Study on the Extraction and Separation of Zinc, Cobalt, and Nickel Using Ionquest 801, Cyanex 272, and Their Mixtures

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Abstract: Both Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) and Ionquest 801 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) are commonly used for metal extraction and separation, particularly for zinc, cobalt, and nickel, which are often found together in processing solutions. Detailed metal extractions of zinc, cobalt, and nickel were studied in this paper using Cyanex 272, Ionquest 801, and their mixtures. It was found that they performed very similarly in zinc selectivity over cobalt. Cyanex 272 performed much better than Ionquest 801 in cobalt separation from nickel. However, very good separation of them was also obtained with Ionquest 801 at its low concentration with separation factors over 4000, indicating high metal loading of cobalt can significantly suppress nickel extraction. Slope analysis proved that two moles of dimeric extractants were needed for one mole extraction of zinc and cobalt, but three moles were needed for the extraction of one mole nickel. A synergistic effect was found between Cyanex 272 and Ionquest 801 for three metal extractions with the synergistic species of M(AB) determined by the Job’s method.

Keywords: solvent extraction; cyanex 272; ionquest 801; zinc; cobalt; nickel

1. Introduction

In nickel laterite processing, zinc, cobalt, and nickel often present together in leach solutions due to their similar chemical properties [1–3]. Ionquest 801 and Cyanex 272 are commonly used for their separations [3–6]. Cyanex 272 has been successfully used in a Murrin Murrin Nickel laterite project, where two solvent extraction circuits are used to separate zinc from cobalt and nickel in the first circuit, and, then, cobalt from nickel in the second circuit [7,8]. Although Cyanex 272 performed very well in their separation, its high manufacturing cost and, accordingly, high price drive some practices to turn to other alternatives, such as Ionquest 801 [9], and this is particularly true in China [10–13].

Ionquest 801 has stronger metal extraction capacity than Cyanex 272, but generally has less selectivity for cobalt over nickel [14,15]. The separation factor of cobalt over nickel normally is over 2000 with Cyanex 272 compared to around 150 with Ionquest 801. However, if cobalt loading is high with Ionquest 801, good separation can also be obtained. For example, the cobalt loading increased from 1.55 g/L to 6.92 g/L with Ionquest 801. The separation factor of cobalt over nickel rapidly increased from 106.5 to 858.0 [16], indicating that the metal separation can be significantly affected by the extraction conditions. Ionquest 801 has been used to simultaneously extract cobalt and magnesium from a concentrated
nickel sulphated solution [17], even though Cyanex 272 could perform better than Ionquest 801 in cobalt and magnesium separation from nickel [18]. Detailed extraction properties of zinc, cobalt, and nickel are still highly required using Cyanex 272 and Ionquest 801 to serve a real process application.

Cyanex 272 and Ionquest 801 both are organophosphorus acidic extractants with very similar structures. They have a strong synergistic effect with chelating extractants for the extraction of zinc, cobalt, and nickel [19,20]. Another organophosphorus acidic extractant D2EHPA (bis(2-ethylhexyl) phosphoric acid) also shows a strong synergistic effect for nickel extraction with N-bearing chelating reagents [21,22]. The synergistic effect of the mixture of Cyanex 272 and Ionquest 801 for cobalt and manganese has been studied for cobalt and manganese and a maximum synergistic effect of around 3–4 was obtained by Zhao et al. [23]. Using the mixture of Ionquest 801 (P 507) and Cyanex 272 was also used to recover cobalt and nickel from a leach solution by Liu et al. [24], and it was found that their optimised synergistic effect at P 507 to Cyanex 272 ratio of 3:2. However, contrary results were reported for rare earth extraction. For instance, Liu et al. [25] revealed that the mixtures of P 507 and Cyanex 272 have a synergistic effect in heavy rare earth extraction with the extraction species of RE(HB₂)₂(HA₂)₂, while Quinn et al. [26] reported that the mixture of Ionquest 801 and Cyanex 272 has an antagonistic effect in their extractions. This is likely due to the fact that the interaction between them strongly depends on extraction conditions. Therefore, a detailed study is required to verify their interaction mechanism for the metal extractions.

The extraction of zinc, cobalt, and nickel with Cyanex 272 and Ionquest 801 has been widely investigated in these years [27–33]. Most research studies focused on the metal separation properties in an attempt to find potential applications. Few research studies focused on their extraction mechanisms with some discrepancies that might be due to the different testing conditions. For example, the extraction of cobalt and nickel with similar types of extractants Cyanex 272, Ionquest 801, and D2EHPA was reported via a complex species combined directly with two molecules of extractant, but four extractant molecules were involved to explain the relationship of LogD against pH [30]. In contrast, Tait [29] reported that the Log\(_D\)(Co) and Log\(_D\)(Ni) against the Log [Cyanex 272] have a linear relationship with the slopes of 2.0 and 3.1, respectively, suggesting that two molecules of Cyanex 272 participated in each metal extraction for cobalt, but three for nickel. The mechanism of metal extraction by Cyanex 272 and Ionquest 801 needs further study.

Herein, the extraction and separation of zinc, cobalt, and nickel with Cyanex 272, Ionquest 801, and their mixtures were studied in detail. Thermodynamic equilibrium calculations and slope analysis were used to study the metal extraction reactions. The synergistic or antagonistic effect of Cyanex 272 and Ionquest 801 on extraction of these three metal extractions was also discussed.

2. Materials and Methods

2.1. Reagents and Solution Preparation

Cyanex 272 was kindly provided by Cytec Industries (Paterson, NJ, USA) and used as received without further purification. Ionquest 801 was obtained from ChemRex (Limassol, Cyprus) with >98% purity, and also used as received. ShellSol D70, which is an aliphatic hydrocarbon, supplied by Shell Chemicals (Brisbane, Queensland, Australia), was used as the diluent. The organic solutions were prepared by dissolving extraction reagents into the diluent to desired concentrations. An aqueous feed solution containing 1.0 g/L each of zinc, cobalt, and nickel was prepared by dissolving their corresponding metal sulphates into de-ionized water.

2.2. Metal Extraction pH Isotherms

The determination of metal extraction pH isotherms was carried out in 300 mL of hexagonal glass jars immersed in a water bath to control temperature at 40 °C unless it is indicated. Aqueous and organic solutions each of 100 mL were added into the jar to obtain
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2.2. Metal Extraction pH Isotherms

The determination of metal extraction pH isotherms was carried out in 300 mL of the aqueous feed solution were determined as shown in Figure 1a,b. By comparison, Ionquest 801 performed stronger for the extraction of all three metals than Cyanex 272. The pH50 (pH against half metal extraction) of 0.3 M Ionquest 801 were 1.70, 3.88, and 5.36 for zinc, cobalt, and nickel, respectively (Figure 1b), while with 0.3 M Cyanex 272, they were 2.09, 4.16, and 6.20 for zinc, cobalt, and nickel, respectively (Figure 1a). This has been well concluded and documented elsewhere [14]. The gaps of ΔpH50(Co/Ni) with Cyanex 272 was clearly larger than that with Ionquest 801. However, the gaps ΔpH50(Zn/Co) with Ionquest 801 was similar to or slightly large than with Cyanex 272. These indicate that Cyanex 272 is advantageous in the selectivity of cobalt over nickel compared to Ionquest 801, but is slightly inferior to Ionquest 801 in zinc selectivity over cobalt. However, some processes used it for zinc separation from cobalt [7].

3. Results and Discussion

3.1. Metal Extraction pH Isotherms of Cyanex 272 and Ionquest 801

The metal extraction pH isotherms of Cyanex 272 and Ionquest 801 with the aqueous feed solution were determined as shown in Figure 1a,b. By comparison, Ionquest 801 performed stronger for the extraction of all three metals than Cyanex 272. The pH50 (pH against half metal extraction) of 0.3 M Ionquest 801 were 1.70, 3.88, and 5.36 for zinc, cobalt, and nickel, respectively (Figure 1b), while with 0.3 M Cyanex 272, they were 2.09, 4.16, and 6.20 for zinc, cobalt, and nickel, respectively (Figure 1a). This has been well concluded and documented elsewhere [14]. The gaps of ΔpH50(Co/Ni) with Cyanex 272 was clearly larger than that with Ionquest 801. However, the gaps ΔpH50(Zn/Co) with Ionquest 801 was similar to or slightly large than with Cyanex 272. These indicate that Cyanex 272 is advantageous in the selectivity of cobalt over nickel compared to Ionquest 801, but is slightly inferior to Ionquest 801 in zinc selectivity over cobalt. However, some processes used it for zinc separation from cobalt [7].

Detailed metal extraction pH50 and ΔpH50(Co-Zn), ΔpH50(Ni-Co) of Cyanex 272 and Ionquest 801 under various concentrations are obtained in Table 1. All of these results showed that Cyanex 272 has higher pH50 and larger ΔpH50(Ni-Co) compared with
Ionquest 801 at the same concentration, suggesting weaker metal extraction and better cobalt selectivity over nickel. The $\Delta p$H50(Co-Zn) of both Cyanex 272 and Ionquest 801 are similar with the latter being slightly larger at the same concentration, indicating slightly better zinc selectivity over cobalt with Ionquest 801 than that with Cyanex 272.

Table 1. Metal extraction $p$H50 and $\Delta p$H50 with various concentrations of Cyanex 272 and Ionquest 801.

| Cyanex 272 Concentration (M) | pH50 | $\Delta$H50 |  |  |  |
|-----------------------------|------|-------------|---|---|---|
|                             | Zn   | Co          | Ni | Co-Zn | Ni-Co |
| 0.1                         | 2.64 | 5.10        | >6.5 | 2.46 | - |
| 0.2                         | 2.32 | 4.42        | >6.5 | 2.10 | - |
| 0.3                         | 2.15 | 4.21        | 6.28 | 2.06 | 2.07 |
| 0.4                         | 2.05 | 4.15        | 6.06 | 2.10 | 1.91 |

| Ionquest 801 Concentration (M) | pH50 | $\Delta$H50 |  |  |  |
|-------------------------------|------|-------------|---|---|---|
|                               | Zn   | Co          | Ni | Co-Zn | Ni-Co |
| 0.1                           | 2.30 | 4.78        | >6.5 | 2.48 | - |
| 0.2                           | 1.80 | 4.05        | 5.85 | 2.25 | 1.80 |
| 0.3                           | 1.71 | 3.89        | 5.40 | 2.18 | 1.51 |
| 0.4                           | 1.55 | 3.70        | 2.15 | 1.35 |  |

Cobalt extraction and its separation factors over nickel with various concentrations of Cyanex 272 and Ionquest 801 at different pH values are calculated in Table 2. Organic percentages by metal loading (% of organic concentration occupied by loaded metals) are also calculated in Table 2. For both organic systems, cobalt extraction grew with increasing pH and the extractant concentrations. The SF$_{Co/Ni}$ (separation factors of cobalt and nickel) is high over 1000 under various pH with Cyanex 272 for its all-tested concentrations. The SF$_{Co/Ni}$ also reached high over 4000 at tested pH values with 0.1 M Ionquest 801, which are much comparable with 0.1 M Cyanex 272. This indicates that, when using low Ionquest 801 concentration, very good cobalt separation from nickel can also be obtained. The SF$_{Co/Ni}$ over decreased rapidly to less than 100 with increasing Ionquest 801 concentration to 0.4 M, suggesting that cobalt selectivity of Ionquest 801 is more sensitive to the concentration than that of Cyanex 272. In Table 2, with the increase of the extractant concentration, the metal loaded organic percentage was clearly decreased, leaving more organic free from metal loading. These organic materials tend to extract nickel more with Ionquest 801 than with Cyanex 272.

Table 2. Cobalt extraction, its separation factor over nickel (SF$_{Co/Ni}$), and organic loading percentages with Cyanex 272 and Ionquest 801.

| Cyanex 272 Concentration (M) | Co Extraction (%) | SF$_{Co/Ni}$ | Metal Loaded Organic (%) |
|------------------------------|-------------------|--------------|--------------------------|
|                              | pH 5.0 | pH 5.5 | pH 6.0 | pH 5.0 | pH 5.5 | pH 6.0 | pH 5.0 | pH 5.5 | pH 6.0 |
| 0.1                          | 37.6   | 69.4   | 88.6   | 2973   | 6640   | 7163   | 42.9   | 53.3   | 59.3   |
| 0.2                          | 89.5   | 98.6   | 99.7   | 4341   | 4725   | 4149   | 29.9   | 31.9   | 33.0   |
| 0.3                          | 97.5   | 99.6   | 99.9   | 2314   | 2479   | 1888   | 20.4   | 21.3   | 23.8   |
| 0.4                          | 37.6   | 69.4   | 88.6   | 2314   | 1630   | 1126   | 17.1   | 18.0   | 21.0   |

| Ionquest 801 Concentration (M) | Co-Extraction (%) | SF$_{Co/Ni}$ | Metal Loaded Organic (%) |
|-------------------------------|-------------------|--------------|--------------------------|
|                               | pH 5.0 | pH 5.5 | pH 6.0 | pH 5.0 | pH 5.5 | pH 6.0 | pH 5.0 | pH 5.5 | pH 6.0 |
| 0.1                           | 64.1   | 85.3   | 96.4   | 4938   | 7313   | 6103   | 51.9   | 59.0   | 62.8   |
| 0.2                           | 97.2   | 99.4   | 99.9   | 549    | 459    | 279    | 32.5   | 36.2   | 41.5   |
| 0.3                           | 98.5   | 99.6   | >99.9   | 207    | 179    | 98     | 23.6   | 27.3   | 30.5   |
| 0.4                           | 99.0   | 99.8   | >99.9   | 104    | 87     | 48     | 21.0   | 24.5   | 25.1   |
3.2. Metal Extraction Analysis

Thermodynamic equilibriums for these metal extractions by Cyanex 272 and Ionquest 801 were analysed in this study to further clearly understand the metal extraction reactions. The extraction of all three metals with Cyanex 272 and Ionquest 801 is expressed in Equation (1) considering that both extractants present as a dimer.

\[
M^{2+} + nH_2A_2 \rightleftharpoons M(H_{2n-2}A_{2n}) + 2H^+ \tag{1}
\]

\[
K_{eq} = \frac{[M(H_{2n-2}A_{2n})][H^+]^2}{[M^{2+}][H_2A_2]^n} \tag{2}
\]

\[
\log D(M) = \log K_{eq} + n \log [H_2A_2]_f + 2\text{pH} \tag{3}
\]

where \(M\) represents the metals of Zn, Co, or Ni. HA represents the extractant of Cyanex 272 or Ionquest 801, hence \(H_2A_2\) is their dimer. The top bar denotes the organic phase. The subscript "f" denotes free extractant concentration (organic free from the metal loading).

Linear relationships of \(\log D(M)\) against \(\log [H_2A_2]_f\) and \(\text{pH}\) of Cyanex 272 and Ionquest 801 for all three metal extractions were fitted as shown in Figures 2 and 3, respectively, and corresponding \(n\) values in Equation (3) are listed in Table 3. For the extraction of zinc and cobalt, \(n\) values were close to 2 with both Cyanex 272 and Ionquest 801. However, for nickel extraction, \(n\) values were close to 3. These results are similar to those reported by Tait [29] with Cyanex 272. It is suggested that one molecule metal extraction requires two-dimer extractant molecules for zinc and cobalt extraction, but three for nickel extraction with both Cyanex 272 and Ionquest 801. Since nickel extraction requires more extractant molecules for coordination, which is not required for charge equilibrium, interpreting why its extraction occurred at a relatively higher \(\text{pH}\) compared to the extraction of zinc and cobalt.

![Figure 2. The relationship of LogD(M) against Log [dimer Cyanex 272]_f. (a) LogD(Zn)-Log[dimer Cyanex 272], (b) LogD(Zn)-Log[dimer Cyanex 272], (c) LogD(Zn)-Log[dimer Cyanex 272].](image)

From Equation (3), \(\log D(M) - n \log [H_2A_2]_f\) versus \(\text{pH}\) will give the straight line with a slope of 2. The linear relationships of \(\log D(M) - n \log [H_2A_2]_f\) against \(\text{pH}\) were obtained and shown in Figures 4 and 5. Then, the value used for the calculation is 2 for zinc and cobalt, and 3 for nickel. The line slopes are listed in Table 4. Although some slope values are approaching the integer of 2 for zinc and cobalt extraction with Cyanex 272, many slope values are deviated from 2, ranging from 1.5 to 1.7. This is possibly caused by ionic activity in both aqueous and organic phases.
The relationship of Log \(D(M)\) against Log [dimer Cyanex 272]: (a) Log\(D(Zn)\)-Log[dimer Ionquest 801], (b) Log\(D(Zn)\)-Log[dimer Ionquest 801], (c) Log\(D(Zn)\)-Log[dimer Ionquest 801].

Figure 3. The relationship of Log\(D(M)\) against Log [dimer Ionquest 801]: (a) Log\(D(Zn)\)-Log[dimer Ionquest 801], (b) Log\(D(Zn)\)-Log[dimer Ionquest 801], (c) Log\(D(Zn)\)-Log[dimer Ionquest 801].

Table 3. Slopes of straight lines in Figures 2 and 3, and the corresponding \(n\) values in Equation (3).

| Metal | pH  | \(n\) Value |
|-------|-----|-------------|
|       |     | Cyanex 272  | Ionquest 801 |
| Zn    | 3.0 | 1.79        | -            |
|       | 2.0 | 1.71        | 1.76         |
|       | 1.5 | 1.75        | -            |
| Co    | 5.0 | 2.29        | -            |
|       | 4.5 | 2.10        | 2.12         |
|       | 4.0 | -           | 2.14         |
|       | 3.5 | -           | 2.35         |
| Ni    | 6.5 | 2.71        | -            |
|       | 6.0 | 2.74        | 2.94         |
|       | 5.5 | -           | 2.96         |
|       | 5.0 | -           | 3.21         |

From Equation (3), Log\(D(M)\)-\(n\)Log \([H_2A_2]_f\) versus pH will give the straight line with a slope of 2. The linear relationships of Log\(D(M)\)-\(n\)Log \([H_2A_2]_f\) against pH were obtained and shown in Figures 4 and 5. Then, the value used for the calculation is 2 for zinc and cobalt, and 3 for nickel. The line slopes are listed in Table 4. Although some slope values are approaching the integer of 2 for zinc and cobalt extraction with Cyanex 272, many slope values are deviated from 2, ranging from 1.5 to 1.7. This is possibly caused by ionic activity in both aqueous and organic phases.

Figure 4. The linear relationship of Log\(D(M)\)-\(n\)Log \([H_2A_2]_f\) and equilibrium pH for the metal extraction with Cyanex 272.
Figure 5. The linear relationship of $\log D(M)-n\log [H_2A_2]^f$ and equilibrium pH for the metal extraction with Ionquest 801.

Table 4. Line slope of the linear relationship of $D(M)-2n\log [HA]^f$ against pH in Figures 4 and 5.

| Metal | Cyanex 272 Concentration (M) | Ionquest 801 Concentration (M) |
|-------|-----------------------------|---------------------------------|
|       | 0.1 | 0.2 | 0.3 | 0.4 | 0.1 | 0.2 | 0.3 | 0.4 |
| Zn    | 1.70 | 1.79 | 1.82 | 1.77 | 1.70 | 1.70 | 1.67 | -   |
| Co    | -   | 1.78 | 1.86 | 1.99 | -   | 1.69 | 1.63 | 1.58 |
| Ni    | -   | 1.68 | 1.69 | 1.77 | -   | 1.54 | 1.49 | 1.51 |

3.3. Synergistic Effect of Cyanex 272 and Ionquest 801

Cyanex 272 has a significant advantage in cobalt selectivity over nickel compared to Ionquest 801, but, for zinc separation from cobalt and nickel, Ionquest 801 is more preferred due to its stronger extraction capacity, slightly better selectivity, and, most importantly, its much lower price. If we take both advantages by using each in a separate process for zinc and cobalt extraction, respectively, two extractants might be blended to some extent via phase carryover. A number of investigations have been carried out on the metal extraction using the mixture of Cyanex 272 with Ionquest 801 or D2EHPA, which is another analogue of acidic organophosphorus acid [31,34,35]. No clear synergistic effect on these metal extractions was found. The synergistic effect of Cyanex 272 and Ionquest 801 on the extraction of zinc, cobalt, and nickel was again studied systematically in this study based on the metal extraction pH isotherms. Metal extraction pH isotherms of different compositions of Cyanex 272 and Ionquest 801 were determined (Figure 6). From Figure 6, it is seen that, when the total concentration was maintained constant, metal extractions were basically increased by increasing Ionquest 801 concentration and decreasing Cyanex 272 concentration. This is due to the stronger metal extraction capability of Ionquest 801 than Cyanex 272. However, metal extraction pH isotherms at 0.2 M Cyanex 272 + 0.2 M Ionquest 801 was very close to those at 0.1 M Cyanex 272 + 0.3 M Ionquest 801, which is even stronger by shifting to the right side for the extraction of zinc and cobalt (Figure 6). This should be attributed to their synergistic effect.
Figure 6. Metal extraction pH isotherms of mixed organic solutions of Cyanex 272 and Ionquest 801 at the total concentration of 0.4 M (in legends: number followed by concentration unit M, C272 is for Cyanex 272, and Ion801 is for Ionquest 801). (a) Zn extraction-pH, (b) Co extraction-pH, (c) Ni extraction-pH.

Half extraction pH50 and ΔpH50 (Co-Zn and Ni-Co) are shown in Table 5. Clearly, the mixtures all have better zinc and cobalt separation than the Cyanex 272 alone system, but are very similar to the Ionquest 801 alone system. However, the mixed systems are poorer than the Cyanex 272 alone system for cobalt selectivity over nickel. As more Ionquest 801 was used in the system, the performance became poorer. The separation factor of cobalt from nickel (SF_{Co/Ni}) dropped rapidly with increasing Ionquest 801 concentration (Table 6), suggesting that lower Ionquest 801 concentration should be used in the mixed system to achieve good cobalt and nickel separation. SF_{Co/Ni} was 300–400 when equal moles of Cyanex 272 and Ionquest 801 were mixed in the extraction system.

Table 5. The half extraction of pH50 and ΔpH50 (Co-Zn and Ni-Co) with various organic compositions composed of Cyanex 272 and Ionquest 801.

| Organic Concentration (M) | pH50 | ΔpH50 |
|--------------------------|------|-------|
| Cyanex 272 | Ionquest 801 | Zn | Co | Ni | Co-Zn | Ni-Co |
| 0.4 | 0 | 2.05 | 4.15 | 6.06 | 2.10 | 1.91 |
| 0.3 | 0.1 | 1.96 | 4.10 | 5.84 | 2.14 | 1.74 |
| 0.2 | 0.2 | 1.74 | 3.89 | 5.48 | 2.15 | 1.59 |
| 0.1 | 0.3 | 1.79 | 3.92 | 5.38 | 2.13 | 1.46 |
| 0 | 0.4 | 1.55 | 3.70 | 5.05 | 2.15 | 1.35 |

Table 6. Separation factor of cobalt over nickel (SF_{Co/Ni}) under various organic compositions and pH values.

| Organic Concentration (M) | SF_{Co/Ni} |
|--------------------------|------------|
| Cyanex 272 | Ionquest 801 | pH 4.0 | pH 4.5 | pH 5.0 | pH 5.5 |
| 0.4 | 0 | 1421 | 2000 | 2314 | 1630 |
| 0.3 | 0.1 | 696 | 884 | 776 | 759 |
| 0.2 | 0.2 | 446 | 555 | 398 | 315 |
| 0.1 | 0.3 | 143 | 196 | 217 | 266 |
| 0 | 0.4 | 83 | 107 | 104 | 87 |

The synergistic coefficient of Cyanex 272 and Ionquest 801 under various organic compositions at two appropriate pH values for each metal extraction were calculated based on Equation (4), as shown in Table 7.

$$SC_M = \frac{D_M}{D_{M(C272)} + D_{M(Ion.801)}}$$  (4)
where $SC_M$ represents a synergistic coefficient, $D_M$ represents a metal extraction distribution ratio, and C 272 and Ion. 801 are abbreviations of Cyanex 272 and Ionquest 801, respectively. $SC_M$ was clearly larger than 1 at 0.2 M of each Cyanex 272 and Ionquest 801 in the mixture, particularly for nickel extraction, indicating their clear synergistic effect. Under some organic compositions, a slightly antagonistic effect was also observed by $SC_M < 1$, particularly at the organic system consisting of 0.1 M Cyanex 272 and 0.3 M Ionquest 801 for the extraction of zinc and cobalt. Although the reason why the synergistic or antagonistic effect occurred at different organic compositions, it can be generally concluded from Table 7 that, when the concentration of Cyanex 272 is equal to or higher than that of Ionquest 801, a synergistic effect most likely occurs. Otherwise, an antagonistic effect will occur. Based on the Job’s method [36], plotting the distribution ratio of $D_{M(s)}$ ($D_{M(s)} = D_M - D_{M(C272)} - D_{M(Ion.801)}$), contributed by the synergistic effect, versus the fraction of Cyanex 272 concentration (Cyanex 272 to the overall concentration) (Figure 7), maximum values were obtained at the fraction of 0.5 for all three metals. It is indicated that the synergistic complex has the structure of one metal molecule combined with each of the Cyanex 272 and Ionquest 801 molecule in the form of $M(AB)$ for all three metal extractions.

### Table 7. Synergistic coefficient for metal extraction ($SC_M$) using the mixture of Cyanex 272 and Ionquest 801.

| Organic Concentration (M) | SC$_{Zn}$ pH = 1.5 | SC$_{Zn}$ pH = 2.0 | SC$_{Co}$ pH = 4.5 | SC$_{Co}$ pH = 5.5 | SC$_{Ni}$ pH = 5.5 | SC$_{Ni}$ pH = 6.0 |
|---------------------------|-------------------|-------------------|-------------------|-------------------|------------------|------------------|
| Cyanex 272                |                   |                   |                   |                   |                  |                  |
| 0.4                       | 1.00              | 1.00              | 1.00              | 1.00              | 1.00             | 1.00             |
| 0.3                       | 1.00              | 0.94              | 1.34              | 1.29              | 4.74             | 4.03             |
| 0.2                       | 1.10              | 1.17              | 1.49              | 1.80              | 2.86             | 3.44             |
| 0.1                       | 0.73              | 0.73              | 0.81              | 0.90              | 1.03             | 0.96             |
| 0.0                       | 1.00              | 1.00              | 1.00              | 1.00              | 1.00             | 1.00             |

**Figure 7.** Job’s plot of $D_{M(s)}$ versus Cyanex 272 concentration fraction in the mixtures. (a) $D_{Zn(s)}$-Cyanex 272 fraction, (b) $D_{Co(s)}$-Cyanex 272 fraction, (c) $D_{Ni(s)}$-Cyanex 272 fraction.

#### 3.4. Discussion of Cyanex 272 and Ionquest 801 Application

Since Ionquest 801 is stronger for metal extraction than Cyanex 272, lower pH is required for the metal extraction with Ionquest 801 when compared to Cyanex 272. In addition, with its additional advantage of low price, Ionquest 801 should be more preferred to Cyanex 272 in some applications.

- In terms of zinc extraction and separation from cobalt and nickel, Ionquest 801 performed similarly to or even better than Cyanex 272.
- Cyanex 272 is much superior to Ionquest 801 for cobalt and nickel separation, while usually having one magnitude order larger separation factors comparatively. Cyanex 272 would be a preferred selection for cobalt and nickel separation.
• Using low concentration of Ionqest 801 to reduce the free extractant availability during the metal extraction, very good separation of cobalt from nickel is also available with the separation factor over 1000, which is comparable to those using Cyanex 272 as discussed before. Therefore, more rigid concentration control is required if Ionqest 801 is used for cobalt and nickel separation by taking its advantage to lower the cost.
• To separate zinc, cobalt, and nickel in an integral process, if Ionqest 801 is selected in the first solvent circuit to separate zinc and it is followed by Cyanex 272 to separate cobalt, leaving nickel in the raffinate. Ionqest 801 could contaminate Cyanex 272 by the phase carryover. However, as discussed previously, very good cobalt and nickel separation is still available when a small amount of Ionqest 801 mixed in the Cyanex 272 system.

4. Conclusions
Good separation of zinc, cobalt, and nickel from each other can be achieved with Cyanex 272 and Ionqest 801 systems, and both extractants performed similar selectivity for zinc over cobalt with the latter performing slightly better. Although Cyanex 272 has much higher selectivity for cobalt over nickel than that of Ionqest 801, separation factors over thousands were also obtained when low Ionqest 801 concentration or a high A/O ratio was used, which were very similar to that of Cyanex 272, indicating that high cobalt loaded in organic can significantly improve the separation of cobalt from nickel with Ionqest 801.

Slope analysis showed that one molecule metal extraction requires two dimer extractant molecules for zinc and cobalt extraction, but three for nickel extraction with both Cyanex 272 and Ionqest 801. The mixture of Cyanex 272 and Ionqest 801 has a slightly synergistic effect for the extraction of zinc and cobalt, particularly with the equal concentration of each in the mixture. A significant synergistic effect was observed for nickel extraction when Cyanex 272 concentration was higher than the Ionqest 801 concentration. The synergistic species was determined to have the form of $M(AB)$.

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