma)^{-2} \quad (8)$$

Similarly, the bound extractant concentration is given by:

$$[(\text{LH})_2]_{\text{complex}} = (2 - \gamma)[\overline{\text{Co}}]_t \quad (9)$$

Two equilibrium constants can be inferred from this analysis. These are:

$$K_{\text{Co},a} = \frac{(1 - \gamma)^2 [\overline{\text{Co}}]_t [\text{H}^+]^2}{[\text{Co}^{2+}] \{[(\text{LH})_2]_{\text{feed}} - (2 - \gamma)[\overline{\text{Co}}]_t\}^2} \quad (10)$$

$$\begin{aligned} K_{\text{Co},p} &= \frac{\gamma [\text{H}^+]^2}{[\text{Co}^{2+}] [(\text{LH})_2]} \\ &= \frac{\gamma [\text{H}^+]^2}{[\text{Co}^{2+}] \{[(\text{LH})_2]_{\text{feed}} - (2 - \gamma)[\overline{\text{Co}}]_t\}} \end{aligned} \quad (11)$$

The value of  $K_{\text{Co},a}$  determined from the extraction of cobalt at low organic phase loading was assumed to be valid for the first stage of the extraction at higher organic

phase loadings. Therefore, by knowing  $K_{Co,a}$  at low loading,  $\gamma$  can be determined, and knowing  $\gamma$  allows calculation of  $K_{Co,p}$ .

A similar development for the extraction of nickel leads to the expressions:

$$K_{Ni,a} = \frac{(1 - \gamma)^2 [\overline{Ni}]_i [H^+]^2}{[Ni^{2+}] \{ [(LH)_2]_f - (3 - \gamma) [\overline{Ni}]_i \}^2} \quad (12)$$

$$K_{Ni,p} = \frac{\gamma [\overline{Ni}]_i}{[Ni^{2+}] \{ [(LH)_2]_f - (3 - \gamma) [\overline{Ni}]_i \}^2} \quad (13)$$

Calculating the values of  $K_{Co,p}$  and  $K_{Ni,p}$  and plotting these against organic phase loading, Komasa et al. found a considerable amount of scatter [28]. They assumed this scatter was due to small errors in the measurement of the organic phase cobalt-nickel concentrations. Using a least squares analysis, assuming that the extraction constants at low loading were valid estimates of  $K_{Co,a}$  and  $K_{Ni,a}$  at high loading, at 25 °C, gave the following results in xylene.

$$K_{Co,a} = 7.53 \times 10^{-7}$$

$$K_{Co,p} = 1.5 \times 10^{-7}$$

$$K_{Ni,a} = 1.5 \times 10^{-11} \text{ m}^3/\text{mol}$$

$$K_{Ni,p} = 1.5 \times 10^{-10} \text{ m}^3/\text{mol}$$

For n-heptane under the same conditions, they found:

$$K_{Co,a} = 3.4 \times 10^{-6}$$

$$K_{Co,p} = 6.0 \times 10^{-6}$$

$$K_{Ni,a} = 2.4 \times 10^{-10} \text{ m}^3/\text{mol}$$

$$K_{Ni,p} = 1.0 \times 10^{-10} \text{ m}^3/\text{mol}$$

The effect of sodium was found to be negligible on the extraction of cobalt and nickel.

Ritcey et al. found that the separation factor for cobalt and nickel under conditions of practical importance, with 20–40% D<sub>2</sub>EHPA was 1.6 [47]. Ritcey and Lucas found that with 20% D<sub>2</sub>EHPA at an equilibrium pH of 6.0 with feed concentrations of 10 g/L cobalt and nickel, a single stage  $\beta_{Co/Ni}$  of 2.29 could be achieved [48]. Golding et al. found that the separation factor varied from 0.67–2.37 depending upon

the ratio of aqueous concentrations of cobalt and nickel [23]. These observations indicate the existence of an interaction between the two metals extracted.

Komasawa et al. noted that even at low loading, experiments with PC-SSA carried out containing both metals indicated, that the extractability of cobalt was greater than that predicted by the single metal extraction relationships described earlier [29]. The extractability of cobalt was also found to increase with the aqueous phase nickel concentration. They found that for D<sub>2</sub>EHPA, cobalt extraction could be increased by as much as 50%, while for PC-SSA, an enhancement by as much as 20% was feasible. Komasawa et al. felt these enhancements in extractability could be explained by the formation of cobalt-nickel-extractant complexes. These reactions were felt to occur in addition to the simple monomeric relations discussed earlier. Experiments designed to maintain equal amounts of cobalt and nickel in the organic phase at low loading with D<sub>2</sub>EHPA and PC-SSA found that the cobalt-nickel-extractant complex could be formed according to the relationship:



For D<sub>2</sub>EHPA, the equilibrium constant,  $K_M$  as found to be  $4.4 \times 10^{-10} \text{ m}^3/\text{mol}$ . and  $4.8 \times 10^{-12} \text{ m}^3/\text{mol}$ . in n-heptane and xylene respectively. For PC-SSA  $K_M$  was found to be  $3.2 \times 10^{-12} \text{ m}^3/\text{mol}$  in n-heptane. The value of  $K_M$  in xylene for PC-SSA was found to be less than  $10^{-14} \text{ m}^3/\text{mol}$ . Values for the separation constant calculated from these relationships (equations 10,11,12,13) were found to compare favourably with experimentally determined separation constants, although some scatter was apparent. Komasawa et al. found that at higher loadings of the organic phase, with binary metal extractions, neither the distribution relationships predicted by the single metal polymerization reactions nor the mixed metal complex reaction could adequately describe the distributions of cobalt and nickel in binary mixtures [29].

It was found that the distribution ratio of both metals increased with an increasing  $\text{Ni}^{2+}$  concentration. The separation factor,  $\beta_{\text{Co/Ni}}$ , also increased, suggesting that the extraction of cobalt was more sensitive to the presence of nickel in the aqueous phase than nickel itself. Komasawa et al. felt that the increases in the

ionic strength of the solutions might be the cause of some of the disagreement between the theoretical distributions and experimental values, because the extraction constants assumed may no longer be valid.

Experimental separation factors  $\beta_{\text{Co/Ni}}$  were found to increase over a loading ratio of 0–0.3 with 100 mol./m<sup>3</sup> and 50 mol./m<sup>3</sup> of extractant. The separation factor,  $\beta_{\text{Co/Ni}}$ , was found to increase from approximately 1000 to 4000 as the concentration of nickel in the feed solution increased from 0–1000 mol./m<sup>3</sup>. The concentration of cobalt in the feed solution was maintained between 60–100 mol./m<sup>3</sup>. Even at cobalt concentrations 300–3000 times the concentration of nickel, the extraction of cobalt was affected. Similarly, the presence of cobalt had a severe effect on the extraction nickel. Beyond an organic loading of 0.3, the separation factors were found to decrease sharply. The sharp decrease in the separation factor at loadings greater than 0.3 was felt to be due to an interaction between cobalt and nickel. Komasaawa et al. felt this behavior indicated that highly aggregated organic cobalt species, present under these conditions, tend to involve nickel. However, no mechanism could be found to explain this hypothesis.

In a practical study of the extraction of cobalt and nickel, Komasaawa et al. used 100, 200, and 400 mol./m<sup>3</sup> (25.7% (v/v)) PC-SSA to extract cobalt and nickel from aqueous solutions containing 500 mol./m<sup>3</sup> NaNO<sub>3</sub> [27]. In most cases an A/O ratio was maintained at a value of 1.0.

They found that for organic phase loadings below the range of 0.75–0.80, the viscosity of the organic phase was relatively constant. For most diluents, such as xylene, n-heptane, or 90% xylene–10% 2-ethylhexanol, the viscosity of the organic phase was approximately 1 centipoise. When 2-ethylhexanol was used as a diluent the viscosity of the solutions were approximately constant at 10 centipoise.

However, when the metal loading in the organic phase increased beyond the 0.75–0.8 range, the viscosity rose sharply for all the diluents except 2-ethylhexanol.

All metal ions tested, decreased the interfacial tension as a function of organic phase loading. This is an undesirable trend because a low interfacial tension will promote the stability of an emulsion. In hydrocarbon diluents, the interfacial tension was lowered moderately from 25 to  $19 \times 10^3 \text{ N} \cdot \text{m}^{-1}$  as cobalt loading increased from

0.001 to 1.0. However the interfacial tension is appreciably lowered (from 25 to  $6 \times 10^3 \text{ N} \cdot \text{m}^{-1}$ ) with an increase in nickel loading over the same range. Similarly, sodium reduced the interfacial tension from 22 to  $2 \times 10^3 \text{ N} \cdot \text{m}^{-1}$  as the loading ratio approached 1.0.

Komasawa et al. noted that a third phase began to form as the loading ratio  $[\overline{\text{Na}}]/[\text{LH}_2]_{\text{feed}}$  exceeded 1.3:1.

Cox et al. found that  $\text{p}K_a$  of PC-SSA (in 75% aqueous ethanol) was 4.10, while for  $\text{D}_2\text{EHPA}$  and Cyanex 272 it was 3.57 and 5.05 respectively [12].

With a small study of the different extractant systems, they found that although the interfacial tension of a  $\text{D}_2\text{EHPA}$  system decreased from  $31\text{--}24 \times 10^{-3} \text{ N/m}$  as the equilibrium pH of the aqueous phase increased, over the pH range 1–6, the interfacial tension of Cyanex 272 and PC-SSA remained essentially constant at  $31 \times 10^{-3} \text{ N/m}$ . The aqueous phase also contained 1M  $\text{NH}_4\text{NO}_3$ . The saturated surface concentration of PC-SSA in heptane or toluene was found to be  $6 \times 10^{-3} \text{ mol/dm}^3$ . These results are similar to those found by Vangrft and Horowitz [52].

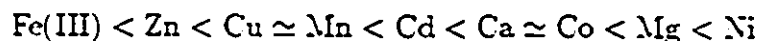
In 1984 Driesinger and Cooper published the results of a series of studies designed to determine the optimum operating conditions for solvent extraction with PC-SSA [16,17]. They found PC-SSA performed slightly better in diluents with a low aromatic content than in diluents with a high aromatic content. Most commercially available aliphatic diluents were acceptable with few apparent differences. Esso's low aromatic diluent Varsol DX3641 was chosen as the optimum diluent, because of its availability and low cost, and because of a marginally superior separating capability with PC-SSA.

They found in agreement with Komasawa et al. that as cobalt loading exceeded 75% of the maximum stoichiometric ratio (2:1), the viscosity of the organic phase became so great as to render the phase unmanageable [28,27].

The optimum equilibrium pH of the aqueous phase at 50 °C with 30% PC-SSA in Varsol DX3641 was approximately 5.1, which gave a separation factor,  $\beta_{\text{Co/Ni}}$ , of 2700 in batch tests with an A/O ratio of 4:1 and initial aqueous phase concentrations of 6 g/L Co and 8 g/L Ni in 1M  $\text{Na}_2\text{SO}_4$ .

Using 20% PC-SSA with an A/O ratio of 2:1 at 50 °C, distribution isotherms

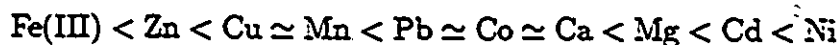
for a variety of metal ions in 1M Na<sub>2</sub>SO<sub>4</sub> were determined. They found, according to the magnitude of the pH<sub>0.5</sub> that the individual metal ions extracted in the order:



for this system. These results were similar to Preston's results with xylene [40,41]. The pH<sub>0.5</sub> for cobalt was found to be approximately 3.5. For nickel under the same conditions, the pH<sub>0.5</sub> was approximately 4.9. It should be noted that Fe(III) has a particularly high affinity for PC-SSA in sulphate media. The pH<sub>0.5</sub> for Fe(III) is approximately 0.1. This affinity was also demonstrated by the degree of difficulty required to strip Fe(III) from the organic phase. Driesinger and Cooper used 6M HCl to strip the solution [17].

Because calcium co-extracts with cobalt, Driesinger and Cooper pointed out that concentration of cobalt in the stripping stages would also cause the concentration of calcium and possible gypsum precipitation. This tendency was noted earlier by MHO [11]. Fitcey and Ashbrook had noted a similar tendency with the extraction of cobalt D<sub>2</sub>EHPA. They suggested that careful control of the number of stripping stages in a contactor could selectively remove cobalt from the organic phase and yet leave the calcium. A bleed stream from the organic phase pretreatment stage would be required to prevent calcium buildup in the organic phase [45,46,47]. In the IPC process, calcium was removed prior to the solvent extraction stages by selective precipitation as the fluoride [46].

Driesinger and Cooper also found the extraction order of the same metal ions in a chloride media. The pH<sub>0.5</sub> for cobalt at 50 °C with 20% PC-SSA with 1M (Na,H)Cl media was 3.0. For nickel the pH<sub>0.5</sub> was 4.3. The order of extraction of metals was determined to be:



The shift in the pH<sub>0.5</sub> values for cobalt and nickel, as well as with the other ions, does not necessarily mean that extraction occurs at a lower *actual* pH<sub>0.5</sub>. As Driesinger and Cooper pointed out, chloride media have been shown to introduce an error in pH measurements by lowering the *measured* pH to a value less than the *actual* pH, through the interaction and complex formation of chlorine atoms.

Chloro-complexation was not found to be a significant factor in the separation of cobalt and nickel. However, a few metals did show reduced extraction in chloride media, after correction of the pH measurement error. The reduced affinity of PC-SSA for these metals, as evidenced by a shift of their  $\text{pH}_{0.5}$  to a higher value was attributed to chloro-complexation. These metals were iron(III), cadmium, zinc, and lead.

Using 20% and 30% PC-SSA in Varsol DX3641 with 1M  $\text{Na}_2\text{SO}_4$  at an A/O ratio of 1, aqueous feed concentrations of 12 g/L Ni and 8 g/L Co were extracted at 25 °C, 40 °C, 50 °C, and 60 °C as a function of pH. Driesinger and Cooper found, as expected, that increasing the temperature of the phases resulted in a marked improvement in the cobalt-nickel separations. These improvements were found to be due primarily to increases in the distribution ratio of cobalt as a function of temperature. The distribution of nickel did not appear to have been affected by changes in temperature.

Several researchers attributed changes in the extraction of cobalt as a function of temperature to be due to a octahedral-tetrahedral conversion with the extractant  $\text{D}_2\text{EHPA}$  [4,45,20,41]. However, both Driesinger and Cooper and Komasaawa et al. indicate that for PC-SSA, no spectral evidence exists of this coordination geometry change, and that the improved separation of cobalt and nickel at higher temperatures must be due to some other mechanism [17,30].

Results similar to Komasaawa et al.'s found that the organic phase loading affected the separation of cobalt and nickel [16,17].

In 1983 a Chinese research team reported on the performance of a new phosphinic acid with the designation 5709 [6]. They found that this extractant had similar extraction properties similar to those of PC-SSA except that 5709 would preferentially extract cobalt over calcium. Unfortunately the structure of this new extractant was not disclosed.

### 1.1.3 Phosphinic Acid Extractants

In 1982, Rickelton et al. patented the use of phosphinic acids, or a salt thereof, as selective extractants of cobalt and nickel from aqueous solutions [44]. The authors

compared several phosphinic acids, and found them all to be superior to D<sub>2</sub>EHPA in regards to the separation of cobalt from cobalt-nickel solutions. Preston studied the behaviour of three extractants, D<sub>2</sub>EHPA, Cyanex CNX and RD 577 in xylene [41]. Cyanex CNX was an undisclosed phosphinic acid residue soluble in organic solvents at temperatures above 40 °C. At a temperature of 50 °C using 0.5 M extractant, as the dimer, in xylene, and an initial aqueous feed of 0.1 M metal nitrate in 1 M NH<sub>4</sub>NO<sub>3</sub>, he found that the p*H*<sub>0.5</sub> for Co was 3.45 while for Ni the p*H*<sub>0.5</sub> was 5.5. This extractant therefore provided a better Co-Ni separation than either D<sub>2</sub>EHPA or RD 577. By adding 25% (v/v) isodecanol to the phosphinic acid the difference in p*H*<sub>0.5</sub> between cobalt and nickel was reduced to 1.45 pH units at 50 °C. This shift would make the separating ability of Cyanex CNX equivalent to RD 577 at 50 °C. At 20 °C, 25% (v/v) isodecanol was required to maintain the solubility of Cyanex CNX in the organic phase. The p*H*<sub>0.5</sub> for Co was found to be 4.22 while that for Ni was found to be 5.20.

Preston found that the enhanced separation of the phosphonic/phosphinic extractants over the phosphoric acid extractants, was due to a shift in the nickel extraction isotherms at the same temperature. At different temperatures differences in the performance of an individual extractant could be attributed to shifts in the cobalt extraction isotherms. Cyanex CNX was later removed from the market due to its poor solubility at low temperatures.

In 1984, Rickelton et al. compared D<sub>2</sub>EHPA, PC-SSA, and Cyanex 272 [42]. Cyanex 272, a phosphinic acid reported to be bis-(2,4,4-trimethylpentyl)-phosphinic acid, HDTMPP, is manufactured by American Cyanamid Co. Using 0.1 M extractant in the diluent MSB 210 with an aqueous phase containing  $2.5 \times 10^{-2}$  M each of cobalt and nickel, at 25 °C, A/O=1, and an equilibrium pH of 4.0, they were able to show that the separation factors increased dramatically from D<sub>2</sub>EHPA, to PC-SSA to Cyanex 272.

One of the reported advantages that Cyanex 272 displayed over the other phosphorus-based extractants was its ability to extract cobalt in preference to calcium. The order of extraction based upon the individual metal ions' p*H*<sub>0.5</sub> were given as

[45.19.17]:

D<sub>2</sub>EHPA Zn < Cu < Co < Ni < Mg < Ca (Ritcey)

D<sub>2</sub>EHPA Zn < Ca < Cu < Mg < Co < Ni (Flett)

PC-SSA Zn < Cu < Ca < Co < Mg < Ni (Flett)

PC-SSA Zn < Cu < Ca  $\approx$  Co < Mg < Ni (Driesinger)

Cyanex 272 Zn < Cu < Co < Mg < Ca < Ni (Rickelton)

It is apparent that Flett's results are similar to those reported by Driesinger and Cooper for PC-SSA. However there appears to be some disagreement about the placement of the  $pH_{0.5}$  for calcium with D<sub>2</sub>EHPA.

If Ritcey's estimate is correct, as MHO tended to believe, then Cyanex 272 may not be any better than D<sub>2</sub>EHPA in terms of potential calcium precipitation. There may however be, for the extraction of Ca, a dependency on other metals in solution, or on the ionic strength, which would explain the reported inconsistencies in the data. Clearly the ability to select cobalt from calcium containing solutions without co-extraction of calcium is of considerable importance. This characteristic, perhaps more than any other, has made Cyanex 272 the most favoured potential cobalt extractant on the market today. There appears to be no debate as to the ability of Cyanex 272 to be more selective than D<sub>2</sub>EHPA for cobalt in cobalt-nickel solutions.

Rickelton et al. developed a continuous countercurrent extraction/scrubbing system which could obtain a cobalt to nickel ratio in the final extractant phase greater than 1000 and a raffinate containing less than 10  $\mu\text{g/L}$  of cobalt. The extractant phase contained 20% (v/v) Cyanex 272 as the  $\text{NH}_4$  salt in MSB 210 with 10% (v/v) nonylphenol. The circuit was maintained at 50 °C and consisted of 4 extraction stages and 2 scrubbing stages. With an A/O ratio in the extraction stages of 2 and an aqueous feed of 2.0 g/L Co and 99 g/L Ni in 20 g/L  $(\text{NH}_4)_2\text{SO}_4$  at a pH of 5.0, the loaded organic phase before scrubbing contained 5.5 g/L  $\text{Co}^{2+}$ , 0.21 g/L  $\text{Ni}^{2+}$ , and 0.016 g/L  $\text{NH}_4^+$  [43].

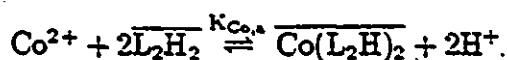
After scrubbing at an O/A ratio of 32 with 40 g/L  $\text{Co}^{2+}$  in two stages, the scrubbed organic phase was found to contain 5.6 g/L  $\text{Co}^{2+}$ , 0.004 g/L  $\text{Ni}^{2+}$  and 0.004 g/L  $\text{NH}_4^+$ .

Rickelton also reported some results for Cyanex 272 in his original patent [44]. Using 180 g/L (0.6M), bis-(2,4,4-trimethylpentyl)-phosphinic acid in Varsol DX3641 with 5% (v/v) isodecanol, he contacted an aqueous phase containing 1.9 g/L  $\text{Co}^{2+}$  and 103 g/L  $\text{Ni}^{2+}$  as sulphate salts, at 50 °C and an A/O ratio of 1. A separation factor,  $\beta_{\text{Co/Ni}}$ , of 407 at a pH of 5.12 was found. With 91% of the cobalt extracted, this result corresponds to a cobalt loading in the extractant phase,  $[\overline{\text{Co}}]/[\overline{\text{LH}_2}]_{\text{feed}}$  of 0.1.

A similar experiment with Solvesso 100 as a diluent instead of Varsol DX3641 contacted 1.97 g/L cobalt with 93.6 g/L nickel at 50 °C and an A/O ratio of 1. All of the cobalt and 3.1% of the nickel was extracted at a pH of 5.52. This of course resulted in a separation factor of infinity [44].

Preston, compared  $\text{D}_2\text{EHPA}$ , PC-SSA, and Cyanex 272. [40]. He too found Cyanex 272 to be a superior extractant to  $\text{D}_2\text{EHPA}$ . Cyanex 272 performed slightly better than PC-SSA on batch countercurrent experiments, but still required the same number of extraction stages to achieve a raffinate with less than 10 ppm of cobalt. The optimum pH for extraction of cobalt consistent with a low co-extraction of nickel was found to be about 5.25–5.5.

Danesi et al. reported that the stoichiometric relationship between cobalt and the extractant Cyanex 272 could be described by the expression [13,14]:



The conditional equilibrium constant,  $K_{\text{Co,a}}$ , was estimated to be  $6.0 \pm 0.1 \times 10^{-8}$  for the reaction in a non-complexing aqueous media, ( $[\text{NH}_4\text{NO}_3]=0.3\text{M}$ ), with toluene as an organic diluent, at 25 °C. A similar experiment for nickel established the stoichiometry as :



The conditional equilibrium constant was estimated to be  $1 \pm 0.2 \times 10^{-10} \text{ m}^3/\text{mol}$ . Both of these experiments were performed using the radioisotopes  $^{63}\text{Ni}$  and  $^{60}\text{Co}$  at tracer level concentrations, ( $10^{-3} - 10^{-6}\text{M}$ ). These equilibrium constants were derived on the assumption that the concentration of the dimer was equal to one half

of the monomer concentration [13,14]. These results were as expected from earlier measurements on D<sub>2</sub>EHPA and PC-SSA.

When the diluent was changed from aromatic to aliphatic, the HDTMPP stoichiometric coefficient for Co dropped from 2 to 1.4 as a result of the non-ideal behavior of the extractant in n-dodecane [13]. The actual nature of the non-idealities are not known, although similar behavior has been demonstrated for D<sub>2</sub>EHPA [45].

It is interesting to note that Danesi recognised the fact that the separation factors quoted by many researchers often appear contradictory and widely varied, and that this was due to the dependence of the separation factor on different extractant concentrations and different extractant loadings [13]. In a later paper he suggested that the behavior of extractants should be compared at a standard set of experimental conditions, namely 1 M extractant in toluene [14]. This standard condition however would bias the results of such a comparison towards those extractants which perform better in aromatic diluents. Furthermore, these conditions do not address the problems of synergism and interferences from other ions in solution.

When an acetate buffer was used in the aqueous phase to control the pH at equilibrium, the selectivity of the reagent, HDTMPP, was reduced [13]. Other experiments using supported liquid membranes with HDTMPP adsorbed on polypropylene film, indicated that the separation factor,  $\beta_{Co/Ni}$ , depended inversely upon the concentration of the unbound extractant, and the pH of the aqueous feed solution, as well as the diffusional parameters used to describe the membrane transport processes. The separation factor in this process was defined as the ratio of the permeability coefficients of cobalt and nickel through the supported membrane [13]. Danesi et al. found that for low metal ion concentrations, more selective cobalt-nickel separations could be achieved by liquid-liquid extraction. At higher metal concentrations, or lower free extractant concentrations, both techniques gave similar results ( $\beta_{Co/Ni} > 10^4$ ) [13]. The advantage of a membrane process is that counter-current extraction and stripping in the same unit is possible. The most significant disadvantage to the process is the fragility of the liquid membrane itself.

Preston's work although valuable in discussing the advantages of commercially

available extractants, did not shed any light onto the structure-selectivity relationship of the organophosphorus extractants [41]. To investigate this relationship, and the influence of extractant concentration, on the separation factor, Danesi et al. examined the role of the acid functional group, and the role of the alkyl side chains on a homologous series of extractants [14]. Using radioactive tracers, in 0.3M  $\text{NH}_4\text{NO}_3$  and toluene as the diluent, they found the apparent extraction coefficients decreased in the order phosphoric > phosphonic > phosphinic. For example, the apparent extraction coefficients for cobalt solutions with extractants with the 2-ethylhexyl side chain were:

$$\begin{aligned} \text{bis-(2-ethylhexyl)-phosphoric acid} &= 4.3 \times 10^{-6} \\ \text{" -phosphonic acid} &= 3.6 \times 10^{-7} \\ \text{" -phosphinic acid} &= 4.4 \times 10^{-8} \end{aligned}$$

For nickel the results were:

$$\begin{aligned} \text{bis-(2-ethylhexyl)-phosphoric acid} &= 2.0 \times 10^{-6} \text{ m}^3/\text{mol} \\ \text{" -phosphonic acid} &= 1.7 \times 10^{-8} \text{ m}^3/\text{mol} \\ \text{" -phosphinic acid} &= 5.8 \times 10^{-10} \text{ m}^3/\text{mol} \end{aligned}$$

At a 1 M free extractant concentration, as the dimer, the separation factor becomes the ratio of the apparent extraction coefficients for cobalt and nickel. This is only valid of course, when one ion acts independently of the others in solution. Therefore:

$$\begin{aligned} \beta_{\text{Co/Ni,phosphoric}} &= 22 \\ \beta_{\text{Co/Ni,phosphonic}} &= 21 \\ \beta_{\text{Co/Ni,phosphinic}} &= 76 \end{aligned}$$

As this relationship was found for a number of extractant series, it seems likely that the phosphinic acids should provide better separations of cobalt from cobalt-nickel solutions in toluene [14].

Introducing side chains to the  $\alpha$  and  $\beta$  positions of the alkyl or alkoxy group tended to decrease the apparent extraction constant for both cobalt and nickel.

However, the nickel extractions were affected more by the inclusion of side chains than the cobalt extractions. Therefore, the separation of cobalt from nickel was in general expected to increase [14]. It appears that steric hinderances affect both cobalt and nickel extraction, but that nickel extraction is affected most severely. Cyanex 272, or HDTMPP, was found to be approximately 190 times as selective as its phosphoric acid homologue under the proposed standard conditions, and almost 350 times as selective as D<sub>2</sub>EHPA .

As with the earlier extractants,[45,30,40] Danesi et al. found that HDTMPP existed as a dimer in the organic phase, even at concentrations as low as 10<sup>-3</sup>M. Spectroscopic studies indicated that cobalt in the cobalt-HDTMPP complex existed in the tetrahedral coordination geometry for all temperatures and extractant concentrations studied. Nickel was found to be octahedrally coordinated [14].

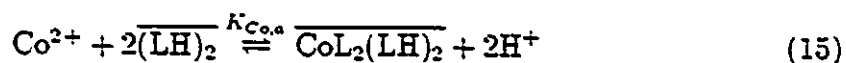
Karl Fisher analysis indicated that nickel co-extracted five molecules of water per molecule of nickel into the organic phase, which is similar to the earlier studies on PC-SSA. Cobalt as expected did not appear to co-extract any water into the organic phase. These results are reasonable when one considers the difference in electronegativity between nickel and cobalt. NMR studies indicated that the water was coordinated in either the first or second coordination shell of the nickel ion [14].

Fu and Golding examined the behavior of Cyanex 273 in Varsol DX 3641 for under both high and low metal loading conditions in the organic phase [54]. They fitted the high cobalt loading isotherms with semiempirical curves of the Langmuir and Freundlich type with good agreement between the predicted and actual responses. Nickel loading was found to vary linearly with the aqueous phase nickel concentration. Temperature was not found to change the coordination geometry of the metal-extractant complex. Evidence of polymerization in the organic phase under conditions of high cobalt loading was observed. Phase modifiers were found to be ineffective in reducing the increase in the organic phase viscosity. Using an analysis similar to that of Komasaawa et al. , Fu and Golding were able to calculate the polymer ratio  $\gamma$ , as a function of the organic phase loading.

### 1.1.4 Summary of Extractant Literature

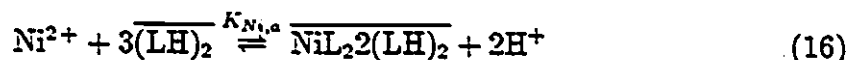
It is apparent that little coherent information can be drawn from the literature on the actual role of an extractant in the solvent extraction process. What data are available is restricted to the experimental conditions under which the measurements were taken.

Many authors have claimed that the characteristics of one phosphorus-based extractant can be extended to others [45]. This statement appears to be correct, in so far as the behavior of the phosphorus-based extractants at low metal loading of the organic phase is concerned. The general equation for the extraction of cobalt with phosphorus-based extractants at low cobalt loading is of the form:[45,28,13]



Variations in the form of the cobalt-extractant complex have been proposed, although little evidence is available to discern between them [45,28,40,13]. Even the stoichiometric coefficients have been observed to vary [13]. These variations are believed to be due to the non-ideal interactions between the diluent and the metal-extractant complex [13].

Similarly, for nickel extraction, the general equation, at low organic phase loadings is of the form:[45,28,13]



Similar difficulties to those with cobalt exist for nickel [45,28,13]. Furthermore, several authors have found that water is associated with the nickel-extractant complex, [45,30,40], although Preston appears to be the only researcher to have attempted to describe the nickel-H<sub>2</sub>O-extractant complex [40].

The actual structure of the organic phase cobalt and nickel species is unknown. Furthermore it is unclear if the dimerized extractant remains dimerized while coordinated to the metal species, or whether the dimer is broken.

The temperature dependency of the various commercial phosphorus-based extractants have been shown to be different. For D<sub>2</sub>EHPA the increase in the organic phase cobalt loading as a function of temperature was attributed to a change in

the coordination geometry of cobalt from an octahedral geometry to a tetrahedral geometry. Several authors have shown that this conversion does not take place in the PC-88A and Cyanex 272 systems. In these systems the cobalt-extractant complexes always appear to be in the tetrahedral geometry [28,29,13]. This difference in the apparent loading dependency on coordination geometry casts some doubt onto the claim that results from one extractant are transferrable to another. At higher metal loadings the metal extractant is observed to undergo a behavior change, and the phase becomes very viscous [9,29]. Polymerization has been proposed as the cause of this change and some researchers have attempted to quantify the reaction mechanism [28,9]. These approximations have met with some success although predicted equilibrium constants have shown significant scatter as a function of the phase loading.

It is interesting to compare the estimates of the single component extraction equilibrium constants  $K_{Co,a}$  and  $K_{Ni,a}$ , for the commercial extractants. (see Table 1)

As one can see, the estimates for the cobalt extraction equilibrium constant are within a factor of 10. However, a large discrepancy is apparent between the various estimates of the nickel extraction coefficients for a number of the commercially available extractants. The reasons for these discrepancies are unclear.

Although little data are available for the behavior of cobalt and nickel in single component extractions, even less information is available about the behavior of binary solutions. Several studies of PC-88A and the other extractants have examined binary mixtures of metal ions. MHO examined the behavior of a binary mixture of cobalt and nickel in sulfate solutions with the extractant PC-88A, using a continuous countercurrent process. They achieved very good separation with this system, however no data were given concerning the equilibrium relationship between the cobalt and nickel concentrations in each phase [11]. Flett et al. [20], indicated that at low metal ion concentrations, the separation factor had a dependency on pH, which was not expected, while Komasaawa et al. found that the extraction of cobalt was sensitive to the amount of nickel in solution [20,29]. Neither the single component equations for low loading of the organic phase nor the polymerization

Reference	Extractant	Diluent	$\frac{[(LH)_2]_{feed}}{M}$	$[anion]_{aqueous\ feed}$ M	$K_{Co,a}$	$K_{Ni,a}$ $m^3/mol.$
Madigan [32]	D <sub>2</sub> EHPA	kerosene	0.05	---	$8 \times 10^{-5}$	$2 \times 10^{-5}$
Brisk and McManemy [9]		kerosene	$\leq 0.5$	---	$1 \times 10^{-3}$	$2 \times 10^{-4}$
Komasawa et al. [28]		heptane	$\leq 0.6$	0.5M NO <sub>3</sub> <sup>-</sup>	$4 \times 10^{-5}$	$4.5 \times 10^{-8}$
Danesi et al. [13]		toluene	$\leq 0.6$	0.5M NO <sub>3</sub> <sup>-</sup>	$4.5 \times 10^{-6}$	$1.5 \times 10^{-9}$
		toluene	1.0	0.3M NO <sub>3</sub> <sup>-</sup>	$4.3 \times 10^{-6}$	$5.8 \times 10^{-10}$
Komasawa et al. [28]	PC-88A	heptane	$\leq 0.6$	0.5M NO <sub>3</sub> <sup>-</sup>	$3.4 \times 10^{-6}$	$2.4 \times 10^{-10}$
Danesi et al. [13]		xylene	$\leq 0.6$	0.5M NO <sub>3</sub> <sup>-</sup>	$7.5 \times 10^{-7}$	$1.5 \times 10^{-11}$
		toluene	1.0	0.3M NO <sub>3</sub> <sup>-</sup>	$3.6 \times 10^{-7}$	$1.7 \times 10^{-8}$
Danesi et al. [13]	Cynex 272	xylene	1.0	0.3M NO <sub>3</sub> <sup>-</sup>	$6 \times 10^{-8}$	$1.6 \times 10^{-10}$
Fu and Golding [54]		Varsol DX3641	$\leq 0.5$	0.2M SO <sub>4</sub> <sup>-2</sup>	$2.6 \times 10^{-8}$	$1.9 \times 10^{-10}$

Table 1: Estimated Extraction Coefficients for Cobalt and Nickel Extractions with Commercial Phosphorus-based Extractants at 25°C.

equations have been able to describe the equilibrium between mixtures of cobalt and nickel and the extractant. Komasaawa proposed another equation to describe the extraction of nickel and cobalt from aqueous sulphate mixtures with PC-SSA, but this equation was valid only under very restricted conditions [29]. At high organic phase loadings from binary mixtures of cobalt and nickel in aqueous solutions, Komasaawa suggested that nickel was not present at a significant level in the organic phase compared to that of cobalt and that the concentration of cobalt could be predicted by the polymerization reactions described earlier [29,27]. For processes which have high concentrations of cobalt in the feed solutions, this approximation may be sufficient. Unfortunately, nickel will always be present in the organic phase, to a greater or lesser extent, and as the solvent-free fraction of cobalt in the equilibrium aqueous phase decreases, nickel can be expected to play a more important role in the extraction of cobalt. Komasaawa's et al. approach may be adequate for the prediction of cobalt loadings, but it gives no indication of the amount of nickel in the organic phase, which is of considerable interest. A few methods have been proposed for the prediction of the equilibrium coordinates for a mixture of metal ions in aqueous solution in equilibrium with an extractant-diluent mixture [24,3].

## 1.2 Diluents

A diluent, or carrier solvent, in a solvent extraction process, is mainly required as a diluting medium, to lower the viscosity of the organic phase, and to facilitate the contacting between the two phases. There are several quite obvious characteristics that a diluent should possess, and these are:

1. The ability to retain in solution both the complexed and uncomplexed forms of the extractant.
2. A low solubility in the aqueous phase.
3. A high flash point and a consistently low rate of evaporation throughout the operating range of the process.

4. Chemical stability over the range of conditions used in the plant operation.
5. Moderate interfacial tensions to allow for relatively quick coalescence and dispersion times in mixing processes, and yet not restrict mass transfer rates.
6. Relatively inexpensive costs, and yet be readily available.

Ritcey and Ashbrook also pointed out that a diluent is used to allow for the adjustment of the extractant concentration to a level adequate for the particular job required. They aptly observed that there is little sense in having a high extractant inventory in a process if it is not required [45, p. 174].

The specific gravity of a diluent is a property which should be considered early in the selection stage of a solvent extraction process design. As a metal is loaded into the organic phase, the density of the phase will in general increase. In cases where the density approaches the density of water, phase disengagement may become difficult. The difference in density between the organic phase, consisting of the extractant, diluent and possibly other cosolutes, and the aqueous phase should be greater than 100 g/L to use gravitational separation [26]. Most commercially available diluents are specific fractions from a petroleum distillation process and are thus a complex mixture of hydrocarbons, which have similar boiling points. Usually the commercial diluents have densities of approximately 800 g/L [45, p.176] but these are increased by the addition of an extractant. Most commercially available extractants have fairly high densities. Densities of the combined organic stream which are less than 900 g/L are normally acceptable [26].

The viscosity of a solvent phase should not exceed 2 centipoise, otherwise the power consumption during agitation, and settling times in the settler will increase beyond acceptable levels [26]. Furthermore, the cost of pumping the solvent phase through piping will become prohibitively expensive.

As Ritcey and Ashbrook pointed out, comparatively little data exists on the role of diluents in the solvent extraction process. Prior to the 1950's diluent selection was usually done by choosing a locally available solvent, or kerosene. The logic of this choice being that the diluent played no role in the extraction of metal ions into the organic phase [45, p.172]. Specifically designed diluents were developed concurrently

with the development of the chelating extractants for copper recovery processes. These diluents were generally characterized by the properties listed above.

In fact, researchers have found that diluents do play a role in the extraction process although this role is not well understood. Unfortunately, little attention has been paid to this important phenomenon. As Ritcey and Lucas pointed out, proper selection of the diluent and modifier in a solvent extraction process can be almost as important as selecting the extractant [48].

The dielectric constant for most commercial diluents, of the kerosene type, is of the range of 2-3 [48]. However, the possibility of using diluents with a higher dielectric constant exists. Ritcey and Lucas found that for uranium extraction with  $D_2EHPA$ , increasing the dielectric constant of the diluent decreased the extraction capability of the extractant [48]. In alkaline solutions with  $D_2EHPA$ , they showed that metal loading decreased and nickel selectivity increased as the dielectric constant of the diluent increased. Variation of the aromatic character of the diluent with 20% (v/v)  $D_2EHPA$  in the Co-Ni- $SO_4$  system at 60°C could not be distinguish any relationship between aromaticity and the organic phase equilibrium Co/Ni ratio. Total metal loading decreased with aromatic content. As the naphthenic content of the diluent increased, both the equilibrium total metal loading and the equilibrium Co/Ni ratio increased in the organic phase [48].

The metal loading and cobalt-nickel selectivity of 20% (v/v)  $D_2EHPA$  was found to be a function of the solvating capacity of the diluent. Maximum metal loadings occurred with diluents with a solubility parameter in the 7.5-8.0 range. Cobalt selectivity with  $D_2EHPA$  was found to decrease with increasing diluent solubility parameters. Yet no relationship could be found between extraction and the Kauri Butanol Number, which is considered to be a measure of the solvating ability of the diluent [48].

Bouboulis found however that for  $D_2EHPA$ , the aromatic content of the diluent tended to increase the separation factor,  $\beta_{Co/Ni}$ . He found the effect to be more pronounced at a pH of 5.9 than at a pH of 7.0 with initial aqueous metal concentrations of 12 g/L Co and 10 g/L Ni as sulphates. At high concentrations of the extractant, (about 15% (v/v)), no effect of aromaticity on  $\beta_{Co/Ni}$  could be discerned. However

if 5% TBP was added the cobalt-nickel ratio in the organic phase was found to increase as the aromatic content increased [8].

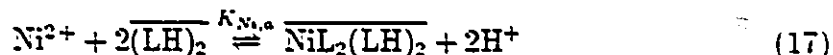
Preston investigated the effect of diluent aromaticity for RD 577 and D<sub>2</sub>EHPA using 0.5F extractant in xylene and n-heptane at 20°C [41]. He found that the  $pH_{0.5}$  for cobalt decreased from 3.68 to 3.47 for D<sub>2</sub>EHPA when the diluent was changed from xylene to heptane. For RD 577 the  $pH_{0.5}$  changed from 3.9 to 3.6. For nickel the changes were from 4.11 to 3.68 for D<sub>2</sub>EHPA and 5.12 to 4.67 for RD 577 respectively. The difference in  $pH_{0.5}$  between cobalt and nickel for an aromatic to aliphatic diluent change decreased for both extractants indicating that the cobalt nickel separation factor had decreased. However, this effect was counterbalanced by an increase in the cobalt loading.

Driesinger and Cooper accepted the fact that diluents of low aromatic character were the preferred diluents for PC-SSA and so investigated diluents with aromatic contents of less than 20% (w/w). They found, using 30% (v/v) PC-SSA, at 50 °C, with an A/O ratio of 4, and an aqueous feed stream with 6 g/L Co and 8 g/L Ni that the optimum pH for extraction was 5.1. At this pH, little difference was apparent between most of the diluents they tested. On the basis of the cobalt-nickel separation factor,  $\beta_{Co/Ni}$ , Esso Varsol DX3641 was determined to be the optimum diluent although most of the diluents could have been equally effective [17]. Unfortunately the organic phase cobalt loadings for these tests were not disclosed. Esso Varsol DX3641 is a low aromatic solvent (% aromatic < 5% (w/w))[31], and is readily available in North America. Driesinger and Cooper could not correlate any solvent properties to the selectivity of the extractant. However, they did note that the use of the diluent ESCAID 100 (20% aromatic (w/w))[45] was not recommended because of its poor selectivity [17].

Komasawa et al. [30] found that cobalt extraction with PC-SSA in a variety of diluents, at low cobalt loadings, followed the same extraction stoichiometry. (see equation 3), but had different extraction coefficients. Of the diluents they studied, the n-heptane-PC-SSA mixture had the highest extraction coefficient for cobalt,  $K_{Co,a} = 3.4 \times 10^{-6}$  while the xylene-PC-SSA mixture had the lowest  $K_{Co,a} = 7.5 \times 10^{-7}$ . For Nickel, they found that in n-heptane  $K_{Ni,a} = 2.4 \times 10^{-10} \text{ m}^3/\text{mol}$

while for xylene.  $K_{Ni,a} = 1.5 \times 10^{-11} \text{m}^3/\text{mol}$ . These single component results indicate that, if the extraction was to behave ideally, increased organic phase cobalt loading is favoured in aliphatic diluents, while increased cobalt/nickel separation is favoured in aromatic diluents. To that end these results were similar to Preston's [41].

It is interesting to note however, that Driesinger and Cooper's work using actual binary mixtures of the metal ions indicate that at least at a pH of 5-5.1, an aliphatic diluent in fact shows the greatest cobalt selectivity in contrast to the work by Preston and Komazawa et al [17,41,30]. Non-polar and moderate electron donor diluents did not affect the stoichiometry of nickel extraction, at low metal loadings. (see equation 4) However, strong electron donor diluents, such as the higher alcohols did tend to increase nickel extraction, by replacing and/or solvating the coordinated water in the Ni-extractant- $\text{H}_2\text{O}$  complex with alcohol [30,40]. The stoichiometry of the reaction also changed to :



From these observations it would seem clear that the diluent of choice for the PC-SSA extraction systems should be one with a low electron donating ability. Furthermore it seems apparent that the diluent should be one with a low aromatic character [40,41,16]. Driesinger and Cooper's results indicate that Esso Varsol DX3641 at an optimum equilibrium pH of 5.0, is the best diluent due to a higher selectivity than the other diluents tested and because of its availability. For this reason Esso Varsol DX3641 was the diluent chosen for this work.

### 1.3 Modifiers

Often in solvent extraction processes, a third phase can develop in the process which can adversely affect the performance of the process with regards to metal ion separation and phase disengagement [45]. These phases are usually of a density intermediate between the solvent phase and the aqueous phase, and are often attributed to the effect of the diluent on the extraction equilibria [45].

Most of the available data on third phase formation suggests that the problem is essentially a solubility problem which can be overcome, in most cases, by increasing the temperature of the extraction process and/or the addition of a third component to the organic phase, namely a modifier [48]. The components are extractants themselves, usually of the solvating type, and thus can be expected to affect the selectivity of a process. The most common modifiers used are long chain alcohols, such as isodecanol or 2-ethylhexanol, or other electron donating compounds such as tributyl phosphate or *n*-nonylphenol [45].

The criteria for choosing a third phase modifier are similar to those for choosing a diluent. The only additional criterion one would include is that the modifier should have the least negative effect on the extraction process as possible. These effects are usually measured in terms of extraction efficiency and separation ratios.

Little evidence is available concerning the effect of a modifier on the extractant-metal complex, although it is well established that modifiers can affect the extractability of a cation [45]. The change is usually deleterious although synergistic effects have been described for some mixtures of extractants [45,25]. Thus, if the extractability of one cation is affected more than another, then differences in the separation coefficient can be expected. It is also obvious that the greater the electron donor strength of a potential modifier, the greater its effect on electron accepting metal-extractant complexes. Thus, 2-ethylhexanol should affect the octahedral Ni-PC-SSA complex more than the tetrahedral Co-PC-SSA complex. Similarly, 2-ethylhexanol should have a greater effect on nickel extraction than tributyl phosphate.

The role of diluents has been reviewed by Ritcey and Lucas and by Bouboulis [48,5]. Both reviews concluded that the effect of modifiers on the extraction of cobalt and nickel with D<sub>2</sub>EHPA is unclear and that laboratory screening tests would be required to determine the best modifier for a particular process. Ritcey and Lucas felt that with D<sub>2</sub>EHPA, isodecanol allowed for a higher loading of metal into the organic phase at equilibrium than other modifiers, but poorer metal ion separations also resulted. TBP was found to give a slightly lower organic phase loading but a much better cobalt-nickel separation.

Fujimoto et al. found that TBP and isodecanol had negligible effects on cobalt loading in the organic phase but more significant effects on cobalt-nickel separation [22]. Using 14 g/L Co and 14 g/L Ni each in a feed solution they found that the addition 5% (v/v) TBP to the organic phase with 20% (v/v) of the ammonium salt of PC-SSA in kerosene at 50°C, and an A/O ratio of 1.0 reduced the percentage of cobalt extracted from 97% to 93% while nickel extraction dropped from 4.7% to 2.9%. Overall the separation factor dropped from 1315 to 491. Using 12 g/L Co and 14 g/L Ni with 5% isodecanol under the same operating conditions gave a separation factor of 241. Although they did not give any reason for using a modifier, MHO used a PC-SSA-TBP-ESCAID 110 mixture (15:5:80 (v/v)) as the solvent phase in a 3-stage countercurrent extraction process at an A/O ratio of 1.7:1 and at 40°C with acceptable results [11].

Flett et al. [20] reported that TBP affected the extraction of cobalt and nickel with SME 418 less than isodecanol, but that it did affect the separation of cobalt and nickel.

Preston investigated the effect of a variety of chemical additives by examining the  $pH_{0.5}$  shifts for cobalt and nickel with and without additives [40]. The addition of 0.5M (13.6% (v/v)) TBP to 0.5M (15.9% (v/v)) RD 577 in xylene shifted the  $pH_{0.5}$  for cobalt from 3.9 to 3.99. For nickel the  $pH_{0.5}$  shifted from 5.12 to 4.98. It is apparent therefore that cobalt loading in the organic phase was decreased while for nickel, loading was increased. These effects are believed to be due to the inhibition of the cobalt equilibrium expression by a competing extraction with the TBP, and to an increased solubility of the Ni-PC-SSA-TBP complex. These effects were similar to those with isodecanol. Although Preston's work indicates that modifiers will affect both the loading and separation of metal ions into the organic phase with PC-SSA, the concentrations he used were much greater than those commonly used. The commonly accepted concentration for modifiers in a solvent extraction system is usually between 0 and 5% (v/v) [45]. The question remains as to whether Preston's observations are significant at practical operating conditions. Komazawa et al. found that 10% ethylhexanol in xylene reduced the cobalt extraction constant from  $7.5 \times 10^{-7}$  to  $2.0 \times 10^{-7}$ . No information was given concerning the effect on

the nickel extraction constant although they noted that the addition of alcohols did increase nickel extraction and thus decrease the cobalt-nickel separation factor [30].

Nickel was found to appreciably reduce the interfacial tension of the systems with xylene as the diluent. Addition of 10% ethylhexanol was found to improve the situation. Third phase formation was found to occur for loading ratios above 1 for sodium extraction with EHPA in xylene. If a pretreatment step was used in a solvent extraction process with NaOH, to adjust the extraction pH to an appropriate level, then a modifier would be recommended to avoid the development of a third phase [30].

Ritcey observed that third phase formation was more likely to occur in aliphatic diluents than in aromatic diluents [45]. In the n-heptane-PC-SSA systems, the surface tension reduced moderately as the nickel loading in the organic phase increased, but Komasaawa et al. felt that the change was not significant enough to warrant any action [30]. Driesinger and Cooper did not use any modifiers for their experiments with the aliphatic diluent Varsol DX3641 because of their reputed deleterious affect on extraction. However, at conditions of high cobalt loading of the organic phase, third phase formation was found to occur under some experimental conditions [16].

It seems that little is actually known about the role of modifiers in the solvent extraction process. Furthermore, because of the diverse experimental conditions used by the previous researchers little information can be concluded from their experiments. What can be concluded is of a general rather than a specific nature.

Apparently TBP is one of the more moderate modifiers that can be used in the PC-SSA extraction systems. This is probably due to its low electron donating ability. Since one of the objectives in the selection of a modifier is that its effect should be the least deleterious, it would appear that TBP should be the modifier of choice. Even so, TBP appears to have an effect on both the loading and selectivity of a cobalt-nickel separation process. There appears to be some disagreement about the use of a modifier in the PC-SSA extraction systems. Several authors have recommended that no modifier be used because of their deleterious effects on the extraction process [40,17,20,8]. Others have felt that the addition a low concentration of modifier was an acceptable safeguard even though it might

reduce the cobalt-nickel separation [45.21.23.30.27.11]. Recognising the fact that third phase formation was a possible experimental danger [16] it was felt that a low concentration of modifier was justified, namely 5% (v/v), as used by Fujimoto et al [21.22].

## Chapter 2

# Mathematical Modeling

There are several ways to relate the operating variables of a system to the properties of that system. The simplest method for relating the properties of a system to its operating variables is to plot the values of those properties determined under different operating conditions and to draw conclusions from the characteristics of the resulting curves. This type of analysis however is very subjective, and can be prone to error, especially when the measurement of the true values of the properties and variables are masked by the effect of random error.

A more objective approach is to analyse the system from a statistical point of view, which allows for the inclusion of random error. Usually the operating variables and properties can be classified into three different classes:

- Independent Variables: Variables which can be set by the experimenter, and are as the name implies, independent of the system of interest.
- Parameters: are characteristics of the system which remain constant throughout the operating range of the system.
- Dependent Variables: Variables which are not explicitly under the influence of the experimenter, but are the result of the state of the system. As the name implies these variables are dependent on the state of the system.

The independent variables, and the parameters of a system determine, through functional relationships with each other, the state of the system and thus the value

of the dependent variables. When the number of functional relationships is equal to the number of dependent variables less the number of independent variables and parameters, the state of the mathematical system of equations is completely specified, and sufficient information exists to allow the experimenter to model the system, and determine the values of unknown parameters.

When one attempts to model the equilibrium behavior of a solvent extraction process from a mechanistic point of view, one is forced to consider the thermodynamic behavior of electrolyte solutions. An electrolyte is defined as a solution of polar or ionic compounds or mixtures of polar and/or ionic compounds which is capable of supporting an electrical current. This type of solution exhibits unusual thermodynamic properties and generally is not well described by classical thermodynamic theory. The equilibrium of an ion in a non-interactive medium has been described by the Debye-Huckel Theory [33]. Strictly speaking, aqueous media are not accounted for in the original Debye-Huckel Theory as they tend to interact with both the ions and themselves through association, solvation and ionization. As a result this theory was found to be valid only at very low ionic concentrations. More modern adaptations to the Debye-Huckel Theory have included terms for these effects, generally of an empirical nature. Recently, the classic Debye-Huckel Theory has been combined with modern vapour-liquid equilibria models such as Redlich-Kister, UNIFAC and UNIQUAC with moderate success [33,34]. However, even with these modern adaptations, the Debye-Huckel Theory is only valid for concentrations of metal ions in an aqueous solution which are below 0.2M [34].

In solvent extraction processes, a second problem exists in that the behavior of the extractant, metal ion, and extractant-metal ion complex must be described in the organic phase. Generally authors have tried to describe the equilibrium behavior of such species using the Scatchard-Hildebrand Solubility Parameter Theory. These models have met only with marginal success however, primarily because this theory is only valid for perfect or regular solutions [33]. Examples of such solutions usually include mixtures of isotopes or optical isomers, but in practice few such mixtures exist.

When one considers that the actual reaction mechanism between a metal ion

and a phosphorus based extractant is still unclear, and that the equilibrium between different solvated metal ions in the aqueous phase is generally unknown, it is not surprising that mechanistic models have so far proved unsatisfactory except under restricted conditions. Many authors have empirically fitted expressions which are similar to those based on a thermodynamic approach [5.1.50.51]. These models have been shown to be useful under limited conditions, such as at very low pH, for very dilute ion concentrations and relatively ideal behaving extractants. For the purpose of description, an ideal extractant is one which shows little departure from the equilibrium position defined by a simple mass action expressions defined by the equations 3 and 4. Other authors have attempted to describe the equilibrium relationships of solvent extraction processes using empirically fitted expressions similar to a simple mass action expression and mass balance requirements [53]. These models for the most part suffer from the same drawbacks as those cited earlier.

Few data have been collected on the behavior of mixtures of two or more ions in the aqueous phase and their equilibria with an extractant in an organic phase. As Mauer pointed out, mixing rules for the calculation of ionic activity coefficients have not been able to adequately describe the behavior of complex electrolyte mixtures [34]. Some researchers have attempted to describe such systems with arbitrary modifications to the mass action expressions but these have met with only limited success [53].

Semi-empirical and empirical modelling are popular methods of describing the behavior of cobalt and nickel solutions in solvent extraction processes. Often analogies to vapour-liquid equilibria and gas adsorption can be drawn [3]. Two such models which adequately describe the characteristics of single component extractions are the Langmuir and Freundlich Adsorption Isotherms [3]. The Langmuir Adsorption Isotherm was developed from the reaction kinetics of gas adsorption reactions. The form of the expression is given by:

$$Y = \frac{\theta_1 x}{1 + \theta_2 x} \quad (18)$$

where  $Y$  is given as the loading of the solid phase in moles solute/kg adsorbant, and  $x$  is the mole fraction of solute in the bulk phase. In the original theory, the

parameter  $\theta_1$  was a measure of the rate of adsorption of a solute from the bulk phase to the solid phase. The ratio  $\frac{\theta_1}{1+\theta_2}$  gave the maximum amount of solute adsorbed by the solid phase.

The Freundlich Adsorption Isotherm is an empirical correlation which is given by the expression:

$$Y = \theta_1 x^{\theta_2} \quad (19)$$

where  $Y$  is again the moles solute/kg adsorbant,  $x$  the solvent free mole fraction, and  $\theta_1$  and  $\theta_2$  are empirically fitted parameters. Analogous forms of these expressions have been used to describe the relationship between the equilibrium phase concentrations of metal ions in a solvent extraction process [3.23]. Although these models have no theoretical basis in solvent extraction their use is common.

Two types of modelling techniques used in binary and multicomponent solvent extraction processes were examined in this thesis. These modelling techniques use the information gathered from single component equilibrium extraction processes and then try to identify how the multicomponent extraction departs from the predicted single component behavior.

The first of these departure function models was proposed by Iannou et al. and is referred to as the Delta-Y ( $\Delta Y$ ) method [24]. This function calculates the difference between the actual and predicted concentrations of a component assuming that the component behaved in an ideal fashion. In this way the Delta-Y departure function is similar to Enthalpy Departure Functions in classical thermodynamics. The Delta-Y Function is given by the equation:

$$\Delta Y_i = Y_i - X_i(Y_i^*) \quad (20)$$

where  $X$  is the solvent free mole fraction of component  $i$  in the aqueous phase, and  $Y_i^*$  is the corresponding single component equilibrium concentration in the organic phase.

The second method used in this work was a method proposed by Barclay, and again takes its origin from classical thermodynamics [3]. The Pseudo Gamma function calculates the relative error between the actual equilibrium concentrations and

the predicted "ideal" concentrations. This function is given by the equation:

$$\gamma_{si} = \frac{Y_i}{X_i Y_i^*} \quad (21)$$

where  $X$  is the solvent free mole fraction of component  $i$  in the aqueous phase, and  $Y_i^*$  is the corresponding single component equilibrium concentration in the organic phase.

The distribution and equilibrium of a metal ion species between two phases is a complex function of several independent variables: The first and probably most important factor in an extraction process is the nature of the organic phase, and the nature of the extractant contained in it. These properties were discussed at length earlier in the sections on extractants, diluents and modifiers. Because the extractant is usually polar in nature the equilibrium pH of the mixture is also of great importance. By adjusting the pH of the solution one is also adjusting the ionic strength of the solution, the reactivity of the extractant molecule, and the individual phase affinities for the ion. Similarly the nature of the ion itself is important in determining how it will distribute between two dissimilar phases. Properties such as the valency, and ionic radius of an ion can affect the relative hydrophobicity of that ion compared to that of another. The temperature of the solution at equilibrium will also have an effect on the distribution of an ion between two phases. This is particularly true of reactive solvent extraction processes. The phase rule indicates that for  $n$  components, reacting with  $r$  reactions, distributed between  $p$  phases,  $n + r + 1 - p$  independent variables are required to completely specify the system. In a single component reactive solvent extraction process, the equilibrium mixture generally consists of two diluents (both organic and aqueous), an extractant, and a metal ion with a reaction occurring between the extractant and the metal ion. In its simplest form therefore, four independent variables would be required to specify the state of the system. Similarly a binary component, reactive solvent extraction process, in its simplest form would be specified by six independent variables.

The methods used for statistically fitting mechanistic, semiempirical, or empirical models to experimental data are well known, and will not be reviewed here. A

complete description of the methods and practices in statistical analysis are available in any of a number of monographs on that subject [15]. Nonlinear statistical modelling was used in this thesis to describe the behavior of the extraction process. Least squares analysis was used to determine the model which best described the experimental data. Least squares analysis minimise the sum of the squared residuals, (SSR), between the actual and predicted data points. The best model is the one which has the minimum number of significant parameters, the minimum SSR, and displays no apparent trends in its residual plots. The statistical modelling performed for this thesis was done using the Statistical Analysis Software, SAS, available on the University of Ottawa's mainframe computer. A sample of a typical SAS program is provided in the Appendix, Section 5.

## Chapter 3

# Experimental Procedure

The equilibrium data for the extraction of cobalt and nickel from aqueous sulfate solutions using 2-ethylhexyl phosphonic acid -2-ethylhexyl ester were obtained by simple shake out experiments.

The organic phase was comprised of 2-ethylhexyl phosphonic acid-2-ethylhexyl ester, tributyl phosphate, and the solvent Esso Varsol DX3641 in a 20:5:75 ratio by volume. This mixture provided good mass transfer characteristics for attaining equilibrium and for minimizing settling times.

The extractant, 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester was used as received from Diahachi Chemical Co. of Japan, under the trade designation PC-SSA. Its purity as measured by non-aqueous titration in 100% ethanol was measured as 99% acid. The phase modifier, tributyl phosphate was used as received from Anachemia, and had a measured density of 0.973 g/L, using calibrated 10 mL density flasks. Tributyl phosphate was included in these experiments because it was felt that third phase formation was a possible experimental danger, especially at high nickel and cobalt concentrations required to measure high binary equilibrium nickel concentrations in the organic phase. A low concentration of tributyl phosphate was used, namely 5% by volume as recommended by Fujimoto et al [21]. Varsol DX3641 is a low aromatic containing hydrocarbon solvent manufactured by Esso Chemical Ltd. and was used as received. Low aromatic diluents were recommended by Driesinger and Cooper as the diluents of choice for the solvent extraction of

cobalt and nickel using PC-SSA. The organic phase was mixed in the specified proportions and then washed with an equivalent volume of 1.0 M sulfuric acid,  $H_2SO_4$ , in a 3 L separatory funnel to remove any aqueous soluble compounds present in the mixture. After the mixture had settled, the phases were separated and the aqueous wash discarded. This procedure was repeated three times.

The resulting organic phase was then washed with an equal volume of water containing 20 g/L ammonium sulfate,  $(NH_4)_2SO_4$ , to remove any residual aqueous acid, and to saturate the organic phase with  $(NH_4)_2SO_4$ . This procedure was repeated three times to ensure a complete washing. The organic phase was then washed with equiformal aqueous ammonium hydroxide in 20 g/L ammonium sulfate. Because incomplete separation of the phases and emulsion formation can present a problem in the solvent extraction of cobalt and nickel, high ionic strengths are required in the aqueous phase. Barclay [3] found that sodium ions present in the aqueous and organic phases interfered with the analysis of cobalt and nickel. To avoid this interference, ammonium sulfate was used to maintain a high aqueous ionic strength. It was found that the conversion of ammonium ions to ammonia and its subsequent volatilization was not a significant factor in the experimental analysis. This was due to two restrictions in any experiment:

1. One of the necessary conditions in the solvent extraction process is the electrical neutrality of both phases, the organic phase and the aqueous phase. Since any  $NH_4^+$  added to the solution was added with an associated anion, almost all  $NH_4^+$  was required to neutralize these components in each phase.
2. The pressure of air left above the solutions in the sample flasks prevented a significant loss of ammonia to the vapor phase. At most, ammonia could build up to its vapor pressure in the sealed flask. This amount of  $NH_4^+$  was negligible when compared to the amount of  $NH_4^+$  required by the experiment. The experimental flasks were not found to be significantly overpressurized during phase contacting or any other subsequent analytical procedure.

The pH values of all solutions were measured with an Orion Research Digital Ionalyzer/501. An Orion 9105 combination electrode with an Orion Temperature compensation electrode were used for each measurement. A constant temperature water bath was used for all experiments and was provided by Fisher. Metal concentrations were determined with a Fisher Jarrel-Ash Dial Atom III Atomic Absorption Spectrometer. This instrument uses an oxygen-acetylene flame to burn a sample whose metal concentration is to be determined. If the metals in the sample are bound to other atoms or molecules, the thermal and chemical reactions in the flame cause the compounds to break down to the free atoms which can absorb and emit light of specific wavelengths. The free atoms in the flame are in an excited state and absorb and emit energy in the form of light to allow the atom to return to a lower energy state. The AAS has two main modes of operation, flame emission and flame absorption spectrophotometry. The use of each mode is governed by the particular metal to be determined. For Cobalt and Nickel, the recommended mode for analysis is the atomic absorption mode. Light is provided to the flame as a monochromatic wavelength by passing the light emitted from a hollow cathode ray lamp through a monochromator. The monochromator is a diffraction grating capable of isolating a particular wavelength of light. The monochromatic light passes through the flame and is absorbed by the excited metal ions. These ions then release the energy gained at a different wavelength than that absorbed, allowing the atoms to attain a lower energy state. By measuring the change in the intensity of the light as it passes through the flame, differences in concentration can be detected. At low concentrations of the analyte, the change in the intensity of the light as it passes through the flame is directly proportional to the concentration of free atoms in the analyte. This proportionality is well described by Beer's Law. By measuring the light absorbed by a sample and then comparing this absorption to that of a set of standard solutions, one can determine the concentration of the analyte in the sample. At low concentrations of cobalt and nickel, neither metal has an influence on the detection of the other. However, when one metal is present in the sample solution at a concentration much higher than the other, interferences in the detection of the metal of present at lower concentration can be detected. The

analytical procedure for removing these interferences is to matrix match the standard solutions to the sample. In other words when one encounters the interferences of one metal upon another, the suggested procedure to analyse the solution is to simulate the concentrations of the metals in the sample in the standard solutions. The recommended operating conditions for the analysis of Cobalt and Nickel are as follows:

- Use a 50  $\mu\text{m}$  monochromator, in the Absorption Mode.
- Use a 12 mA current with a Cobalt light source and measure Cobalt absorbance at a wavelength of 240.7 nm.
- Use an 8 mA current with a Nickel light source and measure Nickel absorbance at a wavelength of 232.0 nm.

Aqueous phase standard solutions were prepared with ammonium sulfate, cobaltous sulfate and nickelous sulfate in distilled water so that the final concentration of ammonium sulfate in the solution was 20 g/L. The final concentration of cobalt or nickel in the solutions were varied depending upon the concentration required. A third solution of 20 g/L ammonium sulfate in distilled water was prepared. The pH of the standard solutions were adjusted to the pH of 4.0 using dilute sulfuric acid or ammonium hydroxide as required. Analytical grade reagents were used for all standard solutions. Sample chemical specifications are given in the appendix. The standard solutions were sealed and used as required. 200 ml. volumetric flasks were used as reaction vessels for the solvent extraction experiments. 50 ml of the treated organic phase were introduced into the clean dry flasks along with a 2 cm teflon coated stirring bar, and the flask sealed with a glass or rubber stopper. Deliveries from each of the standard aqueous solutions were calculated earlier to give particular ion concentrations and ratios and volumes in the initial aqueous phase. These deliveries were made to the reaction flasks with clean dry volumetric pipettes. The initial aqueous phase concentration of ammonium sulfate was maintained at 20 g/L. All samples were calculated to give an initial aqueous phase volume of 50 ml and therefore an A/O ratio of 1.0. The predetermined volumes were delivered to the

reaction vessels and contacted with the treated organic phase. the flasks were again sealed and then shaken by hand for 2 minutes each. After an initial contact, the aqueous-organic phase mixture was placed on a magnetic stirrer and mixed to give a homogeneous mixture. The pH of the mixtures were then adjusted to the required equilibrium level by introducing a pencil thin pH electrode into the mixture. The pH of the mixture was adjusted to the required level using concentrated sulfuric acid and ammonium hydroxide as required. The volumes of acid and base added to the system were recorded and used later to calculate the volumes of each phase. Once the required equilibrium pH was attained the pH probe was removed and the flasks sealed. The reaction flasks were then placed in a thermostatically controlled water bath and allowed to settle overnight under a very mild shaking frequency of 30 oscillations per minute. After the phases had settled, the pH of the equilibrium aqueous phase was measured to ensure that the equilibrium position of the sample had not shifted from that required. If it had, the sample was again mixed and the pH adjusted . Once the sample had reached the required equilibrium position, at the required pH, samples of the organic and aqueous phases (approx. 30 ml each ) were drawn off using a clean dry glass syringe and placed in separate clean dry sample bottles. These sample vials were sealed and used later to determine the concentration of metal in each phase. A portion of each aqueous phase was diluted with distilled water to give an appropriate concentration for the analysis of each metal ion in the atomic absorption spectrophotometer. Five milliliters (ml) of the equilibrium organic phase was placed in a 100 ml. separatory funnel and contacted with 25 mls of 1M sulfuric acid . The funnels were shaken by hand for 2 minutes and then allowed to settle . The aqueous phase was withdrawn and saved in a 200 ml volumetric flask . This procedure was repeated 5 times to ensure complete recovery of the metal ions in the organic phase. The accumulated aqueous phase was then diluted to volume with distilled water. The resulting solution was then diluted with distilled water to an appropriate concentration for the analysis of the metal of interest with the atomic absorption spectrophotometer. Significant curvature was found for standard cobalt and nickel solutions in the absorption vs concentration curves for concentrations above 6 ppm. Standard solutions and sample solutions

were therefore diluted to give concentrations in the range of 1-6 ppm. The aqueous phase samples and the extracted organic phase samples were then analysed along with standard solutions using the atomic absorption spectrophotometer. The standard solutions were checked before, during, and after the samples to ensure that the instrument sensitivity did not drift during the analysis. If it was found to have drifted the spectrophotometer was restandardized and the analysis repeated. The results of the analysis were then used to calculate the original concentrations of the metal ions in each phase at equilibrium. If an adequate mass balance could not be demonstrated the analysis was repeated until it could. A Fortran program was used to calculate the concentration of each of the ions in each phase, and the error for each analysis. The program also calculated the distribution coefficients for each metal, the separation factor and the metal recoveries. The program, a sample data file, and a sample result file are included in the Appendix, Section 4.

Viscosity measurements were taken using Canon-Fenske calibrated viscometers in a temperature controlled water bath. Densities were measured using calibrated 10ml density flasks.

## Chapter 4

# Results and Discussion

As outlined on the section on experimental procedures, the investigation into the relationship between cobalt and nickel ions in aqueous solutions with the extractant PC-SSA took the form of two distinct sections. The first part of the investigations involved the determination of the optimum conditions for maximum separation of the two ions and the characterization of the pure component behaviors. In other words, how each ion behaved when it was extracted from the aqueous phase to the organic phase, in the absence of any other metal ion.

The use of the solvent Varsol DX3641 was suggested by Driesinger and Cooper [16,17] because PC-SSA performed marginally better at 25°C in this diluent than in other commercially available organic diluents. A 20% concentration of PC-SSA was used in the organic phase because this concentration was sufficiently high enough to be feasible as an economic process, and yet not introduce any problems associated with the viscosity of the organic phase. This corresponds to a formal concentration of 0.155 F for the extractant dimer complex.

As stated earlier, the phase modifier tributyl phosphate (TBP), was introduced at a 5% concentration because Driesinger and Cooper [16,17], and Preston [40,41] had noted that some third phase formation was possible.

It was quickly noted that the extraction of cobalt or nickel from aqueous solutions with the organic extractant mixture was prone to emulsions if the ionic strength of the final aqueous phase was not sufficiently high. This was especially true of the

experiments which had low initial metal ion concentrations. This effect was due to the fact that as cobalt or nickel was removed from the aqueous phase to the organic phase, the ionic strength of the aqueous phase would drop to a point where emulsion formation was favored. In order to combat this effect a cosolute was required which would have to satisfy two criteria:

- The cosolute must not interfere with the analysis of cobalt or nickel in either the organic or the aqueous phase.
- The cosolute should, as closely as possible, simulate the conditions in an industrial process.

Since most industrial processes have a high ionic strength working solution which is a complex mixture of inorganic salts, the second condition was a relatively easy one to satisfy. To reduce the complexity of the experiment however, a high ionic strength solution with a minimum number of components was required. The first condition was solved by Barclay for D<sub>2</sub>EHPA solutions, by using NaOH to adjust the pH of the solution and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as a cosolute. However, sodium ions are easily absorbed by the organic phase even in the presence of large amounts of cobalt and nickel. Barclay found that sodium ions had a significant interference in the spectrophotometric determination of cobalt and nickel.

With these problems in mind, it was decided to use (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as a cosolute, in a fashion similar to the work of Barclay, and others, and to use NH<sub>4</sub>OH as a means of adjusting the pH of the solutions. This method was used because NH<sub>4</sub>OH would not interfere with the analysis of either cobalt or nickel because it would break down into the free radicals and elements already present in the flame of the AA spectrophotometer.

Samples of cobalt and nickel sulfate solutions were prepared according to the method outlined in the experimental section. These were prepared with distilled water to a pre-set concentration, using the standard solutions of aqueous cobalt and nickel sulfate which were prepared prior to the experiments. A batch of the organic phase comprised of 20 % PC-SSA , 5 % TBP and 75 % Varsol DX3641 was also prepared as required.

## 4.1 Pure Component Extraction Studies

It is well known that the ability of an extractant to remove a metal ion from an aqueous solution is a strong function of the final pH of that solution at equilibrium. The first series of experiments were designed to determine the equilibrium pH of the aqueous solution which would give the maximum amount of separation between cobalt and nickel ions.

Using the method outlined earlier, mixtures of aqueous cobaltous sulfate were contacted with the prepared organic phase and allowed to come to equilibrium at various pH. Similarly mixtures of aqueous nickelous sulfate were also contacted with the prepared organic phase. A mass balance was performed on the aqueous and organic phase of each sample, for the metal ion. If a total mass balance could not be demonstrated, to within  $\pm 10\%$  with a 95% confidence, the experiment was repeated until this criterion could be demonstrated. The concentration of the metal in each of the phases was calculated using a computer program written by the author. As indicated earlier, sample of the program and its output is included in the appendix. The program used the Atomic Absorption Spectrophotometer's response to a series of standard aqueous cobalt and nickel samples to regress a standard response curve and its 95% confidence interval. This data was then used to estimate the concentration of cobalt and nickel in the sample solutions and assign a confidence interval to these estimates. This data was then used to calculate the mass balance.

A sharp change in the viscosity of the pure cobalt samples was noted as the organic phase loading, increased beyond 70%, as shown in Figure 1. The organic phase loading calculated by dividing the actual organic phase metal concentration by the formal concentration of extractant functional groups in the organic phase. The experimental data is listed in Table 3 and Table 4 in the Appendix. This change was so abrupt that the exact inflection point of the viscosity curve as a function of metal loading was difficult to estimate. The viscosity changed from approximately 2 centipoise at a loading of 70% to an unmanageable viscosity of approximately 2 poise at an organic loading of 80%, an increase of nearly 100

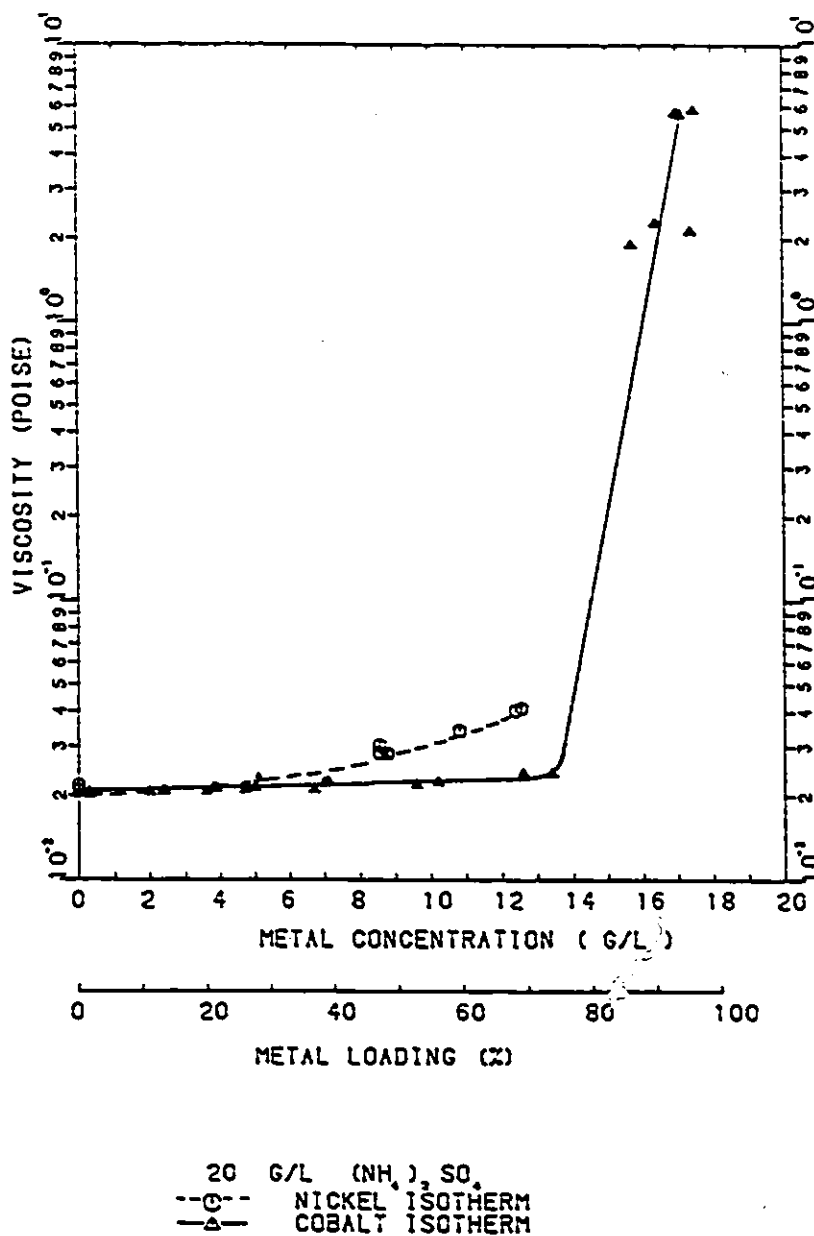


Figure 1: The Viscosity of Metal Loaded Organic Phase at 25°C as a Function of the Phase Loading for Aqueous Cobalt and Nickel with the Extractant PC-SSA

times. This abrupt change in the behavior of the cobalt-PC-SSA complex effectively limits the usable organic loading range for the extraction of cobalt to loadings less than 70% , which corresponds to an equilibrium pH of approximately 6.8. This observation is in agreement with the data found by Driesinger and Cooper[16,17], and that of Komasaawa et al.[30]

The same trend was not apparent for the pure component extraction of nickel in 20 g/L aqueous ammonium sulfate solutions with the extractant solution as shown in Figure 1. The viscosity of the nickel-extractant complex slowly increased from a value of 2 centipoise at a loading of 0% to a value of 4 centipoise at a loading of 70 % . It was found that above a pH of 6.75, the nickel-ammonium double salt precipitated out of solution at a temperature of 25°C. This corresponds to an organic phase loading of 70 % .

The limitations imposed on the practical extraction of cobalt and nickel from sulfate solutions found in this study were that the equilibrium pH must not exceed 6.75, because the nickel-ammonium double salt would precipitate, and that the organic phase loading of cobalt must not exceed 70% to prevent the formation of a viscous cobalt/PC-SSA polymer complex. The nature of this polymer complex is not clear, although Komasaawa et al [28,30], attempted to describe the stoichiometry of such a polymer in toluene, assuming that the ratio of the nth polymer to the (n-1)th polymer was constant. This was discussed earlier in this thesis.

The pure component data for cobalt and nickel were plotted as the percentage of metal ions extracted as a function of the equilibrium pH in Figure 2.

The data can also be shown as the organic phase loading as a function of the equilibrium pH of the aqueous phase, as shown in Figure 3. The data are listed in Table 5.

One of the interesting pieces of information required to evaluate the effectiveness of a particular extractant for potential extractant use is the relationship between the equilibrium aqueous phase metal concentration and the equilibrium organic phase metal concentration. This relationship is a function of the equilibrium temperature and hydrogen ion concentration, so temperature and pH must be remain constant

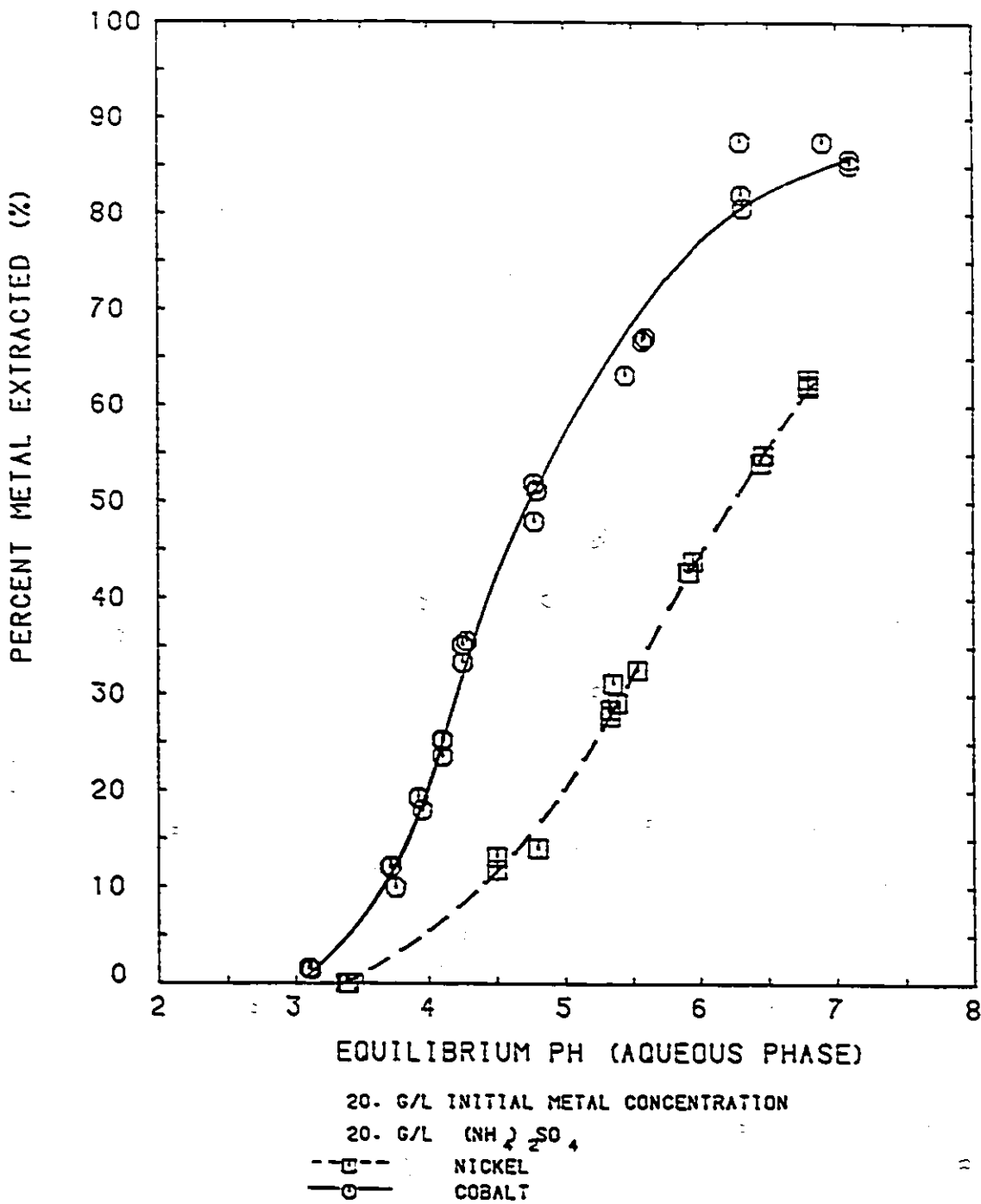


Figure 2: The Pure Component Percent Metal Extracted for Aqueous Cobalt and Nickel at 25°C with PC-SSA as a function of Equilibrium pH

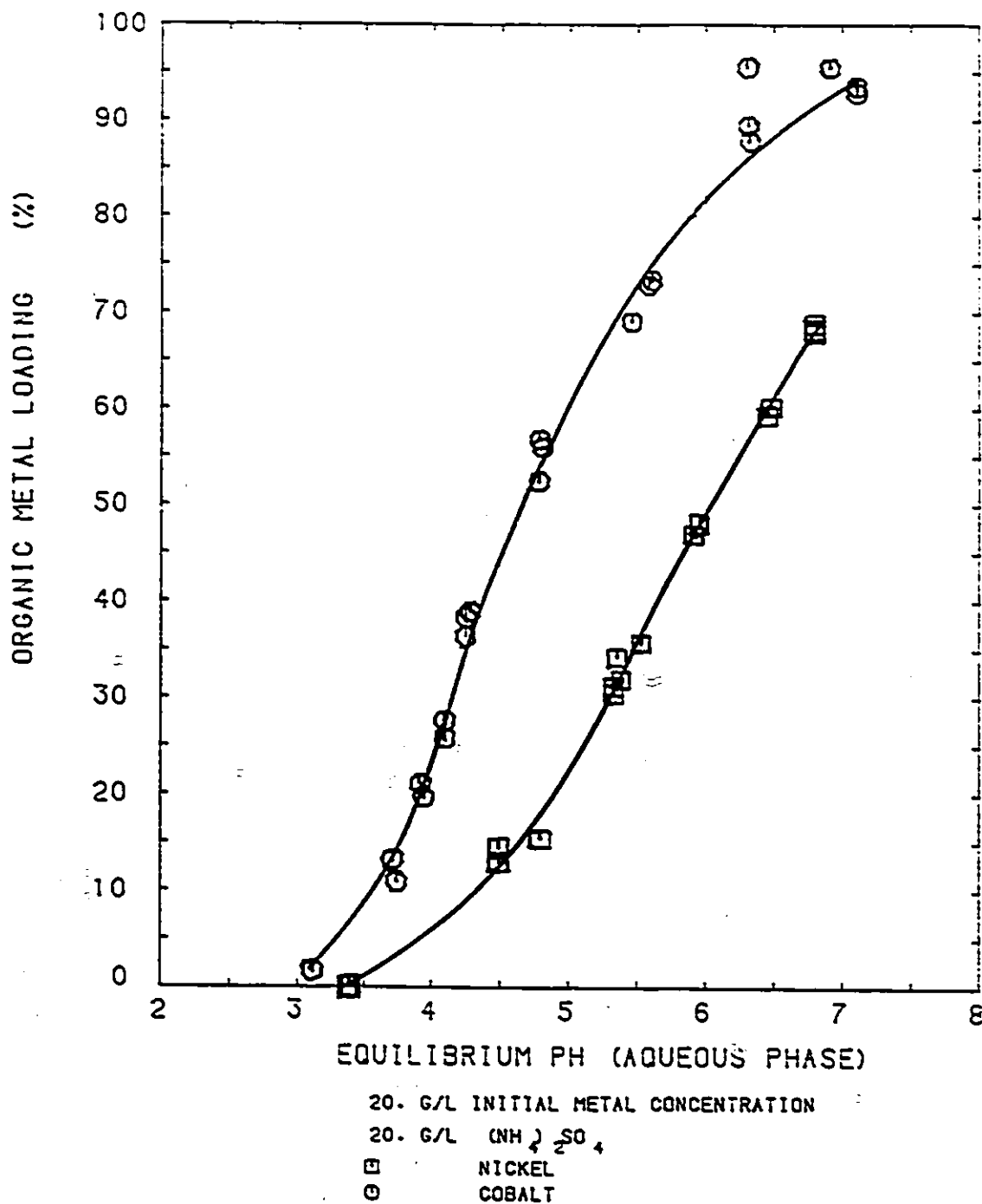


Figure 3: The Pure Component Extraction Phase Loading for Aqueous Cobalt and Nickel at 25°C with PC-SSA as a function of Equilibrium pH

for the relationship to be meaningful. A common method for measuring this relationship is to quote a separation factor,  $\beta_{Co/Ni}$ , as noted in the literature survey. As Ritcey and Ashbrook indicated, if the separation behaves in an ideal fashion, then the separation factor can be determined from the pure component behavior, as the behavior of one ion would be unaffected by the behavior of the other. However, as several researchers have indicated, a separation factor is a function of the phase loading and the concentration of ions in the the aqueous phase. Therefore measuring a separation factor with pure component data would be of little use in predicting the behavior of two metals in a binary extraction scheme.

However in order to develop a consistent set of data, as indicated earlier, a constant pH must be maintained. Ideally one would like to operate at a pH , at which the organic phase has a high affinity for one metal ion as compared to the other metal ion , and displays reasonably fast kinetic behavior. As stated earlier practical limitations were imposed on the system by the viscous behavior of the cobalt-extractant mixture complex, and the precipitation of the nickel ammonium double salt. Taking these into account, a pH of 5.0 was chosen to perform the binary metal experiments at, because at this pH the organic phase displayed the greatest difference in affinity for cobalt over nickel, and is reported to have shown reasonably fast kinetics [16,17]. This is the same pH as that suggested by others [40,41,16,17].

The next series of experiments were designed to determine the pure component extraction isotherms for cobalt and nickel sulfate with 20% PC-SSA, 5% TBP, in Varsol DX3641 at 25°C, and a pH of 5.0. The method used was described in the experimental portion of this thesis. The equilibrium pH of the solution was adjusted by adding a small amount of H<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>OH to the mixture. The volume change was taken into account in the calculations so that no error was made due to volume changes in the solution. Barclay in his experiments with D<sub>2</sub>EHPA had adjusted the initial pH of the organic phase to 4.0 ± 0.2 prior to contacting with the aqueous phase. This allowed the final equilibrium pH values to lie in the 5.3–6.4 range such that both cobalt and nickel loading can be considered independent of the pH. This was because the pH extraction curves for D<sub>2</sub>EHPA are relatively flat in this pH

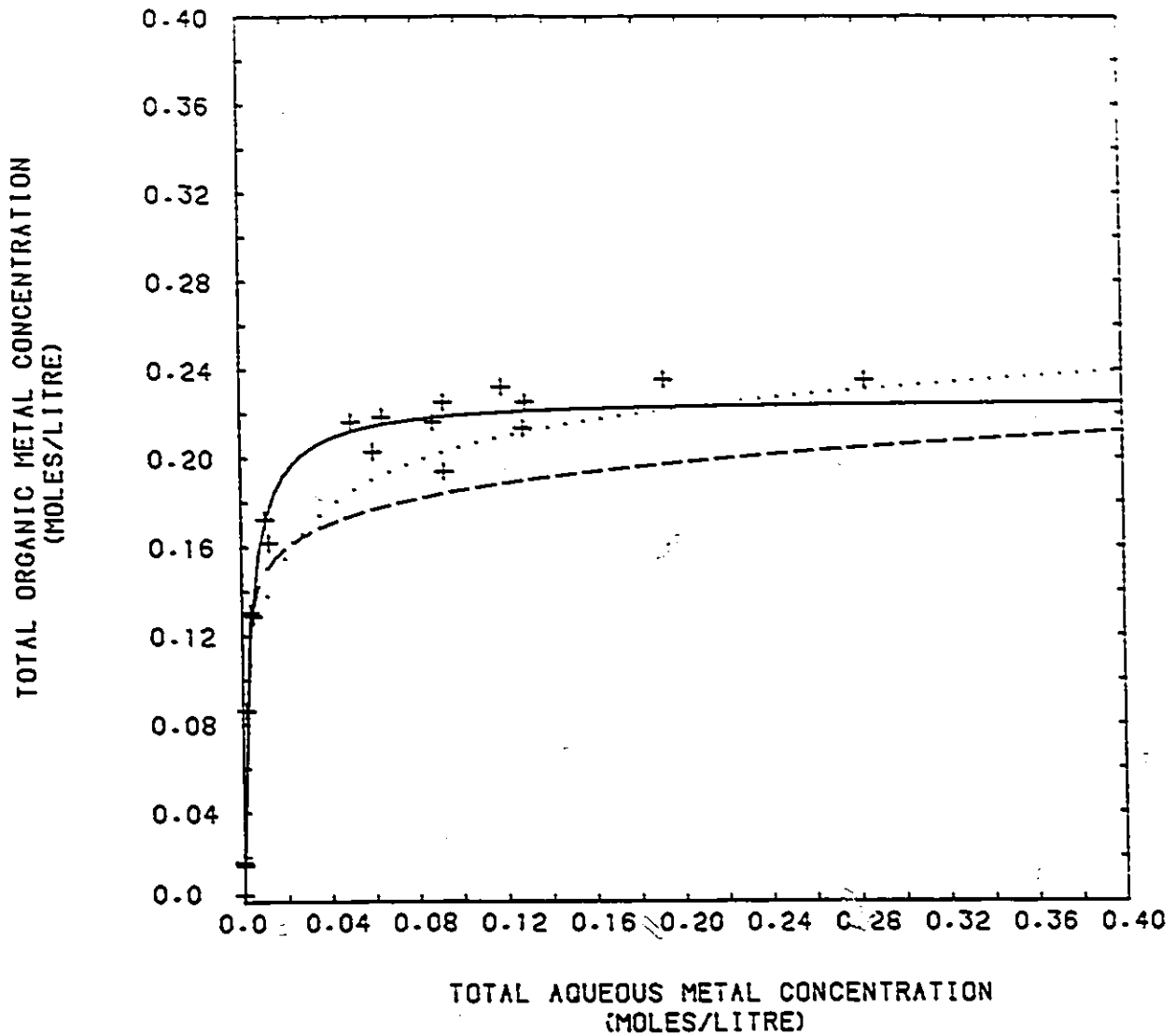
range.

However, for PC-SSA, as shown in Figure 3, the optimum extraction pH of 5.0 is in a range where small changes in the pH can greatly affect the final loadings in the organic phase. A method was developed to control the pH of the final equilibrium to within very tight tolerances, by measuring the pH within the equilibrium solution with a pencil thin pH probe, and adjusting the pH by adding 1M H<sub>2</sub>SO<sub>4</sub>, or 1M NH<sub>4</sub>OH until the final desired pH was achieved. The 95% confidence interval for the equilibrium aqueous pH of all of the remaining samples was  $5.02 \pm 0.01$ .

Samples of cobalt sulfate mixed with 20 g/L aqueous ammonium sulfate were prepared and contacted in the same fashion as in the earlier experiments. After the equilibrium pH had been adjusted to a pH of 5.0, a sample of each of the phases was taken and the concentration of cobalt measured. Again, a mass balance within 10% was required, before the data were considered to be acceptable. Samples of nickel sulfate mixed in the same fashion were similarly analysed. The data are shown in Table 6.

The cobalt organic phase equilibrium metal concentration was then plotted against the aqueous phase cobalt metal concentration, to give the cobalt pure component extraction isotherm for the extractant mixture containing PC-SSA. These data are shown in Figure 4. Three lines are shown in Figure 4. The solid line is the best fit model found for the cobalt-PC-SSA pure component extraction isotherm. Due to the complex reaction stoichiometry involved, semi-empirical curve fitting techniques were used to represent the data. Earlier work by Golding et al. [23] had shown that the Langmuir or Freundlich isotherm were capable of representing equilibrium data. Barclay had used a combination of both isotherms to represent the equilibrium data for cobalt and nickel with the extractant D<sub>2</sub>EHPA, at its optimum extraction pH, and his results are shown with the dotted line [3]. Similarly Fu and Golding's work with the extraction of cobalt with Cyanex 272 at its optimum pH is shown with the dashed line [54]. The general form of the equation used to fit the data is given below:

$$C_{\text{org}} = \frac{\theta_1 \theta_2 C_{\text{aq}}}{1 + \theta_2 C_{\text{aq}}} + \theta_3 C_{\text{aq}}^{\theta_4} + \theta_5 e^{\theta_6 C_{\text{aq}}} \quad (22)$$



ORGANIC PHASE COMPOSITION: 20% EXTR. . 5% TBP. 75% VARSOL DX3641  
 EXTR. —+— = PC-88A      ..... = D2EHPA      - - - - - = CYANEX 272  
 AQUEOUS PHASE COMPOSITION: 20 G/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>  
 PH(AQ) —+— = 5.02±/-0.01      ..... = 5.85±/-0.06      - - - - - = 5.47±/-0.06

Figure 4: The Pure Component Extraction Isotherms for Aqueous Cobalt at 25°C with the Extractants: PC-SSA, D<sub>2</sub>EHPA . and Cyanex 272

where

$C_{org}$  = the organic phase metal ion concentration in moles/Litre.

$C_{aq}$  = the aqueous phase metal ion concentration in moles/Litre.

$\theta_i$  = fitting parameters

It should be noted that Fu did not use this equation form for his analysis of the pure component extraction of nickel. He found that it did not give an adequate fit to the data and as a result used a polynomial regression to fit his data. His equation is given by:

$$C_{org} = \sum_{i=1}^5 \theta_i C_{aq}^{i-1} \quad (23)$$

The three systems were similar in that they employed an organic phase comprised of extractant:TBP:Varsol DX3641, in a 20:5:75 ratio (v/v). Each extractant system was modelled using data at a pH which was optimum for the separation of cobalt and nickel for that system. This was done to allow a direct comparison of the extractants at their optimum performance. The best models which could be determined for these systems are given in Table 2.

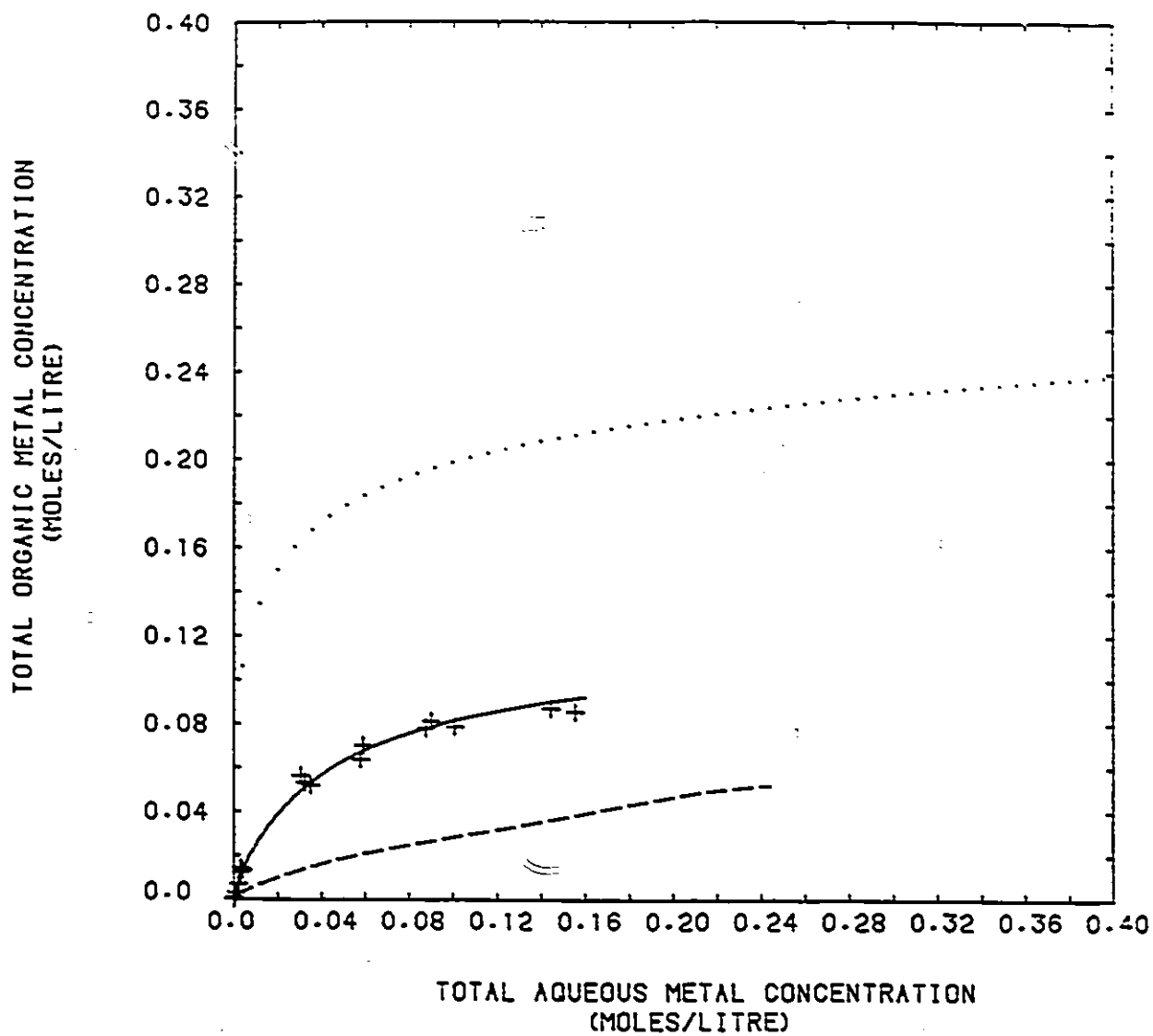
The Residual Plots for the "Best Fit" Models are shown in Figure 12 and Figure 13. The models for the D<sub>2</sub>EHPA and Cyanex 272 extraction systems were taken from the works of Barclay and of Fu, and converted into molar units.

It is clear from the data that there is little difference between the extractants at their optimum pH in terms of the capacity of the extractants for cobalt. The maximum concentration of cobalt achievable for PC-SSA in the organic phase at 25°C and a pH of 5.02 ± 0.01 is 0.2264 moles/L. This corresponds to a organic phase loading of approximately 73 % , based upon the dimer population.

A similar analysis was performed using the pure component data for nickel at 25°C. contained in Table 2. Its pure component extraction isotherm is shown in Figure 5. Again the pure component isotherm for nickel at 25°C was compared to similar isotherms measured by Barclay for D<sub>2</sub>EHPA . and Fu for Cyanex 272 at their optimum extraction pH. It is apparent that for nickel at the optimum equilibrium

Table 2: Fitted Parameters for Pure Component Isotherms of Aqueous Cobalt and Nickel Solutions in Equilibrium with PC-SSA, D2EHPA, and Cyanex 272 at 25°C. Organic Phase = 20% extractant, 5% TBP, 75% Esso Varsol DX3641 Aqueous Phase = 20 g/L  $(\text{NH}_4)_2\text{SO}_4$

	Extractant		
	PC-SSA	D2EHPA	CYANEX 272
pH	$5.02 \pm 0.01$	$5.85 \pm 0.06$	$5.47 \pm 0.06$
	Cobalt		
$\theta_1$	0.2272	0.0767	0.1103
$\theta_2$	276.94	58.933	1007.8
$\theta_3$	0	0.1868	0.1243
$\theta_4$	0	0.1284	0.2140
$\theta_5$	0	0	0
$\theta_6$	0	0	0
SSR	0.0022	see Ref[16,17]	see Ref.[54]
	Nickel		
$\theta_1$	0.1076	.0515	0.0016
$\theta_2$	22.987	58.71	0.4895
$\theta_3$	0	0.2176	-3.9048
$\theta_4$	0	0.147	-20.371
$\theta_5$	0.004	0	-24.711
$\theta_6$	3.633	0	0
SSR	.0013	see Ref[16,17]	see Ref.[54]



ORGANIC PHASE COMPOSITION: 20% EXTR. . 5% TBP. 75% VARSOL DX3641  
 EXTR. —+— = PC-88A      ..... = D2EHPA      - - - = CYANEX 272  
 AQUEOUS PHASE COMPOSITION: 20 G/L  $(\text{NH}_4)_2\text{SO}_4$   
 PH (AQ) —+— = 5.02 $\pm$ 0.01      ..... = 5.85 $\pm$ 0.06      - - - = 5.47 $\pm$ 0.06

Figure 5: The Pure Component Extraction Isotherms for Aqueous Nickel at 25°C with the Extractants: PC-88A, D2EHPA, and Cyanex 272

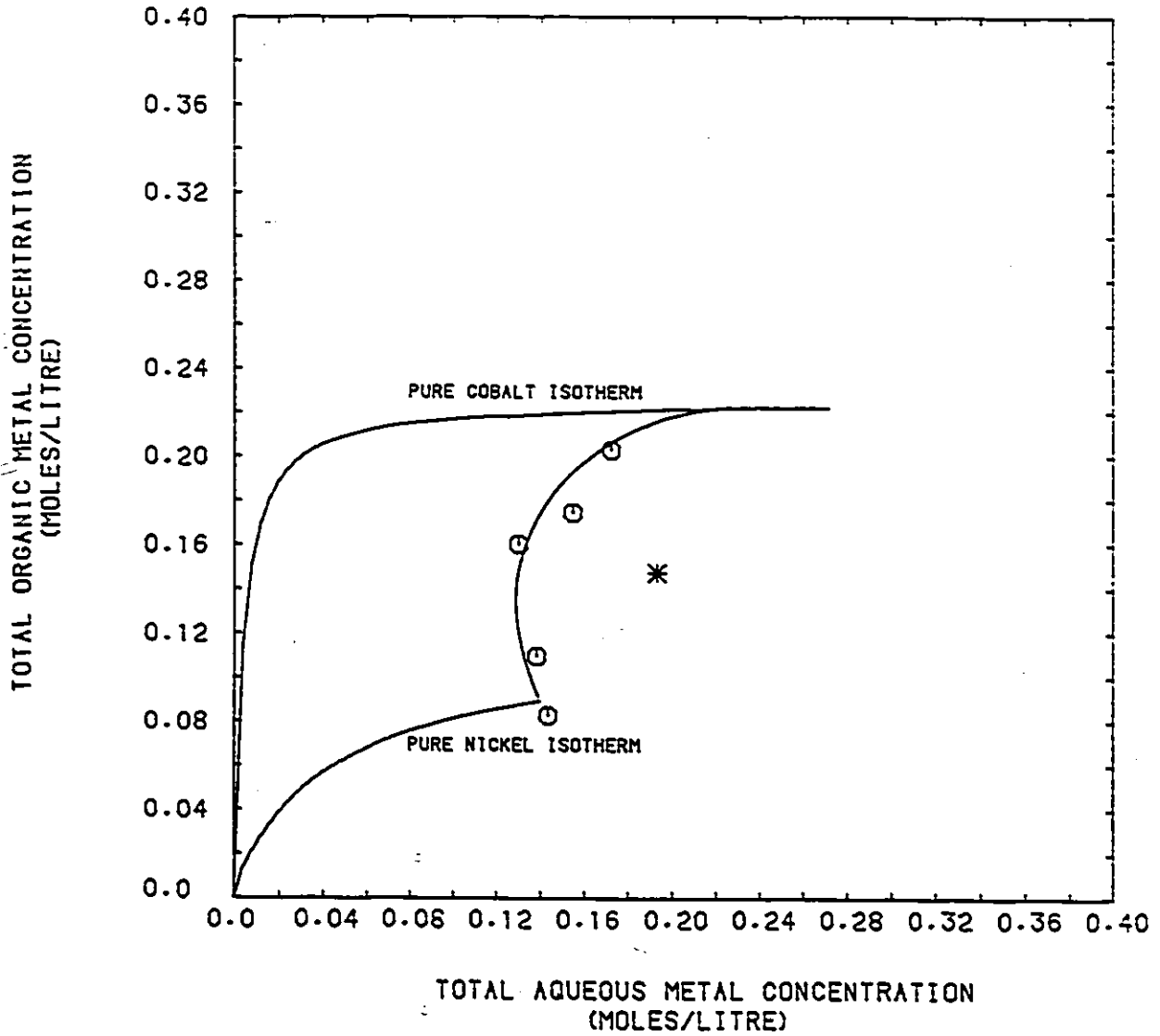
extraction pH, the affinity of PC-88A for nickel is significantly lower than D<sub>2</sub>EHPA, and significantly higher than that for Cyanex 272. This result is similar to those found by others. The maximum concentration of nickel that could be achieved in the organic phase was 0.086 moles/L with an aqueous phase concentration of 0.15 moles/L. This corresponds to a maximum phase loading of approximately 27.7%. Beyond this aqueous phase concentration, the nickel-ammonium double salt precipitated out of solution.

## 4.2 Binary Component Extraction Studies

Samples of cobalt sulfate and nickel sulfate, from standard solutions were added to an aqueous sample of 20 g/L ammonium sulfate to give a predetermined initial aqueous phase concentration, cobalt:nickel ratio, and a total initial aqueous phase volume of 50 ml. As outlined in the experimental section, a preconditioned 50 ml sample of organic phase was added to the sample flask and the sample equilibrated. Final equilibrium pH values were adjusted to a pH of  $5.02 \pm 0.01$  by the addition of small volumes of H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>OH. The analysis of each sample then continued in much the same fashion as earlier samples, ensuring that a mass balance was demonstrated. The data are shown in Table 7.

It was found that the extraction of mixed solutions of cobalt and nickel from ammonium sulfate solutions using PC-88A was limited to a complex operating region, as shown in Figure 6. This region was defined by the pure component equilibrium isotherms for cobalt and nickel and a boundary region which was defined by the solubility limit of the nickel-ammonium, and cobalt-ammonium double salts. This solubility limit was a function of the equilibrium cobalt and nickel concentrations. In 20 °C water, the cobalt ammonium double salt, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> - CoSO<sub>4</sub> - 6H<sub>2</sub>O has a solubility limit of 205 g/L. The double salt of nickel, NiSO<sub>4</sub> - NiSO<sub>4</sub> - 7H<sub>2</sub>O has a solubility limit of 104 g/L. The solubility limit of the nickel-ammonium double salt in 20 °C was approximately 8.8 g/L.

The only other binary datum for the extraction of cobalt and nickel with PC-88A at a pH of 5.0 in the literature can be calculated from the paper by Driesinger



ORGANIC PHASE COMPOSITION: 20% PC-88A . 5% TBP. 75% VARSOL DX3641  
 AQUEOUS PHASE COMPOSITION: 20 G/L  $(\text{NH}_4)_2\text{SO}_4$   
 PH (AQ): 5.02 +/- 0.01  
 PRECIPITATION BOUNDARY (O)  
 DRIESINGER AND COOPER (\*) (1M.  $\text{Na}_2\text{SO}_4$ )

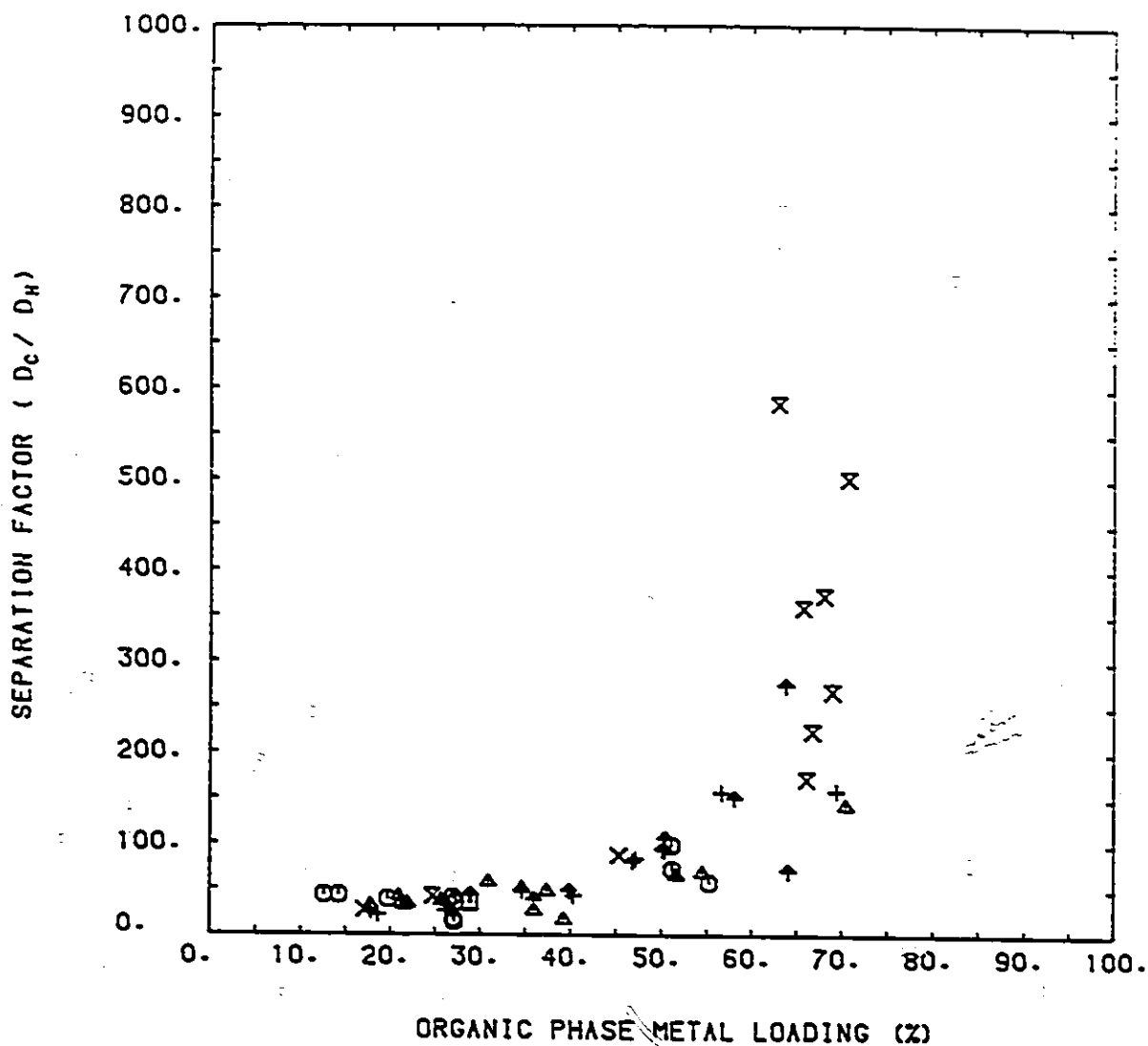
Figure 6: The Operating Region for the Extraction of Binary Mixtures of Aqueous Cobalt and Nickel at 25°C with the Extractant PC-SSA

and Cooper[16.17] and is shown in Figure 6. This data point lies outside of the operating region for the present system because Driesinger and Cooper[16.17] used 1M  $\text{Na}_2\text{SO}_4$  as a cosolute rather than the ammonium sulfate used in this study. As mentioned earlier, sodium was not used in this study because of the analytical interferences which were associated with it [3].

The separation factor,  $\beta_{\text{Co/Ni}}$ , was calculated for each sample and plotted as a function of the organic phase metal loading, and total aqueous phase equilibrium metal ion concentration. This is shown in Figure 7. It is clear that the  $\beta_{\text{Co/Ni}}$  is a function of the organic phase loading. It was not found to be a function of either total aqueous phase metal concentration or the solvent-free aqueous nickel mole fraction.

As stated earlier, Komasaawa et al. indicated that the  $\beta_{\text{Co/Ni}}$  for cobalt and nickel with 0.1-0.2F PC-SSA in a 90:10 xylene:isodecanol diluent was gradually increased from a separation factor of 30 at a phase loading of 2% to a maximum of about 80 at a phase loading of about 75%. Driesinger and Cooper[16.17] indicated a similar trend with a maximum separation factor of 6500 achievable at 50°C with a cobalt organic phase loading of 11.9 g/L with an equilibrium pH 5.5, and an A/O ratio of 2.0, and 20% PC-SSA in Varsol DX3641.

In the present study, the maximum phase loading achievable was approximately 73%, because of the tight control on the equilibrium pH. However, even with this restriction on the phase loading, separation factors of greater than 600 were still achievable. It is apparent that phase loading tended to increase as the total aqueous phase equilibrium metal ion concentration increased. This is not however an unexpected trend. The separation factor also depended upon the equilibrium Co/Ni ratio in the aqueous phase. In fact this appears to have more to do with value of the separation factor, than the organic phase loading. A high equilibrium aqueous phase Co/Ni ratio will give a higher separation factor than a low Co/Ni ratio at the same loading. The separation factor for this study, with equilibrium phase loadings ranging from 5% to 73% ranged from a value of approximately 30 to 600. These separation factors lie between the those values reported by Komasaawa et al. and Driesinger and Cooper. [16.17].



ORGANIC PHASE COMPOSITION: 20% PC-88A . 5% TBP . 75% VARSOL DX3641

AQUEOUS PHASE COMPOSITION: 20 G/L  $(NH_4)_2SO_4$

PH(AQ): 5.02 +/- 0.01

TOTAL AQUEOUS METAL CONCENTRATION:

.005 <  $\odot$  < .015 M.      .045 <  $\diamond$  < .055 M.

.015 <  $\blacktriangle$  < .025 M.      .075 <  $\uparrow$  < .125 M.

.025 <  $+$  < .035 M.      .125 <  $\times$  < .175 M.

.035 <  $\times$  < .045 M.      .175 <  $\nabla$  < .225 M.

Figure 7: The Separation Factor for the Extraction of Aqueous Cobalt and Nickel at 25°C with the Extractant PC-SSA as a function of the Organic Phase Metal Loading and the Total Aqueous Phase Metal Ion Concentration.

From Figure 7 it is apparent that the separation factor cannot be used to make a judgment about the selectivity of an extractant because of its dependence on the experimental conditions. This result is in agreement with observations made by Danesi et al. and Golding et al. about the variability of separation factors and their dependence on experimental conditions [14,23].

It is obvious that a better system for quantifying the selectivity of an extractant between two metals is required, before sound decisions in the design of solvent extraction circuits can be made.

A further requirement for the design of solvent extraction processes is a firm understanding of the interactions between an extractant and two competitive metal ions. As indicated in the literature review, Ritcey et al. proposed that binary extraction isotherms for one metal be constructed at constant equilibrium concentrations of the second metal, and vice-versa. A McCabe-Thiele type analysis could then be performed using the two graphs and the stage concentrations stepped off [45]. However, as Barclay pointed out this method ranges from difficult to impossible especially when highly selective extractants are being used [3]. This study came to much the same conclusion, as the data it collected was not suitable for a McCabe-Thiele analysis.

Similarly, the Delta-Y method proposed by Iannou et al. was attempted [24]. This method draws an analogy to the behavior of mixtures in vapour liquid equilibria and attempts to model a component's departure from its ideal single component state. The departure function can then be modelled for each of the components. The method is an attractive one because it allows the departure function to have a value of unity at a mole fraction of zero and at a mole fraction of 1.0 for any component. Iannou, Bautista and Smutz used this method in their studies of the extraction of Lanthanide metals. The equation for the departure function for any component in an equilibrium mixture can be given by:

$$\Delta Y_i(\text{pH}, T, X_j) = Y_i - X_i(Y_i^*) \quad (24)$$

where:

$\Delta Y_i$  = a function of the equilibrium phase composition, temperature, and pH of the solution. (moles/L)

$Y_i$  = the concentration of component  $i$  in the multicomponent equilibrium organic phase (moles/L)

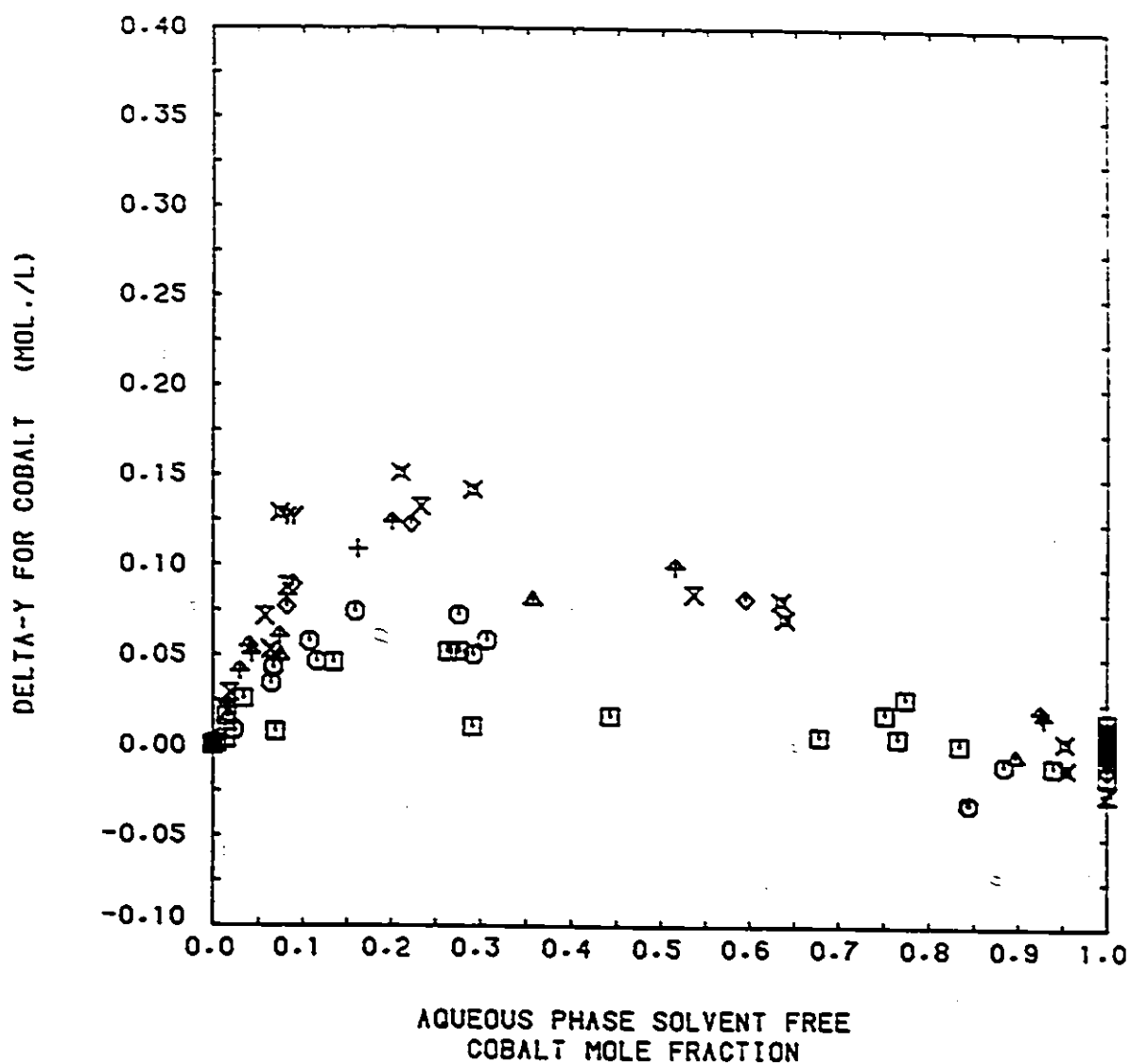
$Y_i^*$  = the concentration of component  $i$  in the single or pure component equilibrium organic phase (moles/L)

$X_j$  = the equilibrium aqueous solvent-free mole fraction of component  $j$  in the extraction equilibrium mixture.

In their study, Iannou et al. discretized data by correlating data with equal concentrations of a particular component in the aqueous phase. In the present study, it was very difficult to collect data in this fashion because of the type of experimental procedure required with isothermal shake out experiments. The Delta-Y method is painstakingly tedious because of the need to maintain constant aqueous equilibrium concentrations of one metal ion while adjusting the equilibrium concentrations of the other ions in the two phases. The utility of the method is also diminished by the fact that the Delta-Y function is by its very definition a function of the concentrations of the various components at equilibrium. Instead of correlating data with equal aqueous component concentrations, attempts were made to discretize the data using the total concentration in the aqueous phase at equilibrium. Although the general shape of the deviation functions are similar to those that Iannou et al. describe for their studies, this investigation could not discretize the data sufficiently to allow for mathematical correlation. The data for the PC-SSA using the Delta-Y method is shown in Figure 8 and Figure 9 and contained in Table 7.

Because of the inability to discretize the data, and develop adequate models for the data, it was felt that the Delta-Y method was not an appropriate method to use for correlating Binary Extraction data. Barclay [3] rejected this method for the same reason when he used it to analyse  $D_2EHPA$ .

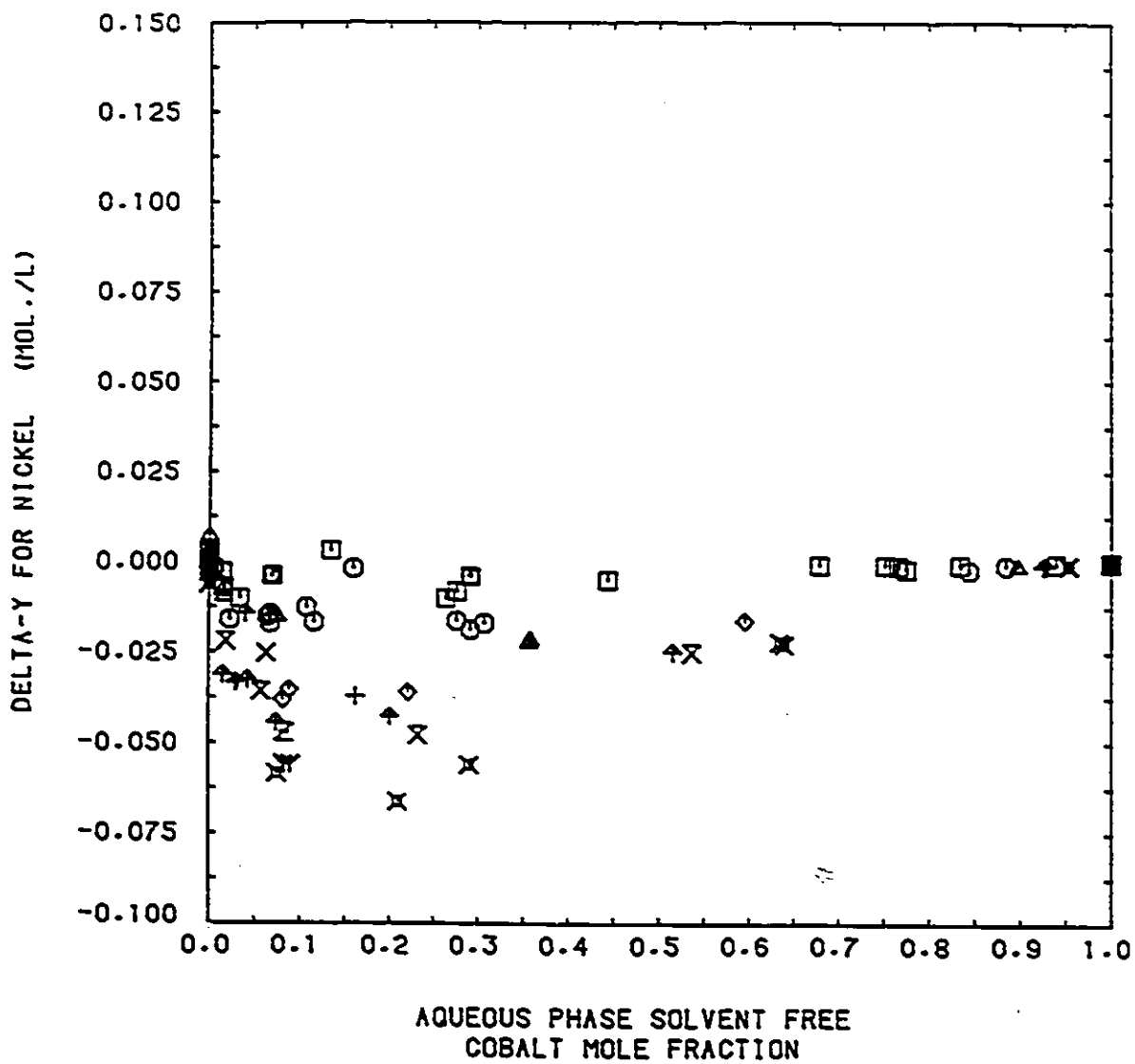
The method proposed by Barclay again drew its analogy from the behavior of mixtures in vapour-liquid equilibria. It proposed that the departure of a metal from



## TOTAL AQUEOUS PHASE METAL ION CONCENTRATION

□	0.000 < XT < 0.015 MOL./L	◇	0.055 < XT < 0.065 MOL./L
○	0.015 < XT < 0.025 MOL./L	†	0.065 < XT < 0.075 MOL./L
▲	0.025 < XT < 0.035 MOL./L	×	0.075 < XT < 0.085 MOL./L
+	0.035 < XT < 0.045 MOL./L	Z	0.085 < XT < 0.095 MOL./L
X	0.045 < XT < 0.055 MOL./L	Y	0.095 < XT < 0.105 MOL./L
		X	0.105 < XT MOL./L

Figure 8: The Delta-Y function for the Extraction of Aqueous Cobalt at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Total Ion Concentration.



TOTAL AQUEOUS PHASE METAL ION CONCENTRATION

□	0.000 < XT < 0.015 MOL./L	◇	0.055 < XT < 0.065 MOL./L
○	0.015 < XT < 0.025 MOL./L	†	0.065 < XT < 0.075 MOL./L
▲	0.025 < XT < 0.035 MOL./L	×	0.075 < XT < 0.085 MOL./L
+	0.035 < XT < 0.045 MOL./L	Z	0.085 < XT < 0.095 MOL./L
×	0.045 < XT < 0.055 MOL./L	Y	0.095 < XT < 0.105 MOL./L
		X	0.105 < XT < MOL./L

Figure 9: The Delta-Y function for the Extraction of Aqueous Nickel at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Total Ion Concentration.

its single, or pure component state could be modeled by the expression:

$$\gamma_{s,1}(\text{pH}, T, X_2) = \frac{Y_1}{X_1 Y_1^*} \quad (25)$$

where:

$\gamma_{s,1}$  = a function of the equilibrium phase composition, temperature, and pH of the solution.

$Y_1$  = the concentration of component 1 in the multicomponent equilibrium organic phase (moles/L)

$Y_1^*$  = the concentration of component 1 in the single or pure component equilibrium organic phase (moles/L)

$X_i$  = the equilibrium aqueous solvent-free mole fraction of component  $i$  in the binary extraction equilibrium

This equation is however not related to the true activity coefficient of the solutions. The equation is arranged so that as the solvent-free mole fraction of component 1 approached one, the pseudo-gamma function would approach 1.

The pseudo-gamma function was calculated for the binary extraction samples discussed earlier and are shown in Table 7 and Table 8. The results are plotted in Figure 10 and Figure 11, for Cobalt and Nickel with a 20% solution of PC-SSA at 25°C and an equilibrium pH of  $5.02 \pm 0.01$ .

For cobalt the pseudo-gamma function has an initial value of 1.0 for a solvent-free nickel mole fraction of 0 and gradually increases to a value of about 10 at a nickel mole fraction of approximately 0.95. The pseudo-gamma continues to rapidly increase to a value approaching 70 as the nickel mole fraction approaches 1.0. Theoretically, PC-SSA should become infinitely selective for cobalt as the mole fraction of nickel approaches 1.0. This is shown experimentally. A Henry's law analogy can be used to estimate a limiting pseudo-gamma at a nickel mole fraction  $\approx 1.0$ . This would correspond to a value of  $\gamma_{s,\text{Co-Ni}-1.0} \approx 70$ . The data for the pseudo-gamma for cobalt in cobalt-nickel sulfate solutions with the extractant PC-SSA was

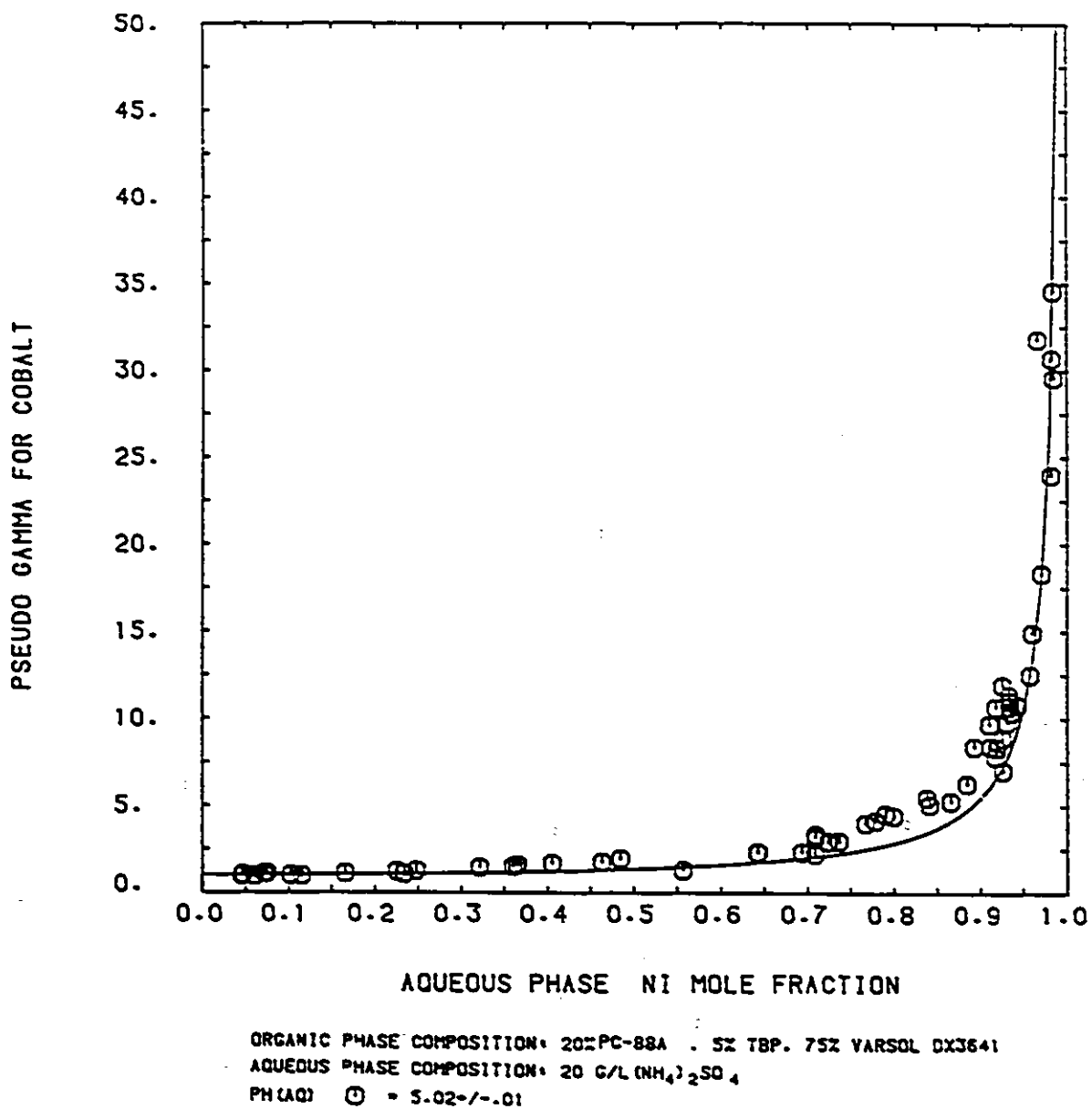


Figure 10: The Pseudo-Gamma function for the Extraction of Aqueous Cobalt at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Solvent Free Nickel Mole Fraction.

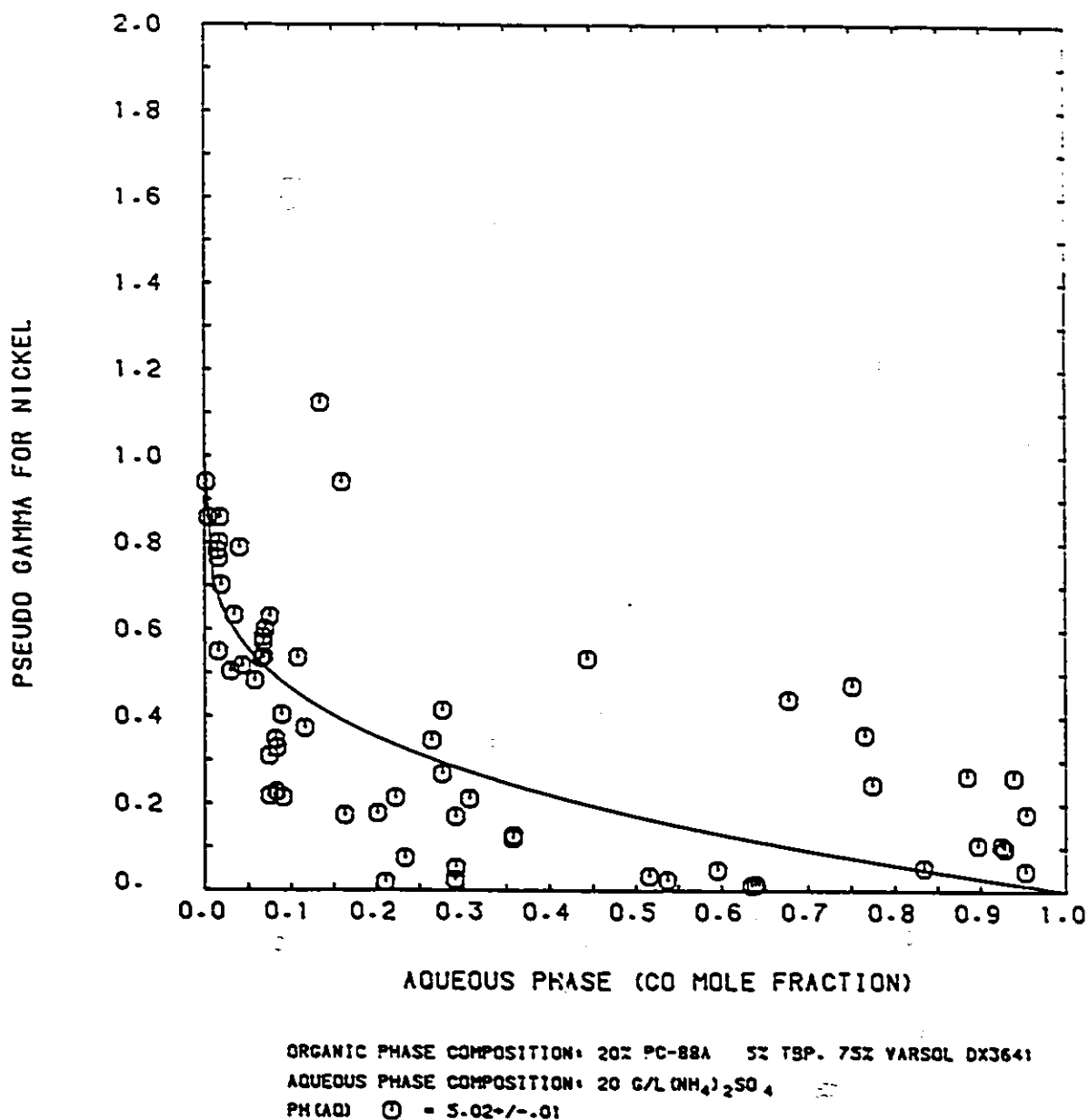


Figure 11: The Pseudo-Gamma function for the Extraction of Aqueous Nickel at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Solvent Free Cobalt Mole Fraction.

regressed using a nonlinear regression and found to agree well with the equation:

$$\gamma_{s,\text{Co}}(25^\circ\text{C}, \text{pH} = 5.02, X_{\text{Ni}}) = \frac{1}{1 - X_{\text{Ni}}^{1.91}} \quad (26)$$

$$\text{SSR} = 28.239 \quad (27)$$

$$\text{MSR} = 397.7 \quad (28)$$

The residual sum of squares for this model appears to be very high but in fact this is due to the scale of the pseudo-gamma function, 0-300, and its shape. The six data points which lie above a solvent-free nickel mole fraction of 0.985 accounted for 98% of the error associated with the fitting. This is not surprising as it was noted earlier that the model does possess an infinite limit as the nickel mole fraction approaches 1.0. The Residual plots for the cobalt and nickel pseudo-gamma functions for PC-SSA at 25 °C are shown in Figure 14 and Figure 15 . The data for D<sub>2</sub>EHPA and Cyanex 272 from the work by Barclay [3] and Fu [54] were also modeled using an equation of the form shown above. The pseudo gamma for Cyanex 272 at a pH of 5.47, and a temperature of 25°C was not significantly different from that of PC-SSA at a pH of 5.02. The fit from the model for D<sub>2</sub>EHPA was significantly better than that proposed by Barclay in his original work, which was a fourth order polynomial, and contained undesirable oscillations in the solvent-free nickel mole fraction range of 0.2 to 0.8. The revised model is given by the equation:

$$\gamma_{s,\text{Co}}(25^\circ\text{C}, \text{pH} = 5.85, X_{\text{Ni}}) = \frac{1 - 0.957X_{\text{Ni}}}{1 - X_{\text{Ni}}^{0.72}} \quad (29)$$

for  $X_{\text{Ni}} < 0.96$ , and

$$\gamma_{s,\text{Co}}(25^\circ\text{C}, \text{pH} = 5.85, X_{\text{Ni}}) = 35.62X_{\text{Ni}} - 31.35 \quad (30)$$

for all  $X_{\text{Ni}} \geq 0.96$ , with

$$\text{SSR} = 1.543 \quad (31)$$

$$\text{MSR} = 0.021 \quad (32)$$

Using Henry's Law the limiting pseudo-gamma for cobalt with D<sub>2</sub>EHPA at 25 °C is approximately 4.3. Barclay's original model had a SSR of 1.68. Barclay's data for

D<sub>2</sub>EHPA at 60 °C gave the following revised equation:

$$\gamma_{s,Co}(60^{\circ}\text{C}, \text{pH} = 5.85, X_{Ni}) = \frac{1 - 0.703X_{Ni}}{1 - X_{Ni}^{0.536}} \quad (33)$$

$$\text{SSR} = 15.95 \quad (34)$$

$$\text{MSR} = 0.249 \quad (35)$$

Barclay's only collected data up to a solvent-free nickel mole fraction of 0.93 for the 60°C  $\gamma_{s,Co}$  data. As indicated earlier, 98% of the error associated with the PC-SSA data is above the 98% range. Qualitatively Barclay's data for D<sub>2</sub>EHPA at 60 °C showed little difference from that of the PC-SSA data at 25 °C .

The pseudo-gamma for nickel with PC-SSA was also calculated and is shown in Figure 11. The values of the pseudo gamma are much smaller than those for cobalt. The pseudo-gamma for nickel as the solvent-free mole fraction of cobalt approaches 1.0 is again by definition equal to 1.0. As the solvent-free mole fraction of cobalt approaches 1.0, the pseudo-gamma for nickel approaches zero. This behavior is typical for all selective extractants. The pseudo-gamma for the favored metal ion will approach infinity as the mole fraction of the less favored metal ion approaches 1.0. Likewise, the converse is true. As the mole fraction of the more favored ion in the solvent extraction approaches 1.0, the pseudo-gamma for the less favored ion will approach zero.

The Pseudo-gamma function for nickel in the binary extraction of nickel and cobalt with a 20 % solution of PC-SSA at 25°C with an equilibrium pH of 5.0 can be modeled by the equation:

$$\gamma_{s,Ni}(25^{\circ}\text{C}, \text{pH} = 5.02, X_{Co}) = 1 - X_{Co}^{0.27} \quad (36)$$

$$\text{SSR} = 3.211 \quad (37)$$

$$\text{MSR} = 0.045 \quad (38)$$

Similarly the pseudo-gamma for D<sub>2</sub>EHPA using the data generated by Barclay [3] gave the equation:

$$\gamma_{s,Ni}(25^{\circ}\text{C}, \text{pH} = 5.85, X_{Co}) = 1 \quad (39)$$

$$\text{SSR} = 3.211 \quad (40)$$

$$\text{MSR} = 0.045 \quad (41)$$

while the pseudo-gamma for D<sub>2</sub>EHPA at 60°C is given by:

$$\gamma_{Ni}(60^{\circ}\text{C}, \text{pH} = 5.55, X_{Co}) = 1 - X_{Co}^{0.305} \quad (42)$$

$$\text{SSR} = 3.211 \quad (43)$$

$$\text{MSR} = 0.045 \quad (44)$$

Again the scale effect can be noted in the fitting of the pseudo-gamma for nickel. These values are all between 1.0 and 0.0 and therefore the SSR for the fitting must take a small value. Although there appears to be a significant amount of scatter in the data compared to the pseudo-gamma for cobalt, the average absolute analytical error from the mass balances for the nickel components in the samples were not significantly different from that of the cobalt component. However a small error in a component with a small concentration will give a much larger percentage error, and this is the effect shown in Figure 11. It is also interesting to note the increase in the data scatter for the pseudo-gamma for nickel as the cobalt solvent-free mole fraction increases beyond 0.7. Barclay displayed a similar increase in the scatter of his data.[3] This result would tend to indicate that an Atomic Absorption analytical method is not sensitive to changes in nickel concentrations at high concentrations of cobalt.

The advantage that these models hold over others that have been proposed is that they are simple, and are capable of accounting for the nonideal interactions displayed by binary extractions in the solvent extraction process. While it is true that the pseudo-gamma model is restricted by an infinite limit for the extraction favored metal ion, the overall ability of the method to overcome a complex problem is good. Most of the error associated with a mathematical modeling using the simple equations proposed above is concentrated to a small region near that infinite limit.

Similarly the method can be used to give an overall measure of the differences in selectivity between different extractants at any pH. The exponential parameter given in pseudo-gamma models increase as the selectivity for the metal ion increases. With a few data points, a good measure of the nonideality of the system can also be found. It is clear that few data points would be required in a practical setting in order to predict with confidence the nonideal behavior of a binary extraction.

Lastly by being able to predict the nonideal behavior of the extraction process, the design of a solvent extraction leaves behind much of the uncertainty formerly associated with the task, allowing extraction profiles for binary solvent extractions to be calculated easily, and with confidence.

## Chapter 5

### Conclusions

The extraction of Cobalt and Nickel sulfate was studied both in single, or pure component and binary systems with the phosphonic acid extractant PC-SSA at 25°C and an equilibrium pH of  $5.02 \pm 0.01$ . Ammonium Sulfate, (20 g/L), was also added to the extraction solutions to maintain a high ionic phase. The A/O phase ratio was maintained as close to 1.0 as possible, and variation with volume included in the subsequent calculations.

It was found that the pure or single component extraction isotherms were well modeled by a combination of the Freundlich and Langmuir Isotherms, as proposed by Barclay.

An operating region exists where the two phases exist in equilibrium. If the aqueous phase total equilibrium concentration is too high, and the Co/Ni ratio too small, the double salts, Cobalt ammonium sulfate and Nickel ammonium sulfate will precipitate. The upper boundary of the region is defined by the Cobalt pure component isotherm, and the lower boundary by the Nickel pure component isotherm.

The maximum concentration of metal which could be practically achieved by a 0.155F solution of PC-SSA based on the dimer population, in Varsol DX3641 with 5% (v/v) TBP, at 25°C and an equilibrium pH of  $5.02 \pm 0.01$  was 0.2264 moles/L. This corresponds to a maximum organic phase loading capacity, of approximately 73%.

In agreement with earlier studies it was found that PC-SSA has extraction characteristics which lie between those of Cyanex 272 and D2EHPA, at the same extractant concentration, ionic strength range, temperature and respective optimum equilibrium pH.

The use of a separation factor was shown to be of little help in determining the nonidealities of an extractant system, or for comparing extractant systems because of its dependence on experimental conditions. It was found that Barclay's pseudo-gamma relationship is the simplest method for modeling binary extraction processes compared to the methods proposed by Iannou et al and Ritcey et al. Although an indefinite limit exists for the method as the solvent-free mole fraction of a component approaches zero, an analogy to Henry's law appears to be able to valid.

The non-ideal interactions displayed by binary solutions of Cobalt and Nickel sulfate can be easily modeled using this method with a minimum number of data points. The best models correlating this method are very simple, and tend to concentrate their error in the regions where the solvent-free mole fraction of one component is extremely high. However, as Henry's law can be used, this difficulty can be easily overcome.

Analytical problems appear to exist for Nickel concentrations in solutions with solvent-free mole fractions above 0.7, in the aqueous phase due primarily to a masking effect of high Cobalt concentrations. Matrix matching may overcome this problem, but it is felt that, in the long run, analytical methods other than Atomic Absorption Spectrophotometry will be required.

Above a phase loading of 75% , a rapid rise in the organic phase viscosity was noted in the pure component Cobalt samples, indicating a polymerization of the extractant-metal complex. This observation is in agreement with conclusions drawn by other researchers.

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# **Chapter 6**

## **Appendix**

### **6.1 Tables and Residual Plots**

Table 3: Viscosity values for Pure Component Aqueous Cobalt Solutions in Equilibrium with PC-SSA at 25°C. Organic Phase = 20% PC-SSA 5% TBP, 75% Esso Varsol DX3641 Aqueous Phase = 20 g/L  $(\text{NH}_4)_2\text{SO}_4$

Concentration g/L	Viscosity Poise
0.00	0.0202
0.30	0.0204
0.30	0.0204
0.30	0.0201
2.00	0.0205
2.40	0.0206
2.40	0.0207
3.60	0.0206
3.80	0.0211
3.90	0.0211
4.70	0.0209
5.00	0.0212
5.10	0.0228
6.70	0.0210
7.00	0.0221
7.10	0.0222
9.60	0.0219
10.20	0.0223
12.60	0.0240
13.40	0.0239
15.70	1.9017
16.40	2.2797
17.00	5.6937
17.10	5.6262
17.40	2.1357
17.50	5.8161

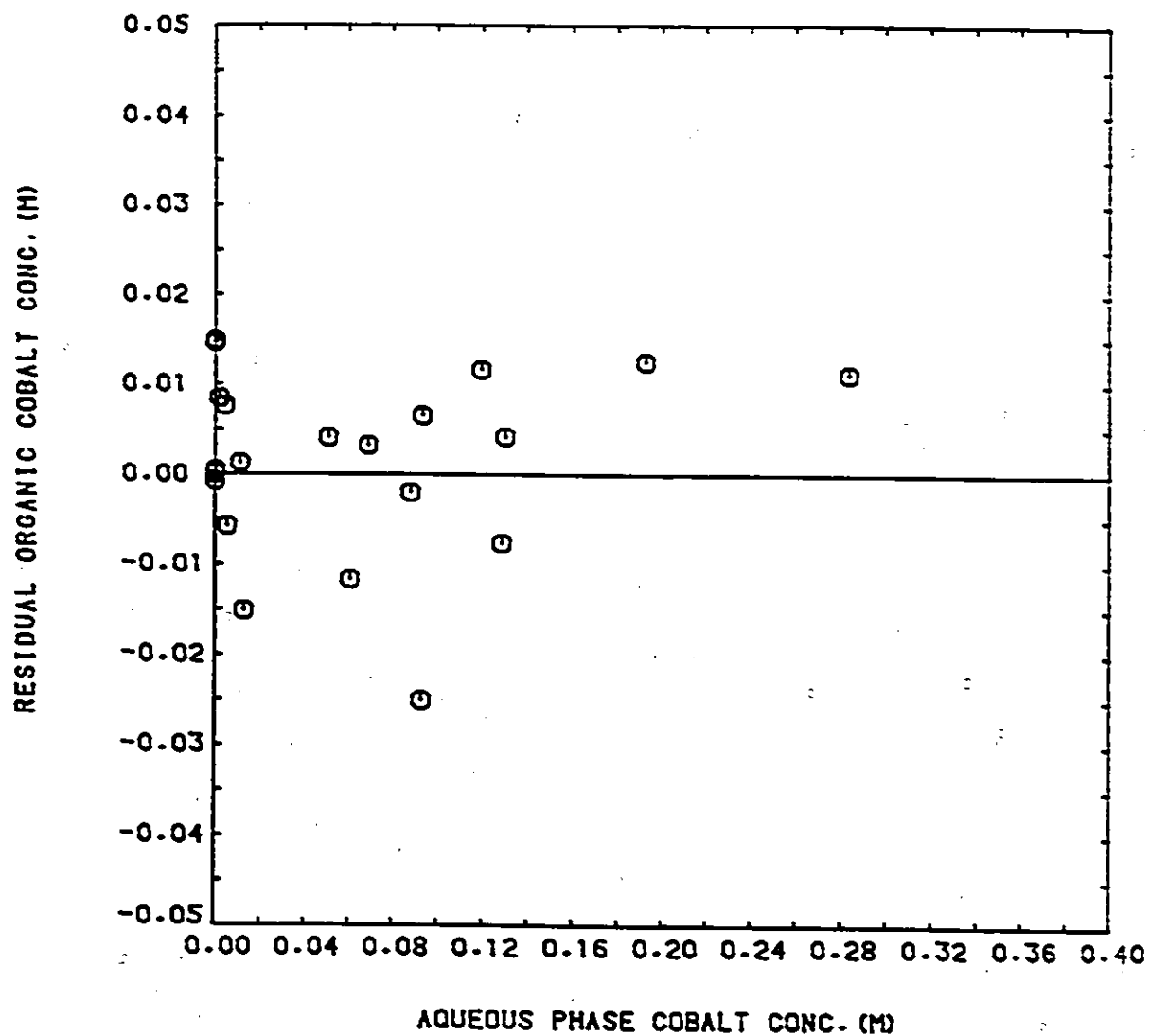


Figure 12: The Residual Organic Phase Cobalt Concentration for the Pure Component Extraction "Best Fit" Model at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Cobalt Concentration

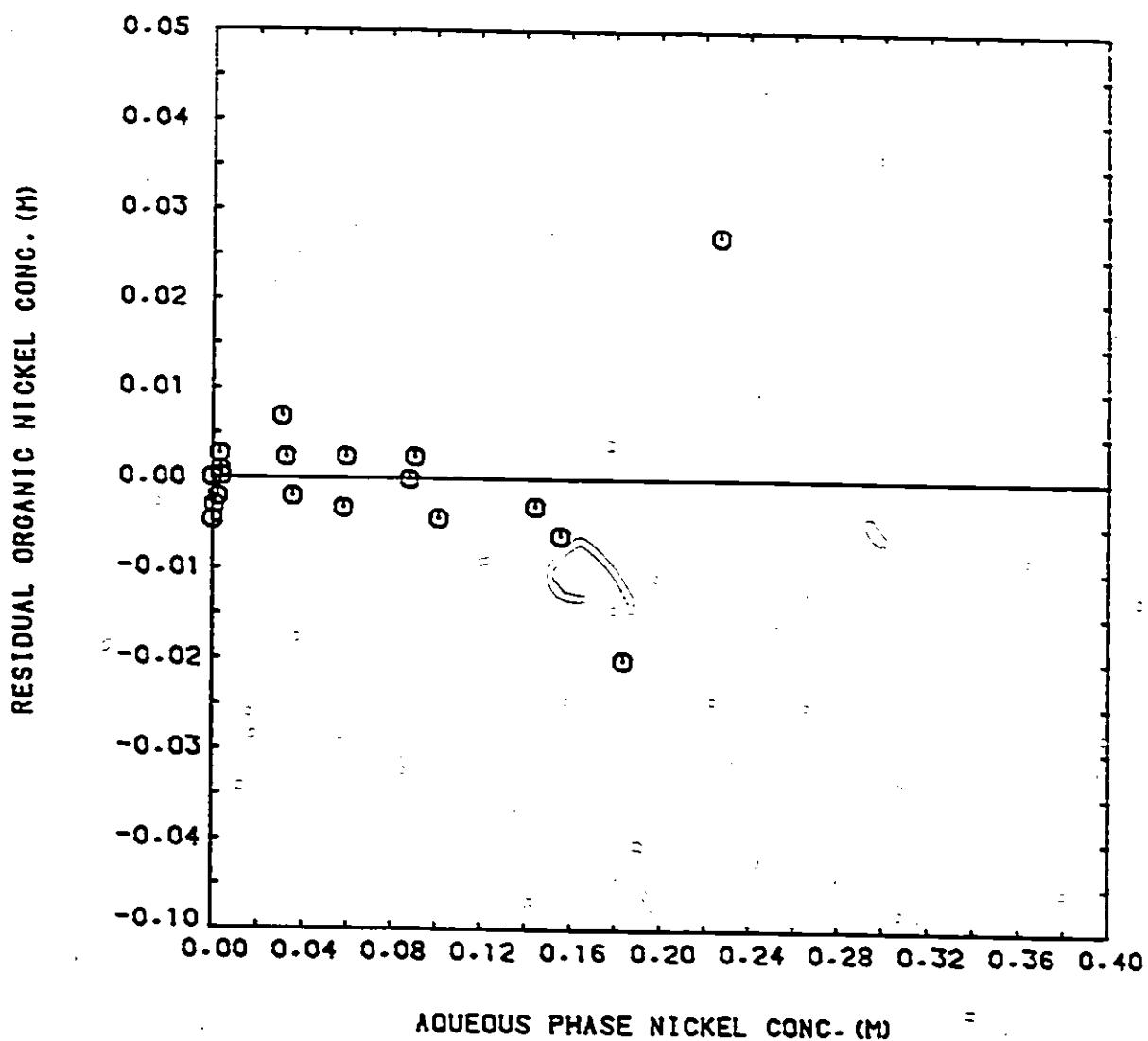


Figure 13: The Residual Organic Phase Nickel Concentration for the Pure Component Extraction "Best Fit" Model at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Nickel Concentration

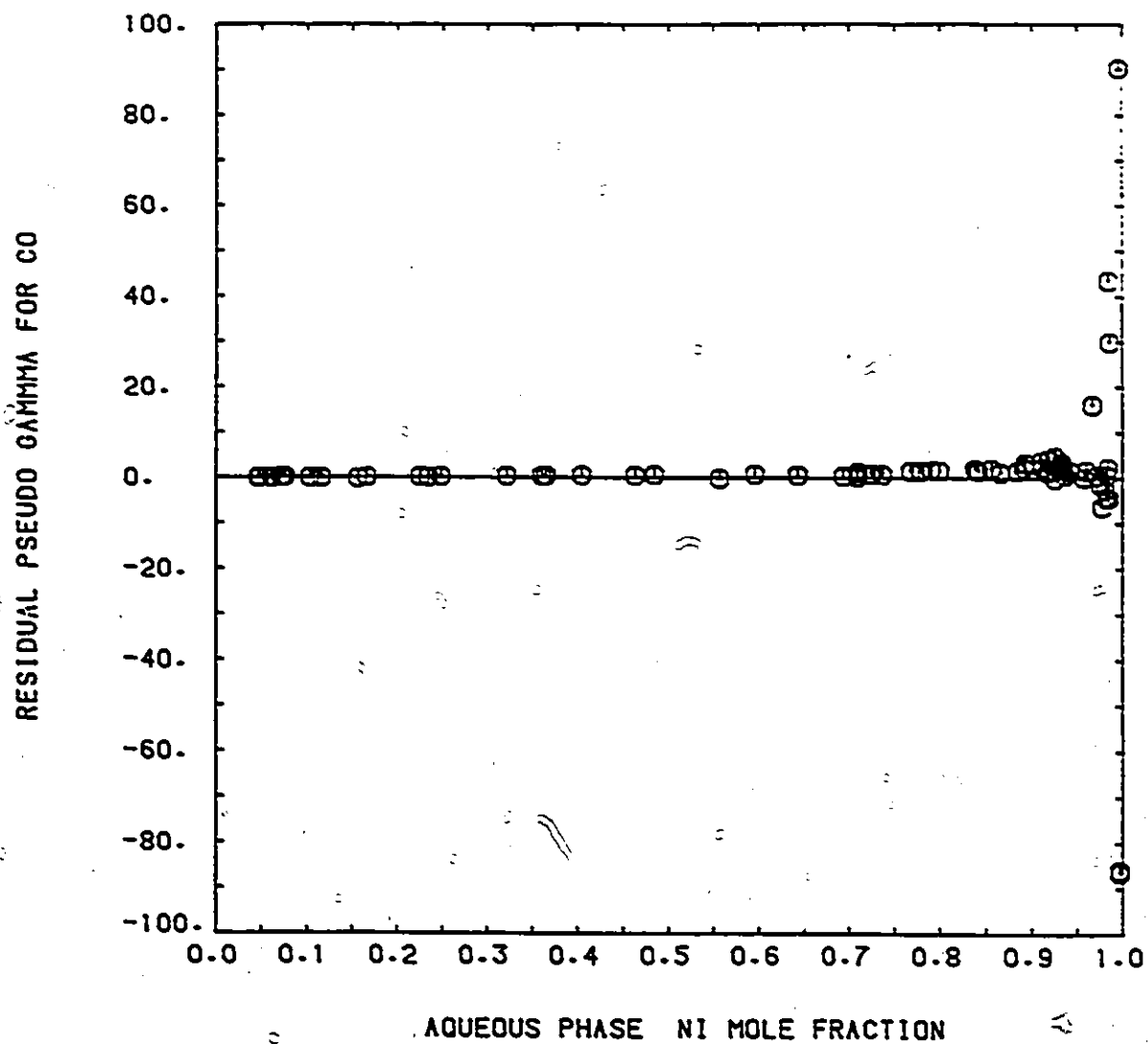


Figure 14: The Residual Pseudo-Gamma Function for the Extraction of Aqueous Cobalt; at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Solvent Free Nickel Mole Fraction.

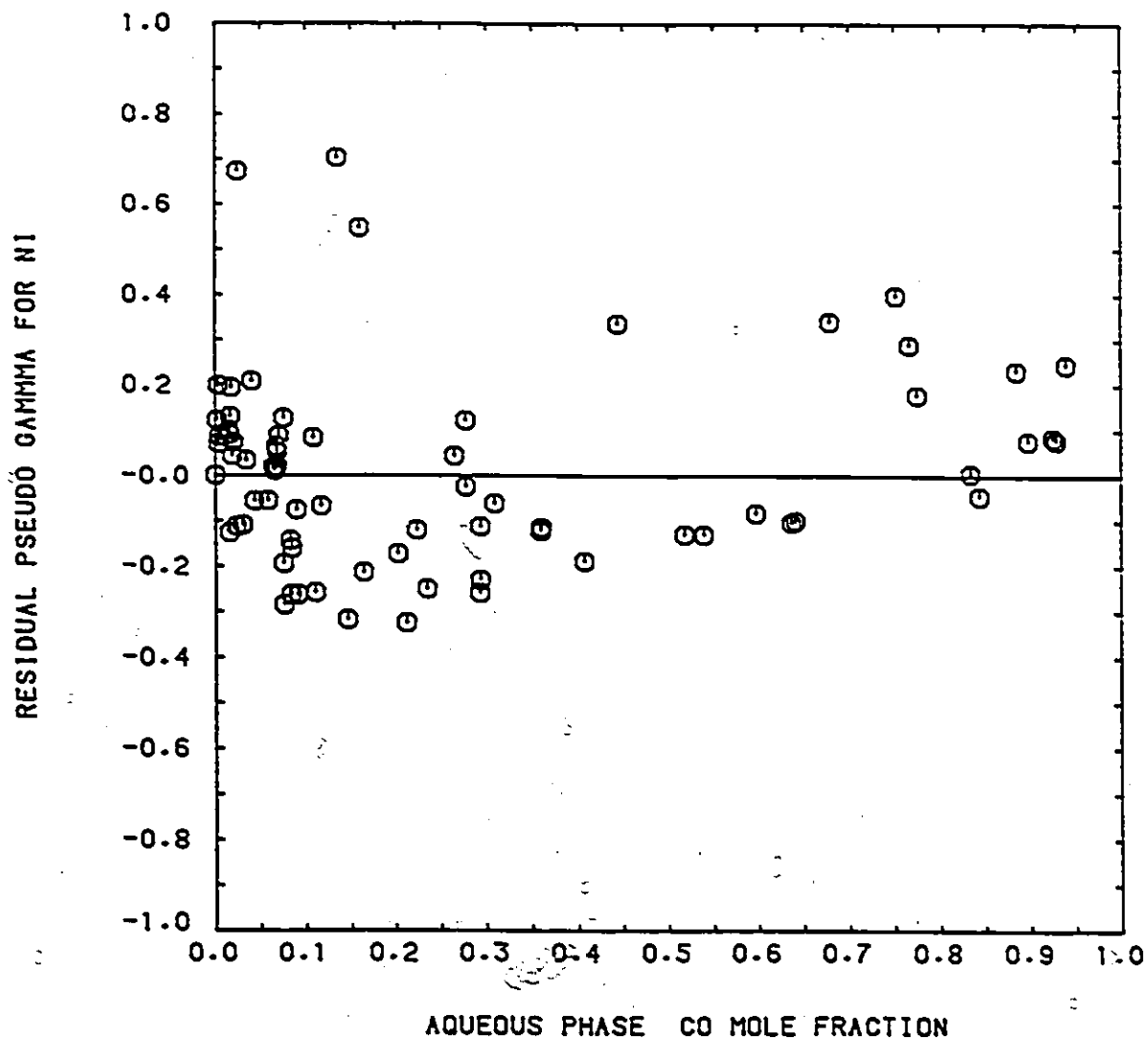


Figure 15: The Residual Pseudo-Gamma Function for the Extraction of Aqueous Nickel at 25°C with the Extractant PC-SSA as a function of the Equilibrium Aqueous Solvent Free Cobalt Mole Fraction.

Table 4: Viscosity values for Pure Component Aqueous Nickel Solutions in Equilibrium with PC-SSA at 25°C. Organic Phase = 20% ext 5% TBP, 75% Esso Var-sol DX3641 Aqueous Phase = 20 g/L  $(\text{NH}_4)_2\text{SO}_4$

Concentration g/L	Viscosity Poise
0.00	0.0208
0.00	0.0208
0.00	0.0217
8.54	0.0284
8.54	0.0302
8.76	0.0283
10.81	0.0341
10.81	0.0342
12.39	0.0403
12.55	0.0412

Table 5: Pure Component Data for aqueous Cobalt and Nickel in equilibrium with an organic phase mixture of PC-SSA, Tributyl phosphate, and Esso Varsol DX3641 (20:5:75 v/v) at 25°C as a function of pH.

pH	Cobalt Conc.(mol/L)		pH	Nickel Conc.(mol/L)	
	Aqueous Phase	Organic Phase		Aqueous Phase	Organic Phase
7.10	.0027	.0171	6.75	.0076	.0109
7.10	.0027	.0170	6.75	.0074	.0110
6.90	.0027	.0175	6.75	.0076	.0109
6.32	.0033	.0157	6.45	.0092	.0102
6.31	.0033	.0164	6.45	.0092	.0101
6.30	.0034	.0174	6.47	.0090	.0101
5.58	.0072	.0134	5.95	.0112	.0076
5.60	.0073	.0134	5.92	.0115	.0074
5.45	.0072	.0126	5.91	.0115	.0076
4.78	.0107	.0104	5.35	.0138	.0054
4.78	.0104	.0096	5.33	.0145	.0056
4.28	.0144	.0071	5.33	.0143	.0056
4.25	.0145	.0070	5.38	.0142	.0057
4.25	.0140	.0067	5.53	.0135	.0055
4.10	.0159	.0051	4.80	.0172	.0024
4.10	.0158	.0050	4.50	.0174	.0024
4.10	.0154	.0047	4.50	.0177	.0026
3.95	.0166	.0036	4.50	.0174	.0023
3.92	.0169	.0038	3.40	.0207	.0012
3.92	.0171	.0039	3.40	.0203	.0010
3.71	.0193	.0024	3.38	.0207	.0013
3.75	.0178	.0020			
3.72	.0190	.0024			
3.12	.0200	.0003			
3.11	.0222	.0003			
3.10	.0216	.0003			

Table 6: Pure Component Aqueous and Organic Phase Concentrations of Cobalt and Nickel in equilibrium with PC-SSA. Organic phase = 20% extractant, 5% TBP, 75% Esso Varsol DX3641: Aqueous phase = 20 g/L  $(\text{NH}_4)_2\text{SO}_4$ , pH =  $5.02 \pm 0.01$

Cobalt Conc.(mol/L)		Nickel Conc.(mol/L)	
Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase
.00004	.01754	.00000	.00000
.00005	.01744	.00036	.00167
.00006	.00314	.00093	.00352
.00027	.01637	.00222	.00750
.00187	.08594	.00315	.01431
.00423	.13020	.00334	.01290
.00524	.12870	.00393	.01344
.01104	.17240	.03072	.05624
.01272	.16180	.03529	.05110
.06054	.20270	.03245	.05319
.05081	.21620	.05808	.06357
.06487	.21840	.05941	.06987
.08808	.21620	.08820	.07786
.09291	.22520	.09041	.08105
.09302	.19360	.10120	.07708
.11910	.23210	.14440	.08693
.12870	.21330	.15560	.08541
.12970	.22520		
.19230	.23550		
.28340	.23550		

Table 7: Equilibrium Phase Concentrations of Cobalt and Nickel at 25°C with the Extractant PC-SSA in Versol DX3641 and TBP (20:75:5) and Water with 20 g/L Ammonium Sulfate at a pH of 5.02

Solvent Free Aqueous Nickel Mole Fraction	Phase Concentrations				$\Delta Y_{Co}$ M	$\%Co$		
	Organic Phase Cobalt M	Nickel M	Aqueous Phase Cobalt M	Nickel M		Actual	Predicted	Residual
0.0462	0.1991	0.0001	0.1142	0.0055	-0.0110	0.9480	1.0030	-0.0550
0.0475	0.2142	0.0000	0.1296	0.0065	0.0037	1.0170	1.0030	0.0145
0.0608	0.1587	0.0001	0.0137	0.0009	-0.0102	0.9400	1.0050	-0.0640
0.0718	0.2157	0.0001	0.0608	0.0047	0.0166	1.0840	1.0070	0.0770
0.0751	0.2188	0.0001	0.0628	0.0051	0.0201	1.1010	1.0070	0.0940
0.1030	0.1759	0.0001	0.0280	0.0032	-0.0046	0.9750	1.0130	-0.0380
0.1158	0.1601	0.0003	0.0196	0.0026	-0.0095	0.9430	1.0160	-0.0730
0.1564	0.1184	0.0000	0.0130	0.0024	-0.0316	0.7896	1.0300	-0.2400
0.1661	0.0195	0.0000	0.0004	0.0001	0.0006	1.0910	1.0330	0.0580
0.2257	0.1585	0.0006	0.0106	0.0031	0.0273	1.2060	1.0610	0.1450
0.2340	0.0915	0.0006	0.0036	0.0011	0.0046	1.0590	1.0660	-0.0070
0.2483	0.0902	0.0008	0.0026	0.0009	0.0187	1.2530	1.0750	0.1780
0.3215	0.0193	0.0007	0.0003	0.0002	0.0075	1.4260	1.1290	0.2970
0.3608	0.2110	0.0003	0.0935	0.0528	0.0712	1.5090	1.1660	0.3435
0.3653	0.2194	0.0002	0.0826	0.0476	0.0812	1.5880	1.1700	0.4177
0.4048	0.2047	0.0008	0.0345	0.0234	0.0823	1.6720	1.2150	0.4572
0.4632	0.1976	0.0006	0.0451	0.0389	0.0847	1.7500	1.2970	0.4520
0.4843	0.2066	0.0009	0.0379	0.0356	0.0996	1.9310	1.3330	0.5988
0.5564	0.0783	0.0058	0.0056	0.0070	0.0170	1.2730	1.4830	-0.2050
0.5951	0.2015	0.0013	0.0696	0.1023	0.1140	2.3040	1.5880	0.7161
0.6416	0.1424	0.0031	0.0112	0.0201	0.0808	2.3120	1.7470	0.5645
0.6426	0.1434	0.0031	0.0117	0.0211	0.0814	2.3090	1.7510	0.5577
0.6928	0.1031	0.0046	0.0063	0.0143	0.0587	2.3170	1.9810	0.3357
0.7083	0.0156	0.0002	0.0003	0.0007	0.0105	3.1420	2.0690	1.0730

Solvent Free Aqueous Nickel Mole Fraction	Phase Concentrations				$\Delta Y_{Co}$ M	Actual	$\tau_{Co}$ Predicted	Residual
	Organic Phase Cobalt M	Nickel M	Aqueous Phase Cobalt M	Nickel M				
0.7083	0.0923	0.0039	0.0062	0.0150	0.0504	2.2070	2.0690	0.1380
0.7090	0.2029	0.0014	0.0408	0.0996	0.1422	3.3400	2.0740	1.2660
0.7235	0.0791	0.0058	0.0027	0.0071	0.0522	2.9450	2.1650	0.7790
0.7238	0.1103	0.0060	0.0054	0.0142	0.0727	2.9290	2.1670	0.7610
0.7360	0.0786	0.0054	0.0029	0.0080	0.0519	2.9610	2.2530	0.7080
0.7670	0.1766	0.0038	0.0182	0.0599	0.1324	3.9980	2.5110	1.4860
0.7781	0.1620	0.0098	0.0124	0.0436	0.1230	4.1470	2.6220	1.5250
0.7897	0.1944	0.0012	0.0319	0.1198	0.1515	4.5290	2.7500	1.7790
0.7988	0.1602	0.0096	0.0138	0.0546	0.1240	4.4240	2.8610	1.5620
0.8374	0.1332	0.0078	0.0070	0.0363	0.1088	5.4540	3.4720	1.9820
0.8405	0.0925	0.0297	0.0036	0.0192	0.0744	5.0820	3.5340	1.5480
0.8553	0.1677	0.0067	0.0224	0.1322	0.1394	5.9240	3.8670	2.0570
0.8652	0.0567	0.0278	0.0019	0.0125	0.0461	5.2650	4.1310	1.1340
0.8839	0.0552	0.0100	0.0018	0.0138	0.0464	6.2730	4.7530	1.5200
0.8905	0.1456	0.0144	0.0142	0.1158	0.1258	7.3380	5.0230	2.3150
0.8922	0.0653	0.0146	0.0017	0.0139	0.0575	8.3870	5.0980	3.2890
0.9096	0.1413	0.0152	0.0089	0.0894	0.1267	9.6760	6.0290	3.6470
0.9109	0.1014	0.0239	0.0053	0.0546	0.0894	8.3960	6.1140	2.2810
0.9163	0.1010	0.0230	0.0076	0.0836	0.0881	7.8240	6.4910	1.3330
0.9171	0.1396	0.0163	0.0082	0.0911	0.1265	10.6500	6.5470	4.1060
0.9179	0.0875	0.0203	0.0046	0.0521	0.0771	8.3330	6.6150	1.7180
0.9247	0.1405	0.0162	0.0080	0.0988	0.1287	11.9000	7.1880	4.7165
0.9248	0.0556	0.0260	0.0021	0.0257	0.0493	8.8740	7.1940	1.6801
0.9252	0.0703	0.0199	0.0052	0.0644	0.0603	7.0090	7.2370	-0.2280

Solvent Free Aqueous Nickel Mole Fraction	Phase Concentrations				$\Delta Y_{Co}$ M	Actual	$\%Co$ Predicted	Residual
	Organic Phase Cobalt M	Nickel M	Aqueous Phase Cobalt M	Nickel M				
0.9302	0.0084	0.0060	0.0002	0.0027	0.0076	9.7870	7.7300	2.0570
0.9322	0.0467	0.0193	0.0013	0.0181	0.0426	11.3300	7.9550	3.3740
0.9323	0.0486	0.0197	0.0015	0.0208	0.0441	10.7100	7.9660	2.7402
0.9328	0.0467	0.0204	0.0014	0.0193	0.0424	10.9900	8.0170	2.9815
0.9350	0.0379	0.0174	0.0012	0.0172	0.0342	10.3400	8.2840	2.0530
0.9363	0.0592	0.0301	0.0030	0.0441	0.0526	9.0230	8.4510	0.5710
0.9423	0.0786	0.0333	0.0045	0.0742	0.0713	10.7570	9.2980	1.4590
0.9571	0.0549	0.0348	0.0030	0.0662	0.0505	12.5000	12.4300	0.0730
0.9600	0.0586	0.0533	0.0028	0.0661	0.0546	14.9100	13.3000	1.6100
0.9663	0.0266	0.0177	0.0004	0.0127	0.0258	31.7600	15.7600	16.0030
0.9704	0.0432	0.0339	0.0019	0.0637	0.0409	18.3200	17.8700	0.4489
0.9755	0.0599	0.1188	0.0042	0.1668	0.0569	19.9900	21.5500	-1.5484
0.9771	0.0086	0.0179	0.0004	0.0180	0.0081	16.6800	23.0300	-6.3540
0.9804	0.0463	0.0631	0.0027	0.1356	0.0444	24.2530	26.9100	-2.6550
0.9813	0.0301	0.0520	0.0015	0.0798	0.0289	23.9800	28.2500	-4.2710
0.9825	0.0161	0.0417	0.0005	0.0308	0.0156	30.6800	30.0800	0.6031
0.9837	0.0161	0.0393	0.0005	0.0314	0.0156	34.5600	32.3500	2.2094
0.9843	0.0160	0.0232	0.0002	0.0140	0.0158	76.9600	33.5600	43.4000
0.9845	0.0232	0.0381	0.0010	0.0662	0.0224	29.5600	34.0100	-4.4490
0.9857	0.0035	0.0105	0.0001	0.0040	0.0034	66.5700	36.7000	29.8700
0.9958	0.0011	0.0128	0.0000	0.0048	0.0011	215.9000	125.7000	90.2800
0.9966	0.0062	0.0763	0.0005	0.1430	0.0061	65.4400	152.0000	-86.5600
0.9967	0.0077	0.0932	0.0006	0.1801	0.0076	72.0200	158.1000	-86.0500
0.9982	0.0024	0.0508	0.0001	0.0367	0.0024	334.8000	291.1001	43.7100

Table 8: Equilibrium Phase Concentrations of Cobalt and Nickel at 25°C with the Extractant PC-SSA in Versol DX3641 and TBP (20:75:5) and Water with 20 g/L Ammonium Sulfate at a pH of 5.02

Solvent Free Aqueous Cobalt Mole Fraction	Phase Concentrations				$\Delta Y_{Ni}$ M	$\gamma_{Ni}$		
	Organic Phase Cobalt M	Nickel M	Aqueous Phase Cobalt M	Nickel M		Actual	Predicted	Residual
0.0018	0.0025	0.0508	0.0001	0.0367	-0.0036	0.9398	0.8185	0.1213
0.0033	0.0077	0.0932	0.0006	0.1801	-0.0246	0.9843	0.7859	0.1984
0.0034	0.0062	0.0763	0.0005	0.1430	-0.0213	0.8531	0.7836	0.0695
0.0042	0.0011	0.0128	0.0000	0.0048	0.0011	0.8577	0.7722	0.0855
0.0143	0.0035	0.0105	0.0001	0.0041	-0.0025	0.7814	0.6820	0.0994
0.0155	0.0232	0.0381	0.0010	0.0662	-0.0253	0.5487	0.6754	-0.1267
0.0157	0.0160	0.0232	0.0002	0.0140	0.0043	0.7634	0.6742	0.0892
0.0163	0.0161	0.0393	0.0005	0.0314	-0.0111	0.8001	0.6710	0.1291
0.0175	0.0161	0.0417	0.0005	0.0308	-0.0110	0.8576	0.6644	0.1932
0.0186	0.0301	0.0520	0.0015	0.0798	-0.0353	0.7017	0.6586	0.0431
0.0196	0.0463	0.0631	0.0027	0.1356	-0.0490	0.7271	0.6541	0.0730
0.0230	0.0086	0.0179	0.0004	0.0170	-0.0135	0.5264	0.6391	-0.1127
0.0245	0.0599	0.1188	0.0042	0.1668	-0.0593	1.3053	0.6324	0.6728
0.0296	0.0432	0.0339	0.0019	0.0637	-0.0328	0.5032	0.6132	-0.1099
0.0337	0.0266	0.0177	0.0004	0.0127	0.0047	0.6327	0.5996	0.0331
0.0400	0.0586	0.0533	0.0027	0.0661	-0.0347	0.7881	0.5806	0.2076
0.0429	0.0549	0.0348	0.0030	0.0662	-0.0438	0.5158	0.5726	-0.0568
0.0577	0.0786	0.0333	0.0045	0.0742	-0.0492	0.4813	0.5369	-0.0536
0.0637	0.0592	0.0301	0.0030	0.0441	-0.0373	0.5421	0.5245	0.0177
0.0650	0.0379	0.0174	0.0012	0.0172	-0.0151	0.5321	0.5218	0.0103
0.0672	0.0467	0.0204	0.0014	0.0193	-0.0125	0.5809	0.5174	0.0635
0.0677	0.0486	0.0197	0.0015	0.0208	-0.0136	0.5356	0.5166	0.0190
0.0678	0.0467	0.0193	0.0013	0.0181	-0.0094	0.5693	0.5164	0.0529
0.0698	0.0084	0.0060	0.0002	0.0027	-0.0027	0.5997	0.5125	0.0872

Solvent Free Aqueous Cobalt Mole Fraction	Phase Concentrations				$\Delta X_i$ M	Actual	$\hat{X}_i$ Predicted	Residual
	Organic Phase Cobalt M	Nickel M	Aqueous Phase Cobalt M	Nickel M				
0.0747	0.0703	0.0199	0.0052	0.0644	-0.0538	0.3088	0.5034	-0.1946
0.0752	0.0556	0.0260	0.0021	0.0257	-0.0217	0.6286	0.5026	0.1260
0.0753	0.1405	0.0162	0.0080	0.0988	-0.0043	0.2170	0.5025	-0.2855
0.0821	0.0875	0.0203	0.0047	0.0521	-0.0304	0.3466	0.4908	-0.1442
0.0829	0.1396	0.0163	0.0082	0.0911	-0.0051	0.2260	0.4893	-0.2633
0.0837	0.1010	0.0230	0.0076	0.0836	-0.0401	0.3270	0.4881	-0.1610
0.0890	0.1014	0.0239	0.0053	0.0546	-0.0217	0.4031	0.4794	-0.0763
0.0904	0.1413	0.0152	0.0089	0.0894	-0.0057	0.2137	0.4773	-0.2636
0.1078	0.0653	0.0146	0.0017	0.0139	0.0004	0.5347	0.4518	0.0828
0.1095	0.1456	0.0144	0.0142	0.1158	-0.0157	0.1907	0.4495	-0.2588
0.1161	0.0552	0.0100	0.0018	0.0138	-0.0116	0.3733	0.4408	-0.0675
0.1348	0.0567	0.0278	0.0020	0.0125	-0.0134	1.1214	0.4178	0.7036
0.1447	0.1677	0.0067	0.0224	0.1322	0.0004	0.0887	0.4065	-0.3178
0.1595	0.0925	0.0297	0.0036	0.0192	-0.0028	0.9385	0.3907	0.5478
0.1626	0.1332	0.0078	0.0070	0.0363	0.0077	0.1731	0.3875	-0.2144
0.2012	0.1602	0.0093	0.0138	0.0546	0.0164	0.1778	0.3513	-0.1735
0.2103	0.1944	0.0012	0.0319	0.1198	0.0332	0.0185	0.3435	-0.3250
0.2219	0.1620	0.0098	0.0124	0.0436	0.0251	0.2130	0.3339	-0.1209
0.2330	0.1766	0.0039	0.0182	0.0599	0.0312	0.0742	0.3251	-0.2509
0.2640	0.0786	0.0054	0.0028	0.0080	0.0056	0.3451	0.3019	0.0431
0.2762	0.1103	0.0060	0.0054	0.0142	0.0118	0.2686	0.2934	-0.0247
0.2765	0.0791	0.0058	0.0027	0.0071	0.0088	0.4140	0.2932	0.1208
0.2910	0.2029	0.0014	0.0409	0.0996	0.0549	0.0239	0.2834	-0.2595
0.2917	0.0156	0.0002	0.0003	0.0007	0.0033	0.0518	0.2829	-0.2311

Solvent Free Aqueous Cobalt Mole Fraction	Phase Concentrations				$\Delta Y_i$ M	Actual	$\hat{Y}_i$ Predicted	Residual
	Organic Phase		Aqueous Phase					
	Cobalt M	Nickel M	Cobalt M	Nickel M				
0.2917	0.0923	0.0039	0.0062	0.0150	-0.0094	0.1700	0.2829	-0.1129
0.3072	0.1031	0.0046	0.0063	0.0143	0.0030	0.2111	0.2728	-0.0617
0.3574	0.1434	0.0031	0.0117	0.0211	0.0318	0.1192	0.2425	-0.1233
0.3584	0.1424	0.0031	0.0112	0.0201	0.0322	0.1268	0.2419	-0.1151
0.4049	0.2015	0.0013	0.0696	0.1023	0.0730	0.0275	0.2165	-0.1891
0.4436	0.0783	0.0058	0.0056	0.0070	0.0014	0.5328	0.1970	0.3358
0.5157	0.2066	0.0009	0.0379	0.0356	0.1061	0.0336	0.1637	-0.1301
0.5368	0.1976	0.0006	0.0451	0.0389	0.1002	0.0240	0.1546	-0.1306
0.5952	0.2047	0.0008	0.0345	0.0234	0.1214	0.0473	0.1307	-0.0533
0.6347	0.2194	0.0003	0.0826	0.0476	0.1399	0.0112	0.1155	-0.1042
0.6392	0.2110	0.0003	0.0935	0.0528	0.1321	0.0138	0.1138	-0.1000
0.6785	0.0193	0.0007	0.0003	0.0002	0.0137	0.4394	0.0994	0.3400
0.7517	0.0902	0.0008	0.0026	0.0009	0.0666	0.4726	0.0741	0.3984
0.7660	0.0915	0.0006	0.0036	0.0011	0.0650	0.3581	0.0694	0.2887
0.7743	0.1585	0.0006	0.0106	0.0031	0.1203	0.2440	0.0667	0.1773
0.8339	0.0195	0.0000	0.0004	0.0001	0.0157	0.0532	0.0478	0.0053
0.8436	0.1184	0.0000	0.0130	0.0024	0.0906	0.0000	0.0449	-0.0449
0.8842	0.1601	0.0003	0.0196	0.0026	0.1379	0.2648	0.0327	0.2321
0.8970	0.1759	0.0001	0.0280	0.0032	0.1552	0.1061	0.0289	0.0772
0.9249	0.2188	0.0001	0.0628	0.0051	0.2027	0.1056	0.0208	0.0847
0.9282	0.2157	0.0001	0.0608	0.0047	0.2003	0.0982	0.0199	0.0783
0.9392	0.1587	0.0001	0.0137	0.0009	0.1478	0.2623	0.0168	0.2455
0.9525	0.2142	0.0000	0.1296	0.0065	0.2037	0.0458	0.0131	0.0327
0.9538	0.1991	0.0001	0.1142	0.0055	0.1889	0.1779	0.0127	0.1652

## 6.2 Reagent Specifications

### 6.2.1 Cobalt Sulfate, 7-Hydrate

Manufacturer	J.T.Baker Chemical Co.
Formula	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$
Formula Weight	281.1
Assay (by EDTA titration as Hydrate)	98.4%
pH of 5% solution at 25 C	4.1
Insoluble matter	< 0.0003%
Chloride	< 0.001%
Nitrate	0.001%
Copper (by AAS)	0.0004%
Iron (by AAS)	0.001%
Lead (by AAS)	0.001%
Nickel (by AAS)	0.04%
Zinc (by AAS)	0.002%

### 6.2.2 Nickelous Sulfate, 6-Hydrate

Manufacturer	Fisher Scientific
Formula	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
Formula Weight	262.86
Assay (by EDTA titration as Hydrate)	99.6%
Insoluble matter	< 0.002%
Chloride	0.0003%
Nitrogen compounds as N	0.0007%
Copper (by AAS)	0.002%
Iron (by AAS)	0.0003%
Cobalt and Manganese as Co (by AAS)	0.04%

### 6.2.3 Ammonium Sulfate

Manufacturer	Fisher Scientific
Formula	$(\text{NH}_4)_2\text{SO}_4$
Formula Weight	132.1
Assay (by formol method)	99.8%
Insoluble matter	<0.001%
Residue after ignition	0.004%
Chloride	<2 ppm
Nitrate	0.0003%
Phosphate	<1 ppm
Iron	<3 ppm
Heavy Metals (as Pb)	<2 ppm

### 6.2.4 Varsol DX3641

Manufacturer	Esso Chemicals Ltd.
Average Formula Weight	158
Density	0.793 at 20 C.
Flash Point	57.2 C
Solubility Parameter	7.7
Viscosity	1.165 cP at 25 C
Aromatic Content	6% (w/w)
Paraffinic Content	45% (w/w)
Napthenic Content	49% (w/w)

### 6.2.5 n-Tributyl Phosphate

Manufacturer	Anachemia Ltd.
Formula Weight	266.32
Density	0.973 at 25 C.

## 6.3 Sample Calculation

This calculation is a sample of the calculations used in this thesis. All of the calculations used in this thesis were calculated using the program included in the appendix.

### Basic Data

Standard concentrations of Cobalt and Nickel were measured before, during, and after the measurement of the sample. These standards were used to check for any baseline drift during the measurements and to develop a standard curve for Cobalt and Nickel using a linear regression calculation. This calculation is included in the program provided.

Example Run 8612032CN Sample 7

### Initial Data:

#### Concentrations of Standard Solutions

Delivery of Cobalt Sulfate to Cobalt Std.	= 230.6705 g
Purity of Cobalt Sulfate	= 98.4 %
Nickel Impurity in Cobalt Sulfate	= 0.04 %
Volume of Cobalt Sulfate Solution	= 1000 ml

Delivery of Nickel Sulfate to Nickel Std. = 50.0058 g  
Purity of Nickel Sulfate = 99.6 %  
Nickel Impurity in Nickel Sulfate = 0.001%  
Volume of Nickel Sulfate Solution = 1000 ml

Concentration of Cobalt in Cobalt Std =

$230.6705 \text{ g} * 98.4/100 * (58.9332/281.1)/1000 \text{ ml} = 0.0476 \text{ g/ml}$

Concentration of Nickel in Cobalt Std =

$230.6705 \text{ g} * 0.04/100/1000 \text{ ml} = 9.23\text{e-}5 \text{ g/ml}$

Concentration of Nickel in Nickel Std =

$50.0058 \text{ g} * 99.6/100 * (58.71/262.86)/1000 \text{ ml} = 0.0111 \text{ g/ml}$

Concentration of Cobalt in Nickel Std =

$50.0058 \text{ g} * 0.001/100/1000 \text{ ml} = 5.0\text{e-}7 \text{ g/ml}$

Volume of Cobalt Standard delivered to Sample = 4.53 ml

Volume of Nickel Standard delivered to Sample = 32.37 ml

Volume of H<sub>2</sub>SO<sub>4</sub> delivered to Sample = 0.90 ml

Volume of NH<sub>4</sub>OH delivered to Sample = 0.00 ml

Concentration of H<sub>2</sub>SO<sub>4</sub> = 7.5 mol/L

Concentration of NH<sub>4</sub>OH = 6.6 mol/L

Temperature at Equilibrium = 25 C

pH at Equilibrium = 5.04

The Standard Curves were calculated from the Cobalt and Nickel Standards and found to be:

for Cobalt: Concentration(ppm) =  $-0.1026 + 31.36$  (reading)

for Nickel: Concentration(ppm) =  $-0.0440 + 30.46$  (reading)

(see program or Draper (Ref. [15] for details).

Average Reading from AAS for Organic Phase Cobalt = 0.1512  
Dilution factor (1) of Organic Phase Cobalt = 0.05 ml/ml  
Dilution factor (2) of Organic Phase Cobalt = 1.00 ml/ml  
Sample Volume to which Org. Co aliquot delivered = 250 ml  
Aliquot Volume of Org. Co taken for analysis = 5 ml  
Original Volume of Organic Phase = 50 ml

Average Reading from AAS for Aqueous Phase Cobalt = 0.046  
Dilution factor (1) of Aqueous Phase Cobalt = 0.50 ml/ml  
Dilution factor (2) of Aqueous Phase Cobalt = 1.00 ml/ml  
Sample Volume to which Aq. Co aliquot delivered = 500 ml  
Aliquot Volume of Aq. Co taken for analysis = 5 ml  
Original Volume of Aqueous Phase = 50 ml

Average Reading from AAS for Organic Phase Nickel = 0.1300  
Dilution factor (1) of Organic Phase Nickel = 0.10 ml/ml  
Dilution factor (2) of Organic Phase Nickel = 1.00 ml/ml  
Sample Volume to which Org. Ni aliquot delivered = 250 ml  
Aliquot Volume of Org. Ni taken for analysis = 5 ml  
Original Volume of Organic Phase = 50 ml

Average Reading from AAS for Aqueous Phase Nickel = 0.073  
Dilution factor (1) of Aqueous Phase Nickel = 0.50 ml/ml  
Dilution factor (2) of Aqueous Phase Nickel = 0.10 ml/ml

Sample Volume to which Aq. Ni aliquot delivered = 500 ml  
 Aliquot Volume of Aq. Ni taken for analysis = 5 ml  
 Original Volume of Aqueous Phase = 50 ml

Calculations:

Aqueous/Organic Ratio

$$= (\text{Original Aqueous Volume} + \text{Volume Acid Del.} \\ + \text{Volume Base Del.}) / \text{Original Organic Volume} \\ = (50 + 0.9 + 0) / 50 = 1.018$$

Concentration of Estimated Equilibrium Cobalt in  
 Sample Organic Phase from Standard Curve

$$= -0.1026 + 31.36 * 0.1512 = 4.639 \text{ ppm}$$

Concentration of Estimated Equilibrium Organic Cobalt in g/ml

$$= (4.639 * 1e-6) / (1 - 4.639 * 1e-6) = 4.639e-6 \text{ g/ml}$$

Concentration of Estimated Equilibrium Organic Cobalt  
 before Dilutions

$$= (4.639e-6 \text{ g/ml}) / (0.05 \text{ ml/ml}) / (1.0 \text{ ml/ml}) * (250 \text{ ml}) / (5 \text{ ml}) \\ = 4.64e-3 \text{ g/ml}$$

The error for the Estimated Equilibrium  
 Organic Cobalt Concentration was based on the statistical fit

of the cobalt and nickel standard solutions was calculated to be:

( See the program for details as to how this was calculated.)

$$= 0.10e-3 \text{ g/ml}$$

Converting Cobalt concentration to Molar Units

$$= 4.64e-3 \text{ g/ml} * 1\text{mol}/58.9332\text{g} * 1000\text{ml}/\text{L}$$

$$= 0.079 \text{ +/-} 0.002 \text{ M.}$$

Similar Calculations were performed for Cobalt in the Aqueous phase and Nickel in the Organic and Aqueous Phases

Concentration of Cobalt in the Aqueous Phase

$$= 0.30\text{+/-}0.00e-3 \text{ g/ml}$$

$$= 0.0051\text{+/-}0.000 \text{ M.}$$

Concentration of Nickel in the Organic Phase

$$= 2.00\text{+/-}0.00e-3 \text{ g/ml}$$

$$= 0.0341\text{+/-}0.000 \text{ M.}$$

Concentration of Nickel in the Aqueous Phase

$$= 4.40\text{+/-}0.10e-3 \text{ g/ml}$$

$$= 0.0749\text{+/-}0.002 \text{ M.}$$

Estimated Aqueous Phase Solvent Free Cobalt Mole Fraction

$$X_{co} = 0.0051 / (0.0749 + 0.0051) = 0.064$$

Estimated Aqueous Phase Solvent Free Nickel Mole Fraction

$$X_{ni} = 1 - 0.064 = 0.936$$

Estimated Cobalt Distribution Coefficient (Organic/Aqueous)

$$D_{co} = C_{org}/C_{aq}$$

$$= ((4.64 \pm 0.1) \cdot 10^{-3}) / ((0.3 \pm 0.0) \cdot 10^{-3}) = 17 \pm 1$$

Estimated Nickel Distribution Coefficient (Organic/Aqueous)

$$D_{ni} = C_{org}/C_{aq}$$

$$= ((2.0 \pm 0.0) \cdot 10^{-3}) / ((4.4 \pm 0.1) \cdot 10^{-3}) = 0.45 \pm 0.01$$

Estimated Separation Factor (Cobalt/Nickel)

$$S_{(co/ni)} = D_{co}/D_{ni}$$

$$= (17 \pm 1) / (0.45 \pm 0.01) = 38.5 \pm 2.8$$

Percentage of Cobalt Extracted from Equilibrium Sample:

Estimated Total Cobalt in Organic Phase

$$= C_{org} \cdot V_{org}$$

$$= 4.639 \times 10^{-3} \text{ g/ml} \cdot 50 \text{ ml} = 0.232 \text{ g}$$

Total Cobalt Delivered to Sample

$$= (\text{Vol of Co Std}) \cdot (\text{Conc. of Co in Co Std}) +$$

$$(\text{Vol of Ni Std}) * (\text{Conc of Co Impurity in Ni Std})$$

$$=(4.53 \text{ ml}) * (0.0476 \text{ g/ml}) + (32.37 \text{ ml}) (5.0 \times 10^{-7} \text{ g/ml}) = 0.216 \text{ g}$$

Percentage of Cobalt Extracted

$$= (\text{Est. Co in Organic Phase}) / (\text{Total Co Delivered to Sample})$$

$$= (0.232) / (0.216) * 100 = 107 \pm 2 \%$$

Calculation of Mass Balance for Cobalt and Nickel:

Estimated Total Cobalt in Aqueous Phase

$$= 0.3 \times 10^{-3} \text{ g/ml} * (50 + 0.9 + 0) \text{ ml} = 0.015 \text{ g}$$

Total Estimated Cobalt Recovered = 0.247 g

Estimated Total Nickel in Organic Phase = 0.100 g

Estimated Total Nickel in Aqueous Phase = 0.224 g

Total Estimated Nickel Recovered = 0.324 g

Percentage of Cobalt Recovered by analysis

for Mass Balance, (as before errors were estimated using standard procedures)

$$= (\text{Total Estimated Co recovered}) / (\text{Total Co Delivered to Sample}) * 100$$

$$= 0.247\text{g}/0.216\text{g} * 100 \qquad = 114 \text{ +/- } 3 \%$$

Similarly for Nickel, percent Nickel Recovered by analysis for Mass Balance

$$= 0.324\text{g}/0.365\text{g} * 100 \qquad = 88.8 \text{ +/- } 2 \%$$

Percent Total Mass of Cobalt and Nickel Recovered

$$= (\text{Total Co and Ni recovered}) /$$

$$(\text{Total Co and Ni delivered}) * 100$$

$$= (0.247\text{ g} + 0.324\text{g}) / (0.216\text{g} + 0.365\text{g}) * 100 = 98.2 \text{ +/- } 2 \%$$

Non-linear Regression of Pure Component Extractions at a pH of 5.02 gave the following "Best fit" equations (concentrations in Moles/L):

$$\text{Cobalt} \quad C_{org} = 0.2272 * (276.94) * C_{aq} / (1 + 276.94 * C_{aq})$$

$$\text{Nickel} \quad C_{org} = 0.1076 * (22.987) * C_{aq} / (1 + 22.987 * C_{aq}) +$$

$$0.004 \exp(3.663 * C_{aq})$$

Predicted Organic Concentrations from Pure Component Regressions

For Cobalt:

$$C_{org} = 0.2272 * 276.94 * 0.0051 / (1 + 276.94 * 0.0051)$$

$$= 0.1330 \text{ M}$$

For Nickel:

$$\text{Corg} = 0.1076 * 22.987 * 0.0749 / (1 + 22.987 * 0.0749) \\ + 0.004 \exp(3.663 * 0.0749)$$

$$= 0.0733 \text{ M}$$

Therefore the estimated pseudo-gamma function of Cobalt for this sample is

$$\text{gamma}(\text{Co}) = (\text{actual Corg}) / (\text{Xco}) * (\text{predicted Corg})$$

$$\text{gamma}(\text{Co}) = 0.079 \text{ M} / (0.064 * 0.1330 \text{ M}) = 9.28$$

Similarly the estimated psuedo-gamma function for Nickel for this sample is

$$\text{gamma}(\text{Ni}) = 0.0341 \text{ M} / (0.936 * 0.0733 \text{ M}) = 0.497$$

From the "Best fit" Non-Linear Regression of the pseudo gamma data, the following predicted relationships were developed.

$$\text{gamma}(\text{Co})^* = 1 / (1 - (\text{mole fraction Ni})^{1.91})$$

$$\text{gamma}(\text{Ni})^* = 1 - (\text{mol fraction Co})^{0.27}$$

Therefore the predicted pseudo-gamma function values for this

## CHAPTER G. APPENDIX

sample are:

$$\text{gamma (Co)} = 1 / (1 - (0.936)^{1.91}) = 8.43$$

$$\text{gamma (Ni)} = 1 - (0.064)^{0.27} = 0.524$$

Therefore the Residual values for the Sample predicted pseudo-gamma values are:

$$\text{Residual(Co)} = 9.28 - 8.43 = 0.85$$

$$\text{Residual(Ni)} = 0.497 - 0.524 = -0.027$$

## 6.4 Fortran Data Analysis Program

### 6.4.1 Executive Program Code

```
FORTVS &1
GLOBAL TXTLIB VLNKMLIB FORTLIB VFORTLIB CMSLIB PLOTLIB IMSLSLIB
FI 15 DISK TEMPRY DATA A (LRECL 240 RECFM F BLKSIZE 240
FI 10 DISK MASTER DATA A (LRECL 240 RECFM F BLKSIZE 240
FI 5 DISK &1 DATA A (LRECL 80 RECFM F
FI 6 DISK &1 RESULT A
FI 7 TERMINAL
LOAD &1 (CLEAR START
&TYPE DO YOU WISH THIS DATA SAVED IN THE MASTER DATA FILE (DEF=N)
&TYPE (ONLY DO IF MOL FRACTIONS WERE CALC.)
&READ VARS &ANS
&IF .&ANS = .YES &GOTO -PRE
&IF .&ANS = .Y &GOTO -PRE
&GOTO -DEF
-PRE
COPYFILE TEMPRY DATA A MASTER DATA A (APPEND COMPRESS
ERASE TEMPRY DATA A
-DEF
```

## 6.4.2 Program Code

```
C-----  
C   A PROGRAM TO ANALYZE DATA FROM BINARY EXTRACTION EXPERIMENTS  
C   NOMENCLATURE:  
C  
C   STANDARD CONCENTRATED SOLUTIONS:  
C   COCOD=CONCENTRATED COBALT SULFATE DELIVERY (G)  
C   CONID="          " NICKEL "          " (G)  
C   COCP=PURITY OF COSO4 (%)  
C   CONP=PURITY OF NISO4 (%)  
C   COCIM=NI IMPURITY IN COSO4 (%)  
C   CONIM=CO IMPURITY IN NISO4 (%)  
C   COCV=VOLUME OF COSO4 CONCENTRATED SOLUTION (ML)  
C   CONV=VOLUME OF NISO4 CONCENTRATED SOLUTION (ML)  
C   COCOC=CONCENTRATION OF CONCENTRATED COSO4 SOLN (G/ML)  
C   CONOC=CONCENTRATION OF CONCENTRATED NISO4 SOLN (G/ML)  
C   COCIC=CONCENTRATION OF NI IMPURITY IN CONCENTRATED COSO4 SOLN(G/ML)  
C   CONIIC=CONCENTRATION OF CO IMPURITY IN CONCENTRATED NISO4 SOLN(G/ML)  
C  
C   STANDARD CURVE VARIABLES (AA READINGS ASSUMED INDEPENDENT );  
C   N- NUMBER OF OBSERVATIONS  
C   SAA-SUM OF AA READINGS STANDARDS  
C   SCON-SUM OF CONC.STANDARDS (PPM)  
C   SSAA-SUM OF SQUARED AA READINGS  
C   SSSCON-"          "CONC. "  "  
C   SACON-SUM OF READINGS&CONC.PRODUCTS  
C   SAA2-(SUM AA READINGS)**2  
C   SCON2-"  "CONC"          "  
C   B- INTERCEPT OF BEST FIT LINE  
C   A- SLOPE"          "  
C   TR- TOP OF REGRESSION COEFFICIENT
```

C BR- BOTTOM "

C R- REGRESSION COEFFICIENT

C SCONAA-STANDARD ERROR OF ESTIMATE

C SB- STANDARD ERROR OF REGRESSION

C

C PREDICTIONS;

C NPTS-NUMBER OF SAMPLES TO BE ANALYSED

C SN-SAMPLE NUMBER

C READ(1)-AVERAGE READING FROM AAS FOR ORGANIC PHASE CO.

C DF1(1),DF2(1)-DILUTION FACTORS REQD TO ANALYSE FOR CO IN ORG.

C SV(1)-SAMPLE VOLUME (ML) TO WHICH (CO,ORG) ALIQUOT IS DELIVERED

C AV(1)-ALIQUOT VOLUME (ML) ORGANIC PHASE REQD FOR CO ANALYSIS

C OV(1)-ORIGINAL VOLUME OF THE ORGANIC PHASE (ML)

C DELC-VOLUME OF COSO<sub>4</sub> CONCENTRATED SOLUTION DELIVERED (ML)

C READ(2)-AQUEOUS PHASE READING FOR CO ANALYSIS

C DF1(2),DF2(2)- DILUTION FACTORS FOR AQUEOUS CO ANALYSIS

C SV(2),AV(2),OV(2)-SAME AS ABOVE EXCEPT FOR AQUEOUS CO (ML)

C DELN-VOLUME OF NISO<sub>4</sub> CONC. SOLN. DELIVERED (ML)

C READ(3),DF1(3),DF2(3),SV(3),AV(3),OV(3)-SAME AS ABOVE EXCEPT FOR

C NI ANALYSIS IN ORGANIC PHASE

C PH-PH OF AQUEOUS PHASE AT EQUILIBRIUM

C VACID,VBASE-VOLUME (ML) OF H<sub>2</sub>SO<sub>4</sub> OF NH<sub>4</sub>OH ADDED TO ADJUST PH

C CACID,CBASE- CONCENTRATION (MOL/L) "

C T- TEMPERATURE OF SAMPLE AT EQUIL. (C)

C PPT- PRECIPITATE OBSERVED DURING EXTRACTION

C READ(4),DF1(4),DF2(4),SV(4),AV(4),OV(4)-SAME AS ABOVE EXCEPT FOR

C NI ANALYSIS IN AQUEOUS PHASE

C C(J)-CONC OF DILUTED SAMPLE IN PPM (J=1-4 =CO ORG--NI AQ, AS ABOVE

C CORC(J)-CORRECTED CONC OF DIL. SAMPLE ( G/ML)

C CA=CONC OF ALIQUOT(G/ML)

C G-WT OF METAL IN ALIQUAT  
 C CO-ORIGINAL CONCENTRATION OF PHASE BEFORE DILUTION (G/ML)  
 C GO-" " WEIGHT" " G  
 C D- DISTRIBUTION FACTOR (ORG/AQ)  
 C ODC-ORIGINAL DELIVERY OF CO TO SAMPLE (G)  
 C ODN-" " NI " "  
 C OD- ORIGINAL DELIVERY OF TOTAL METAL TO SAMPLE (G)  
 C PRX(1)-PERCENT CO EXTRACTED  
 C PRX(2)-" " NI" "  
 C REC(1)-RECOVERY OF CO (%)  
 C REC(2)" "NI (%).  
 C TREC-"% TOTAL RECOVERY  
 C S- SEPARATION FACTOR (CO/NI)  
 C CN- CO/NI RATIO  
 C STCON- STARTING CONCENTRATION OF TOTAL METAL (G/ML)  
 C RE\_\_\_\_\_ - RELATIVE ERROR OF VARIABLE  
 C E\_\_\_\_\_ - ESTIMATED ERROR IN MEASUREMENT OF VARIABLE  
 C MOL(K) - MOLAR CONC. OF METAL IN EACH PHASE(CO-ORG=1.NI-AQ=4)  
 C TMOL(K)- TOTAL MOL OF (CO-ORG=1.,NI-AQ=4, AS BEFORE) IN PHASE  
 C FMCO- MOL FRACTION CO IN ORGANIC PHASE(SOLVENT FREE)  
 C FMCA- " "AQUEOUS" "  
 C EKS04,EKNH3,EKH20-EQUILIBRIUM CONSTANTS ESTIMATED USING VAN'T HOFF  
 C ESTS04- ESTIMATED SO4 AQUEOUS CONC (MOL/L)  
 C CH- AQUEOUS CONCENTRATION OF H (MOL/L)  
 C COH- AQUEOUS CONCENTRATION OF OH (MOL/L)  
 C CHS04- AQUEOUS CONCENTRATION OF HSO4 (MOL/L)  
 C CS04- AQUEOUS CONCENTRATION OF SO4 (MOL/L) CORRECTED  
 C ESTNH4- EST.AQUEOUS CONCENTRATION OF NH4 (MOL/L)  
 C CNH3- AQUEOUS CONCENTRATION OF NH3 (MOL/L)  
 C CNH4- AQUEOUS CONCENTRATION OF NH4 (MOL/L) CORRECTED

C IONIC- IONIC STRENGTH AQUEOUS

C AO= AQUEOUS/ORGANIC RATIO

C

-----  
CHARACTER\*11 RUN, METAL, ANSWER, PPT

REAL MOL, IONIC

DIMENSION N(2), SAA(2), SCON(2), SSAA(2), SCON(2), SACON(2), SAA2(2)

\* , SCON2(2), B(2), A(2), TR(2), BR(2), R(2), SCONAA(2), SB(2)

\* , READ(4), DF1(4), DF2(4), SV(4), AV(4), GV(4), C(4), CO(4)

\* , GO(4), EC(4), ED(4), EGO(4), D(2), RED(2), ED(2), PRX(2)

\* , EPRX(2), REC(2), EREC(2), TMOL(4), REPRX(2), REREC(2), MOL(4)

WRITE(7,1)

READ (7,11) ANSWER

1 FORMAT(T1, 'DO YOU WISH SOLVENT FREE MOL. FRACTIONS ? (Y/N)')

11 FORMAT(T1, A10)

TRIP=0.

READ (5,41) RUN

41 FORMAT (T1, A10)

C CALCULATE THE CONCENTRATIONS OF THE ORIGINAL STANDARD SOLN(G/ML)

READ (5,\*)COCOD, COCP, COCIM, COCV, CONID, CONP, CONIM, CONV

COCOC=COCOD\*COCP/100.\*58.9332/281.1/COCV

CONOC=CONID\*CONP/100.\*58.71/262.86/CONV

COCIC=COCD\*COCIM/100./COCV

CONIIC=CONID\*CONIM/100./CONV

C

-----  
C CALCULATE THE STANDARD CURVE PARAMETERS FOR METAL1 &METAL2

C FROM AAS DATA

C \*\*\*\*\* ENTER COBALT STANDARD CURVE FIRST THEN NICKEL \*\*\*\*\*

C

```

DO 10 I=1,2
  READ (5,*)N(I)
  DO 20 J=1,N(I)
    READ (5,*)AA,CONC
    SAA(I)=SAA(I)+AA
    SSAA(I)=SSAA(I)+AA**2
    SCON(I)=SCON(I)+CONC
    SCON(I)=SSCON(I)+CONC**2
    SACON(I)=SACON(I)+AA*CONC
20  CONTINUE
  SAA2(I)=(N(I)*SSAA(I)-SAA(I)**2)/(N(I)*(N(I)-1.))
  SCON2(I)=(N(I)*SSCON(I)-SCON(I)**2)/(N(I)*(N(I)-1.))
  B(I)=(N(I)*SACON(I)-SAA(I)*SCON(I))/(N(I)*SSAA(I)-SAA(I)**2)
  A(I)=(SCON(I)-B(I)*SAA(I))/N(I)
  TR(I)=(N(I)*SACON(I)-(SAA(I)*SCON(I)))**2
  BR(I)=(N(I)*SSAA(I)-SAA(I)**2)*(N(I)*SSCON(I)-SCON(I)**2)
  R(I)=SQRT( TR(I)/BR(I))
C-----
C          CALCULATE THE STANDARD ERRORS
C-----
  SCONAA(I)=SQRT((N(I)-1.)/(N(I)-2.)*(SCON2(I)-B(I)**2*SAA2(I)))
  SB(I)=SCONAA(I)/(SQRT(SAA2(I)*(N(I)-1.)))
10  CONTINUE
C-----
C          WRITE THE PRELIMINARY INFORMATION
C-----
  WRITE(6,22)RUN
  WRITE(15,22)RUN
22  FORMAT(/,T5,'RUN NUMBER:',T47,A10,/)
  DO 30 I=1,2
    IF (I.EQ.1) THEN

```

```

    METAL='COBALT'
    ELSE
    METAL='NICKEL'
    ENDIF
    WRITE (6,23) METAL
23    FORMAT(/,T5,A10,T16,'STANDARD CURVE',/)
7    FORMAT (T5,F7.4,T15,F4.2,T25,F7.4,T35,F7.4,T45,F7.4,T55,F4.2,
*      T60, F4.2)
    WRITE (6,2)A(I),B(I)
    WRITE (6,3)SCONAA(I)
    WRITE (6,4)SB(I)
    WRITE (6,5)R(I)
    WRITE (6,6)N(I)
30   CONTINUE
2    FORMAT (T5,'REGRESSION ANALYSIS: ESTIMATE; Y=',T40,E12.4,'+(
*      ',T55,E12.4,')*X')
3    FORMAT (T5,'STANDARD ERROR OF ESTIMATE =',T45,E12.4)
4    FORMAT (T5,'STANDARD ERROR OF REGRESSION =',T45,E12.4)
5    FORMAT (T5,'CORRELATION COEFFICIENT =',T45,E12.4)
6    FORMAT (T5,'NUMBER OF FITTED POINTS =',T45,I3)
C-----
C      PREDICT CONCENTRATIONS
C-----
    READ (5,52) NPTS
    WRITE (15,52)NPTS
52   FORMAT (T5,I2)
    DO 40 I=1,NPTS
        READ (5,7)SN,READ(1),DF1(1),DF2(1),SV(1),AV(1),OV(1)
        READ (5,7)DELC,READ(2),DF1(2),DF2(2),SV(2),AV(2),OV(2)
        READ (5,7)DELN,READ(3),DF1(3),DF2(3),SV(3),AV(3),OV(3)
        READ (5,7)PH,READ(4),DF1(4),DF2(4),SV(4),AV(4),OV(4)
```

```

      READ (5,51) VACID,CACID,VBASE,CBASE,T,PPT
51  FORMAT (T5,F7.4,T15,F7.4,T25,F7.4,T35,F7.4,T45,F7.4,T55,A11,/)
      AO=(OV(4)+VACID +VBASE)/OV(3)
      DO 50 J=1,4
          IF (J.LE.2) THEN
              INDEX=1
          ELSE
              INDEX=2
          ENDIF
      C      CALCULATE THE CONCENTRATION IN PPM
      C      C(J)=(A(INDEX)+B(INDEX)*READ(J))
      C      CHANGE CONC. TO G/ML (1PPM=1.E-6 G/ML)
      C      CORC= C(J)*1.E-6/(1.-C(J)*1.E-6)
      C      CALCULATE CONC BEFORE DILUTIONS
      C      CA=CORC/DF1(J)/DF2(J)
      C      G=CA*SV(J)
      C      CALCULATE CONC IN THE ORIGINAL PHASE SAMPLE (G/ML)
      C      CO(J)=G/AV(J)
      C      CALCULATE THE TOTAL METAL IN G. IN THE ORIGINAL PHASE
      C      IF ((J.EQ.1).OR.(J.EQ.3)) THEN
      C      GO(J)=CO(J)*OV(J)
      C      ELSE
      C      GO(J)=CO(J)*(OV(J)+VACID+VBASE)
      C      ENDIF
      C      EC(J)= 2.*SCONAA(INDEX)*SQRT((1./N(INDEX)+(READ(J)-
      *      (SAA(INDEX)/N(INDEX)))**2)
      *      /((N(INDEX)-1.)*SAA2(INDEX)))
      C      CALCULATE THE RELATIVE ERROR FOR CORRECTED CONCENTRATION
      C      RECOR=SQRT((EC(J)/C(J))**2+(EC(J)*1.E-6
      *      /(1.-C(J)*1.E-6))**2)

```

```

        ECOR=CORC*RECOR
        EA=ECOR/DF1(J)/DF2(J)
        EG=EA*SV(J)
        EO(J)= EG/AV(J)
        EGO(J)=EO(J)*OV(J)
50      CONTINUE
        D(1)=CO(1)/CO(2)
        D(2)=CO(3)/CO(4)
C      AGAIN CALC. THE RELATIVE ERROR FOR D
        RED(1)=SQRT((EO(1)/CO(1))**2+(EO(2)/CO(2))**2)
        ED(1)=RED(1)*D(1)
        RED(2)=SQRT((EO(3)/CO(3))**2+(EO(4)/CO(4))**2)
        ED(2)=RED(2)*D(2)
        ODC=COCOC*DEL C+CONIIC*DEL N
        ODN=CONOC*DEL N+COCIC*DEL C
        EODC=(COCOC+CONIIC)*0.05
        EODN=(CONOC+COCIC)*0.05
        PRX(1)=GO(1)/ODC*100.
        PRX(2)=GO(3)/ODN*100.
        REPRX(1)=SQRT((EGC(1)/GO(1))**2+(EODC/ODC)**2)
        REPRX(2)=SQRT((EGO(3)/GO(3))**2+(EODN/ODN)**2)
        EPRX(1)=PRX(1)*REPRX(1)
        EPRX(2)=PRX(2)*REPRX(2)
        REC(1)=(GO(1)+GO(2))/ODC*100.
        REC(2)=(GO(3)+GO(4))/ODN*100.
        REREC(1)=SQRT(((EGO(1)+EGO(2))/(GO(1)+GO(2)))**2+(EODC/ODC)**
*           2)
        REREC(2)=SQRT(((EGO(3)+EGO(4))/(GO(3)+GO(4)))**2+(EODN/ODN)**
*           2)
        EREC(1)=REC(1)*REREC(1)

```

```

EREC(2)=REC(2)*REREC(2)
OD=ODC+ODN
EOD=EODC+EODN
TREC=(GO(1)+GO(2)+GO(3)+GO(4))/OD*100.
RETREC=SQRT( ((EGO(1)+EGO(2)+EGO(3)+EGO(4))/(GO(1)+GO(2)+
*          GO(3)+GO(4)))**2+(EOD/OD)**2)
ETREC=TREC*RETREC
S=D(1)/D(2)
RES=SQRT((ED(1)/D(1))**2+(ED(2)/D(2))**2)
ES=RES*S
IF (ODN.NE.0.) THEN
CN=ODC/ODN
ENDIF
RECN=SQRT((EODC/ODC)**2+(EODN/ODN)**2)
ECN=CN*RECN
STCON=OD/50.*1000.
ESTCON=EOD/50.*1000.
IF ((ANSWER.EQ.'Y').OR.(ANSWER.EQ.'YES')) THEN
  IF (TRIP.EQ.0.) THEN
    WRITE (6,53)
    TRIP=1.
  ENDIF
53  FORMAT(/,T40,'SOLVENT FREE MOLE FRACTIONS',/,T35,'CONC. (MOL/L)
*,T85,'FRACTIONS',/,T5,'SN',T10,
*  'INIT M+',T20,'TOT OR',2X,'TOT AQ',T40,'ORG.CO',2X,'AQ. CO',
*  2X,'ORG.NI',2X,'AQ. NI',
*  T80,'AQ. CO ',T90,'ORG..CO',T100,'ION.ST.',/,T10,'(G/ML)',/)
C  CALCULATE SOLVENT FREE MOL FRACTIONS AND THE AQ. IONIC STRENGTH
    DO 54 K=1,4
      IF (K.LE.2) THEN

```

```

        ATW=58.9332
    ELSE
        ATW=58.71
    ENDIF
    IF ((K.EQ.1).OR.(K.EQ.3)) THEN
        MOL(K)=CO(K)/ATW*1000.
        TMOL(K)=MOL(K)*OV(K)/1000.
    ELSE
        MOL(K)=CO(K)/ATW*1000.
        TMOL(K)=MOL(K)*(OV(K)+VACID+VBASE)/1000.
    ENDIF
54      CONTINUE
C  CALC. THE MOL FRACTIONS OF COBALT ORGANIC&AQUEOUS
        OMOL=MOL(1)+MOL(3)
        AMOL=MOL(2)+MOL(4)
        FMCO=TMOL(1)/(TMOL(1)+TMOL(3))
        FMCA=TMOL(2)/(TMOL(2)+TMOL(4))
C  CALCULATE THE IONIC STRENGTH [(NH4)2SO4]=20G/L=0.1514MOL/L
C  CALC.THE EQUILIBRIUM CONSTANTS
        EKS04=EXP(5.2/1.987E-3*(1/(T+273.15)-1/298.15))+
*          LOG(1.242E-2))
        EKNH3=EXP(-0.9404/1.987E-3*(1/(T+273.15)-1/298.15))+
*          LOG(1.807E-5))
        EKH2O=EXP(-13.36/1.987E-3*(1/(T+273.15)-1/298.15))+
*          LOG(1.E-14))
C  CALC THE MOLAR CONCENTRATIONS OF THE IMPORTANT IONS
C  ASSUME (NH4)SO4,COSO4,NISO4 DISSOLVE
        ESTS04=(CO(2)/58.9332+CO(4)/58.71)*1000+20./132.1
*          +VACID/1000.*CACID
        CH=10.**(-PH)

```

```

COH=EKH20/CH
CHS04=(CH*ESTS04)/(CH+EKS04)
CS04=ESTS04-CHS04
C  ASSUME ALL EXTRACTANT IS INITIALLY SATURATED AND 1 ORG.CO OR ORG.NI
C  REPLACES 2 NH4 MOLECULES AND THESE ARE TRANSFERED TO THE AQ PHASE.
ESTNH4=0.3027+(VBASE*CBASE/1000.+2*(TMOL(1)+TMOL(3)))
*      /((OV(2)+VACID+VBASE)/1000.)
CNH3=ESTNH4*COH/(COH+EKNH3)
CNH4=ESTNH4-CNH3
IONIC=((CO(2)/58.9332+CO(4)/58.71)*1000.*4
*      +CH+CHS04+CS04*4.+COH+CNH4)/2.
WRITE (6,55)SN,STCON,OMOL,AMOL, .
*      MOL,FMCA,FMCO,IONIC,PPT
55  FORMAT(T5,F3.0,T10,F6.3,T20,2(F6.4,2X),T40,
*      4(F6.4,2X),T80,
*      F6.4,T90,F6.4,T100,F6.4,T110,A11)
WRITE (8,57)STCON,OMOL,AMOL,
*      MOL,FMCA,FMCO
57  FORMAT(9(F6.4,2X))
ELSE
WRITE(6,13)RUN
13  FORMAT('-----',
*  '-----',A10)
WRITE (6,14) SN,T
14  FORMAT(//,T5,'SAMPLE NUMBER',2X,F3.0,T30,'T= ',F6.2,'C')
WRITE (6,15)PH,CN,ECN,STCON,ESTCON
15  FORMAT(/,T5,'PH =',T11,F5.2,T30,'C/N =',T36,F7.3,'+/-',
*  F7.3, T55,'INIT.M+ CONC. = ',T70,F6.3,' +/- ',F6.4,'(G/L)')
WRITE(6,16)

```

```

16      FORMAT (///,T25,'(ORG.)(G/ML)',T42,
*          '(AQ. )(G/ML)',T60,'D (O/A)',T79,'%EXTRACTED',T97,
*          '% RECOVERED')
        WRITE (6,17)
17      FORMAT(T25,11('-'),T42,12('-'),T60,8('-'),T79,10('-'),T97,11('-')
*          ))
        WRITE(6,18)CO(1),EO(1),CO(2),EO(2),D(1),ED(1),PRX(1),EPRX(1),
*          REC(1),EREC(1)
18      FORMAT (T15,'CO :',T23,F5.4,' +/- ',F5.4,T40,F5.4,
*          ' +/- ',F5.4,T57,F6.2,' +/- ',F6.2,T77,F5.1,
*          ' +/- ',F5.1,T97,F5.1,' +/- ',F5.1)
        WRITE(6,19)CO(3),EO(3),CO(4),EO(4),D(2),ED(2),PRX(2),EPRX(2),
*          REC(2),EREC(2)
19      FORMAT (T15,'NI :',T23,F5.4,' +/- ',F5.4,T40,F5.4,
*          ' +/- ',F5.4,T57,F6.2,' +/- ',F6.2,T77,F5.1,
*          ' +/- ',F5.1,T97,F5.1,' +/- ',F5.1)
        WRITE (6,21)S,ES,TREC,ETREC,PPT
21      FORMAT(/,T10,'S(C/N)= ',F7.3,' +/- ',F7.3,T50,
*          'TOTAL %RECOVERY= ',F7.3,' +/- ',F7.3,/,T50,A11,/)
        WRITE(6,13)
        ENDIF
C      WRITE (8,122)SN,PH,CO
122     FORMAT(T1,F3.0,/,T5,F6.4,2X,4(E10.4,2X))
        WRITE(15,123)SN,CO,EO,REC,TREC,MOL,FMCA,IONIC,PH,AO
123     FORMAT(T2,F3.0,5X,19(E10.4,2X))
40     CONTINUE
        STOP
        END

```

## 6.4.3 Sample Result File

RUN NUMBER: 8612032CN

COBALT STANDARD CURVE

REGRESSION ANALYSIS: ESTIMATE;  $Y = -0.1026E+00 + (0.3136E+02) * X$

STANDARD ERROR OF ESTIMATE = 0.1228E+00

STANDARD ERROR OF REGRESSION = 0.2801E+00

CORRELATION COEFFICIENT = 0.9981E+00

NUMBER OF FITTED POINTS = 50

NICKEL STANDARD CURVE

REGRESSION ANALYSIS: ESTIMATE;  $Y = -0.4400E-01 + (0.3046E+02) * X$

STANDARD ERROR OF ESTIMATE = 0.9631E-01

STANDARD ERROR OF REGRESSION = 0.2155E+00

CORRELATION COEFFICIENT = 0.9985E+00

NUMBER OF FITTED POINTS = 63

---

SAMPLE NUMBER 7. T= 25.00C

PH = 5.04

C/N = 0.599 +/- 0.007 INIT.M+ CONC. = 11.513 +/- 0.0476 (G/L)

	(ORG.) (G/ML)	(AQ.) (G/ML)	D (O/A)	%EXTRACTED
CO :	.0046 +/- .0001	.0003 +/- .0000	17.29 +/- 1.16	107.5 +/- 2.3
NI :	.0020 +/- .0000	.0044 +/- .0001	0.45 +/- 0.01	27.2 +/- 0.4

COBALT %RECOVERY= 113.8 +/- 2.6

NICKEL %RECOVERY= 88.8 +/- 1.9

S(C/N)= 38.489 +/- 2.812

TOTAL %RECOVERY= 98.2 +/- 2.0

---

## 6.4.4 Sample Input Data File

8612032CN

230.6705 98.4 .04 1000. 50.0058 99.6 .001 1000.

50

.031 1

.032 1.

.033 1.

.031 1.

.032 1.

.067 2.

.066 2.

.068 2.

.065 2.

.132 4.

.131 4.


.131 4.

.131 4.

.190 6.

.191 6.

.191 6.

.192 6. 

.191 6.

.033 1.

.031 1.

.034 1.


.033 1.

.064 2.

.065 2.

.064 2.

.065 2.

.128 4. 

.131 4.  
.128 4.  
.129 4.  
.189 6.  
.189 6.  
.190 6.  
.192 6.  
.040 1.  
.040 1.  
.040 1.  
.040 1.  
.070 2.  
.071 2.  
.071 2.  
.073 2.  
.135 4.  
.139 4.  
.137 4.  
.138 4.  
.199 6.  
.200 6.  
.198 6.  
.200 6.  
63  
.195 6.  
.195 6.  
.195 6.  
.196 6.  
.193 6.  
.033 1.  
.032 1.

.033 1.  
.031 1.  
.061 2.  
.065 2.  
.062 2.  
.064 2.  
.095 3.  
.096 3.  
.096 3.  
.096 3.  
.096 3.  
.128 4.  
.131 4.  
.130 4.  
.129 4.  
.128 4.  
.034 1.  
.036 1.  
.035 1.  
.033 1.  
.066 2.  
.068 2.  
.069 2.  
.069 2.  
.102 3.  
.103 3.  
.103 3.  
.102 3.  
.134 4.  
.136 4.  
.136 4.

.136 4.  
 .198 6.  
 .198 6.  
 .200 6.  
 .200 6.  
 .035 1.  
 .036 1.  
 .036 1.  
 .038 1.  
 .070 2.  
 .069 2.  
 .069 2.  
 .068 2.  
 .105 3.  
 .103 3.  
 .106 3.  
 .104 3.  
 .136 4.  
 .136 4.  
 .136 4.  
 .136 4.  
 .200 6.  
 .203 6.  
 .197 6.  
 .200 6.

1

7.	.1512	0.05	1.00	250.	5.	50.
4.53	.0460	0.50	1.00	500.	5.	50.
32.37	.1300	0.10	1.00	250.	5.	50.
5.04	.0730	0.50	0.10	500.	5.	50.

0.90

7.5

0.

6.6

25.

## 6.5 Sample SAS Program used to Calculate Non-linear Models

```
DATA FRED;
CMS FILEDEF HWDATA DISK BIG1 DATA A;
INFILE HWDATA;
TITLE ANALYSIS OF PC88A DATA BY C WELLS ;
INPUT MCO 142-152 MCA 154-164 MNO 166-176 MNA 178-188
      XFCA 190-200 PH 214-224 ;
IF XFCA>=1.0 THEN DELETE;
IF XFCA<=0.0 THEN DELETE;
IF MCA<0. THEN MCA=0.;
IF MNA<0. THEN MNA=0.;
IF MCO<0. THEN MCO=0.;
IF MNO<0. THEN MNO=0.;
YSTC= 62.91999699*MCA/(1.+276.9429577*MCA);
YSTN= 2.47395*MNA/(1.+22.98688*MNA)+4.333E-03*EXP(3.63303*MNA) ;
XN=1.-XFCA;
TOT=MNA+MCA;
IF YSTC=0 THEN DELETE;
IF YSTN=0 THEN DELETE;
GC=MCO/XFCA/YSTC;
GN=MNO/XN/YSTN;
PROC NLIN DATA=FRED ;
TITLE NONLINEAR MODEL FOR GAMMA C;
PARAMETER A1=1 ;
MODEL GC= 1/(1-XN**A1 ) ;
DER.A1=(-1)/(1-XN**A1)**2*(-1)*LOG(XN)*XN**A1 ;
OUTPUT OUT=A P=PRED R=RESID ;
PROC PRINT ;
PROC PLOT DATA=A;
```

```
PLOT GC*XN='A' PRED*XN='P' /OVERLAY HPOS=40 VPOS=18;
LABEL GC='GAMMAC';
LABEL XN= 'MOL FRAC N';
PLOT RESID*XN /VREF=0 HPOS=40 VPOS=18;
PLOT RESID*PRED/VREF=0 HPOS=40 VPOS=18;
```

```
DATA FRED ;
TITLE ANALYSIS OF PC88A DATA BY C WELLS ;
CMS FILEDEF HWDATA DISK BIG1 DATA A;
INFILE HWDATA;
TITLE ANALYSIS OF PC88A DATA BY C WELLS ;
INPUT MCO 142-152 MCA 154-164 MNO 166-176 MNA 178-188
      XFCA 190-200 PH 214-224 ;
IF XFCA>=1.0 THEN DELETE;
IF XFCA<=0.0 THEN DELETE;
IF MCA<0. THEN MCA=0.;
IF MNA<0. THEN MNA=0.;
IF MCO<0. THEN MCO=0.;
IF MNO<0. THEN MNO=0.;
YSTC= 62.91999699*MCA/(1.+276.9429577*MCA);
YSTN= 2.47395*MNA/(1.+22.98688*MNA)+4.333E-03*EXP(3.63303*MNA) ;
XN=1.-XFCA;
TOT=MNA+MCA;
IF YSTC=0 THEN DELETE;
IF YSTN=0 THEN DELETE;
GC=MCO/XFCA/YSTC;
GN=MNO/XN/YSTN;
IF GC>50 THEN DELETE;
IF GN>50 THEN DELETE;
PROC NLIN DATA=FRED;
TITLE NONLINEAR MODEL FOR GAMMA C WITH HENRYS LAW;
```

```

PARAMETER A1=1 A3=0.8 ;
BOUNDS A3<=1.0;
IF XN < A3 THEN DO;
MODEL GC= 1/(1-XN**A1) ;
DER.A1=(-1)/(1-XN**A1)**2*(-1)*LOG(XN)*XN**A1 ;
DER.A3=0;
END ;
IF XN >= A3 THEN DO;
A2=0.;
SLOPE=(-A2*(1-A3**A1)-(-A1*A3**(A1-1))*(1-A2*A3))/(1-A3**A1)**2;
DSD1=((A2*LOG(A3)*A3**A1+(1-A2*A3)*(-A3**(A1-1)-A1*LOG(A3)*A3**(A1-1)))*
(1-A3**A1)**2-2*(1-A3**A1)*(-LOG(A3)*A3**A1)*
(-A2*(1-A3**A1)-(-A1*A3**(A1-1))*(1-A2*A3)))/(1-A3**A1)**4;
DSD3=((A2*A1*A3**(A1-1)-
(-A1*((A1-1)*A3**(A1-2)*(1-A2*A3)+(A3**(A1-1)*(-A2)))))*(1-A3**A1)**2-
2*(1-A3**A1)*(-A1*A3**(A1-1))*
(-A2*(1-A3**A1)-(-A1*A3**(A1-1))*(1-A2*A3)))/(1-A3**A1)**4;
C=-SLOPE*A3+(1-A2*A3)/(1-A3**A1);
DCD1=-DSD1*A3-(1-A2*A3)/((1-A3**A1)**2)*(-LOG(A3)*A3**A1);
DCD3=-DSD3*A3+SLOPE+
(-A2*(1-A3**A1)-(-A1*A3**(A1-1))*(1-A2*A3))/(1-A3**A1)**2;
MODEL GC=SLOPE*XN+C;
DER.A1=DSD1*XN+DCD1;
DER.A3=DSD3*XN+DCD3;
END;
OUTPUT OUT=A P=PRED R=RESID;
PROC PRINT ;
PROC PLOT DATA=A;
PLOT GC*XN='A' PRED*XN='P' /OVERLAY HPOS=40 VPOS=18;
LABEL GC='GAMMAC';
LABEL XN='MOL FRAC N';

```

```
PLOT RESID*XN /VREF=0 HPOS=40 VPCS=18;
PLOT RESID*PRED/VREF=0 HPOS=40 VPOS=18;
DATA A;
PROC PRINT;

DATA FRED;
CMS FILEDEF HWDATA DISK BIG1 DATA A;
INFILE HWDATA;
TITLE ANALYSIS OF PC88A DATA BY C WELLS ;
INPUT MCO 142-152 MCA 154-164 MNO 166-176 MNA 178-188
      XFCA 190-200 PH 214-224 ;
IF XFCA>=1.0 THEN DELETE;
IF XFCA<=0.0 THEN DELETE;
IF MCA<0. THEN MCA=0.;
IF MNA<0. THEN MNA=0.;
IF MCO<0. THEN MCO=0.;
IF MNO<0. THEN MNO=0.;
YSTC= 62.91999699*MCA/(1.+276.9429577*MCA);
YSTN= 2.47395*MNA/(1.+22.98688*MNA)+4.333E-03*EXP(3.63303*MNA) ;
XN=1.-XFCA;
TOT=MNA+MCA;
IF YSTC=0 THEN DELETE;
IF YSTN=0 THEN DELETE;
GC=MCO/XFCA/YSTC;
GN=MNO/XN/YSTN;
PROC NLIN DATA=FRED ;
TITLE NONLINEAR MODEL FOR GAMMA N;
PARAMETER A1=1;
MODEL GN= 1-XFCA**A1;
DER.A1=(-1)*LOG(XFCA)*XFCA**A1 ;
OUTPUT OUT=A P=PRED R=RESID;
```

```
PROC PRINT ;
PROC PLOT DATA=A;
PLOT GN*XFCA='A' PRED*XFCA='P' /OVERLAY HPOS=40 VPOS=18;
LABEL GN='GAMMAN';
LABEL XFCA= 'MOL FRAC C';
PLOT RESID*XFCA /VREF=0 HPOS=40 VPOS=18;
PLOT RESID*PRED/VREF=0 HPOS=40 VPOS=18;
```