

## Article

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

Wensen Liu <sup>1,2,3</sup>, Jian Zhang <sup>3,4,5</sup>, Zhenya Xu <sup>6</sup>, Jie Liang <sup>1,\*</sup> and Zhaowu Zhu <sup>2,3,4,\*</sup><sup>1</sup> School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China; liuwensen@ipe.ac.cn<sup>2</sup> Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, China<sup>3</sup> National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Beijing 100190, China; zhangjian01@ipe.ac.cn<sup>4</sup> Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China<sup>5</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China<sup>6</sup> The College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100028, China; 2018200201@mail.buct.edu.cn

\* Correspondence: liangjie@cumtb.edu.cn (J.L.); zhwzhu@ipe.ac.cn (Z.Z.)

**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

**Citation:** Liu, W.; Zhang, J.; Xu, Z.; Liang, J.; Zhu, Z. Study on the Extraction and Separation of Zinc, Cobalt, and Nickel Using Ionquest 801, Cyanex 272, and Their Mixtures. *Metals* **2021**, *11*, 401. <https://doi.org/10.3390/met11030401>

Academic Editor: Dariush Azizi

Received: 9 February 2021

Accepted: 24 February 2021

Published: 1 March 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 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  $\text{RE}(\text{HB}_2)(\text{HA}_2)_2$ , 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  $\text{Log}D$  against pH [30]. In contrast, Tait [29] reported that the  $\text{Log}D(\text{Co})$  and  $\text{Log}D(\text{Ni})$  against the  $\text{Log} [\text{Cyanex 272}]$  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

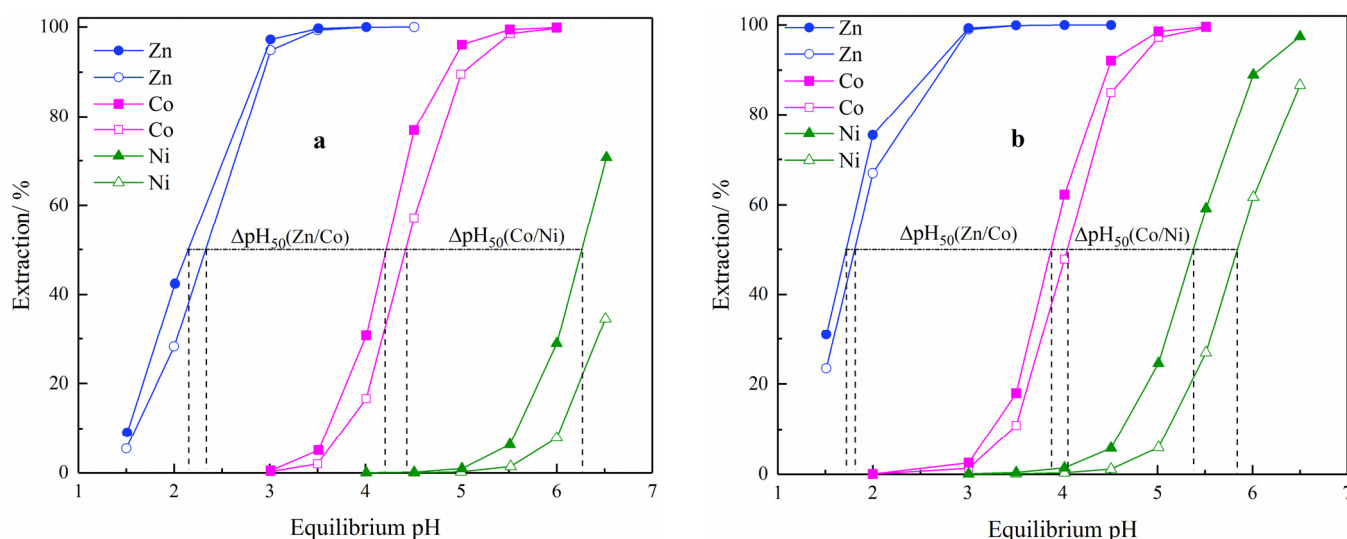
The determination of metal extraction pH isotherms was carried out in 300 mL of hexagonal glass jars immersed in a water bath to control temperature at 40 °C unless it is indicated. Aqueous and organic solutions each of 100 mL were added into the jar to obtain

the A/O ratio of 1:1. Two phase solutions were mixed by an impeller with  $\Phi 40$  mm six-bottom-bladed disc stirrer equipped to an overhead motor. After the temperature increased to 40 °C, a 200 g/L NaOH solution was used to adjust pH to the desired values. The pH was monitored using a ROSS Sure Flow pH probe (model 8127BN, Thermo Fisher Scientific, Waltham, MA, USA) connected to a Hanna portable pH meter (model HI9125, Hanna Instruments, Woonsocket, RI, USA). The mixed solutions about 20 mL were taken using a syringe with a plastic extension at each desired pH point after pH maintains constant for 2 min, and then two phases were separated using Whatman 1PS filter paper, which only allowed organic solution to pass through. Aqueous solutions were then filtered again using membrane syringe filters to completely remove entrained organic and analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300V, Perkin-Elmer, Waltham, MA, USA). Organic solutions were stripped with 100 g/L H<sub>2</sub>SO<sub>4</sub> at an A/O ratio of 1:1 and 40 °C. The loaded strip liquors were then filtered and then analysed by ICP-OES. Mass balance was calculated based on the metal in the feed solution and distributed in the two phases. The analysis results with a mass balance in the range of 95 to 105% were adopted.

### 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 pH<sub>50</sub> (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  $\Delta\text{pH}_{50}(\text{Co/Ni})$  with Cyanex 272 was clearly larger than that with Ionquest 801. However, the gaps  $\Delta\text{pH}_{50}(\text{Zn/Co})$  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].



**Figure 1.** Metal extraction pH isotherm of Cyanex 272 (a) and Ionquest 801 (b) at an A/O ratio of 1:1 and 40 °C (Organic concentrations: solid-label curve, 0.3 M, and open-label curve, 0.2 M).

Detailed metal extraction pH<sub>50</sub> and  $\Delta\text{pH}_{50}(\text{Co-Zn})$ ,  $\Delta\text{pH}_{50}(\text{Ni-Co})$  of Cyanex 272 and Ionquest 801 under various concentrations are obtained in Table 1. All of these results showed that Cyanex 272 has higher pH<sub>50</sub> and larger  $\Delta\text{pH}_{50}(\text{Ni-Co})$  compared with

Ionquest 801 at the same concentration, suggesting weaker metal extraction and better cobalt selectivity over nickel. The  $\Delta\text{pH}_{50}(\text{Co-Zn})$  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  $\text{pH}_{50}$  and  $\Delta\text{pH}_{50}$  with various concentrations of Cyanex 272 and Ionquest 801.

Cyanex 272 Concentration (M)	$\text{pH}_{50}$			$\Delta\text{pH}_{50}$	
	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)	$\text{pH}_{50}$			$\Delta\text{pH}_{50}$	
	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  $\text{SF}_{\text{Co/Ni}}$  (separation factors of cobalt and nickel) is high over 1000 under various pH with Cyanex 272 for its all-tested concentrations. The  $\text{SF}_{\text{Co/Ni}}$  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  $\text{SF}_{\text{Co/Ni}}$  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 ( $\text{SF}_{\text{Co/Ni}}$ ), and organic loading percentages with Cyanex 272 and Ionquest 801.

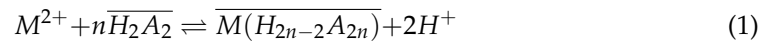
Cyanex 272 Concentration (M)	Co Extraction (%)			$\text{SF}_{\text{Co/Ni}}$			Metal Loaded Organic (%)		
	pH 5.0	pH 5.5	pH 6.0	pH 5.0	pH 5.5	pH 6.0	pH 5.0	pH 5.5	pH 6.0
0.1	37.6	69.4	88.6	2973	6640	7163	42.9	53.3	59.3
0.2	89.5	98.6	99.7	4341	4725	4149	29.9	31.9	33.0
0.3	96.0	99.4	99.9	2514	2479	1888	20.4	21.3	23.8
0.4	97.5	99.6	99.9	2314	1630	1126	17.1	18.0	21.0

Ionquest 801 Concentration (M)	Co-Extraction (%)			$\text{SF}_{\text{Co/Ni}}$			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 equilibria 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.

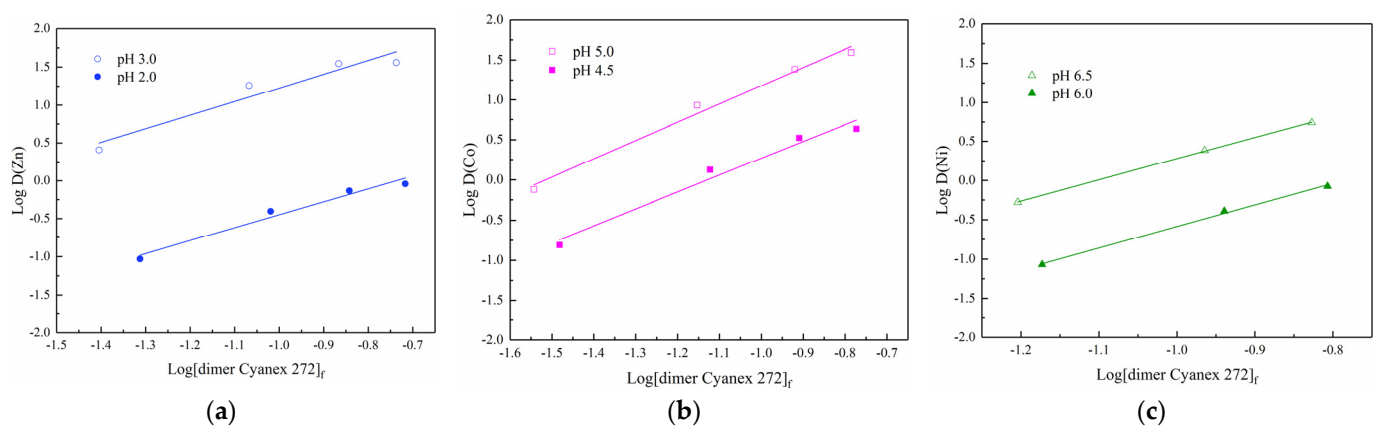


$$K_{eq} = \frac{[\overline{M(H_{2n-2}A_{2n})}][H^+]^2}{[M^{2+}][\overline{H_2A_2}]_f^n} \quad (2)$$

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

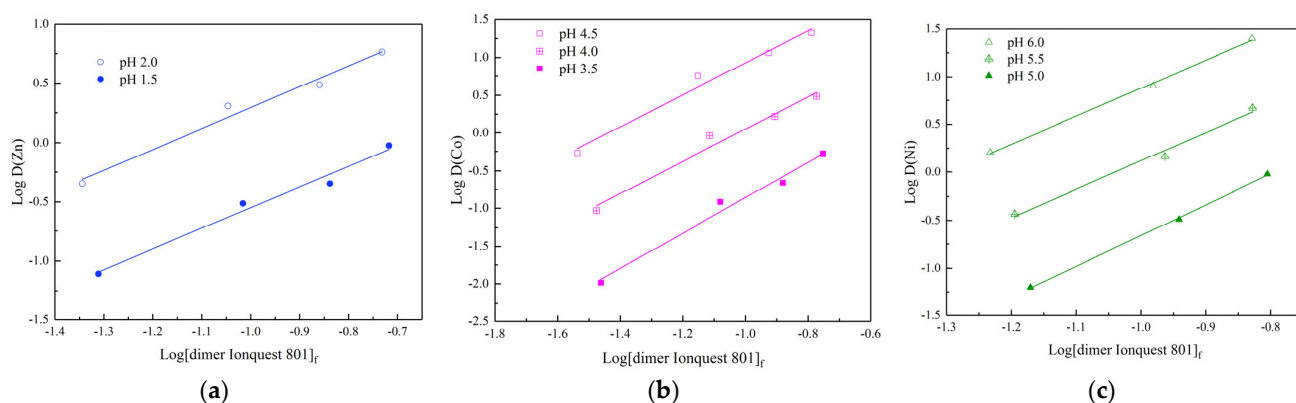
where  $M$  represents the metals of Zn, Co, or Ni.  $HA$  represents the extractant of Cyanex 272 or Ionquest 801, hence  $H_2A_2$  is their dimer. The top bar denotes the organic phase. The subscript “ $f$ ” denotes free extractant concentration (organic free from the metal loading).

Linear relationships of  $\text{Log}D(M)$  against  $\text{Log}[H_2A_2]_f$  and 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 pH compared to the extraction of zinc and cobalt.



**Figure 2.** The relationship of  $\text{Log}D(M)$  against  $\text{Log}[\text{dimer Cyanex 272}]_f$ . (a)  $\text{Log}D(\text{Zn})$ - $\text{Log}[\text{dimer Cyanex 272}]_f$ , (b)  $\text{Log}D(\text{Co})$ - $\text{Log}[\text{dimer Cyanex 272}]_f$ , (c)  $\text{Log}D(\text{Ni})$ - $\text{Log}[\text{dimer Cyanex 272}]_f$ .

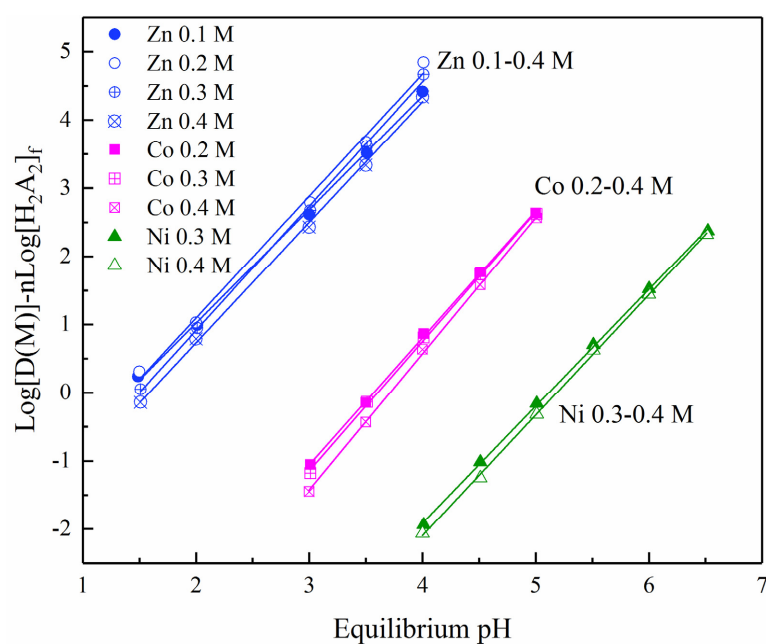
From Equation (3),  $\text{Log}D(M) - n\text{Log}[H_2A_2]_f$  versus pH will give the straight line with a slope of 2. The linear relationships of  $\text{Log}D(M) - n\text{Log}[H_2A_2]_f$  against pH were obtained and shown in Figures 4 and 5. Then, the value used for the calculation is 2 for zinc and 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 3.** The relationship of  $\text{Log}D(M)$  against  $\text{Log} [\text{dimer Ionquest } 801]_f$ . (a)  $\text{Log}D(\text{Zn})$ - $\text{Log}[\text{dimer Ionquest } 801]_f$ , (b)  $\text{Log}D(\text{Co})$ - $\text{Log}[\text{dimer Ionquest } 801]_f$ , (c)  $\text{Log}D(\text{Ni})$ - $\text{Log}[\text{dimer Ionquest } 801]_f$ .

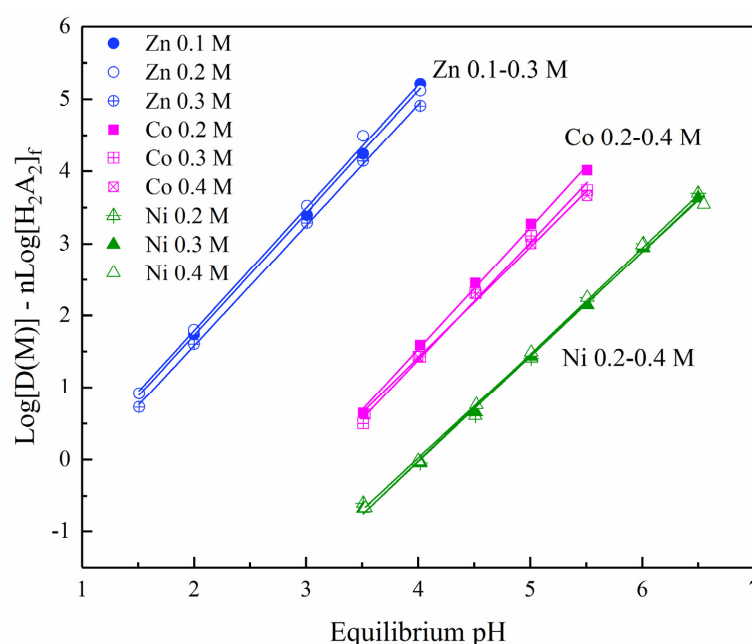
**Table 3.** Slopes of straight lines in Figures 2 and 3, and the corresponding  $n$  values in Equation (3).

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



**Figure 4.** The linear relationship of  $\text{Log}D(M) - n\text{Log} [H_2A_2]_f$  and equilibrium pH for the metal extraction with Cyanex 272.





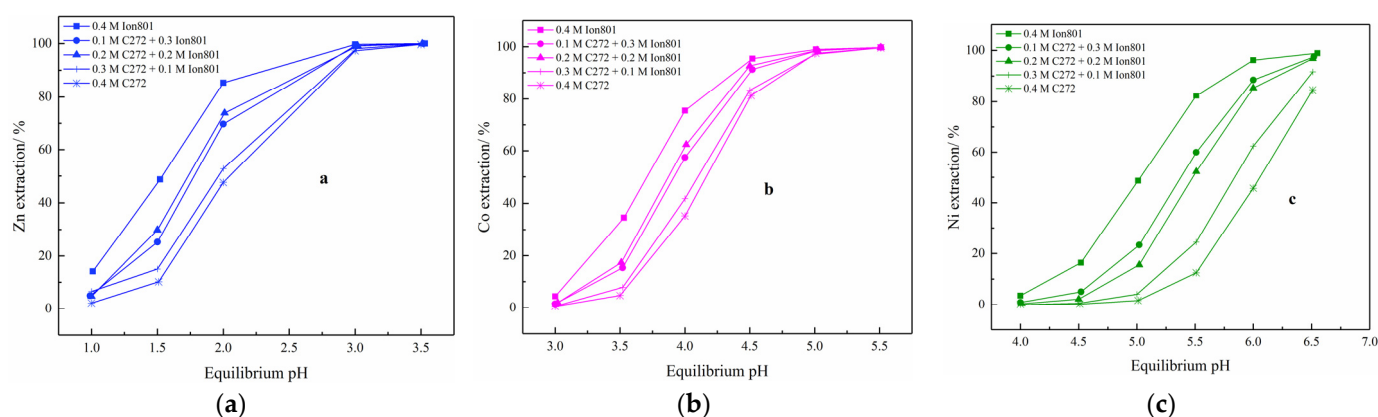
**Figure 5.** The linear relationship of  $\text{Log}D(M) - n\text{Log}[H_2A_2]_f$  and equilibrium pH for the metal extraction with Ionquest 801.

**Table 4.** Line slope of the linear relationship of  $D(M) - 2n\text{Log}[HA]_f$  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  $\text{pH}_{50}$  and  $\Delta\text{pH}_{50}$  (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 ( $\text{SF}_{\text{Co/Ni}}$ ) 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.  $\text{SF}_{\text{Co/Ni}}$  was 300–400 when equal moles of Cyanex 272 and Ionquest 801 were mixed in the extraction system.

**Table 5.** The half extraction of  $\text{pH}_{50}$  and  $\Delta\text{pH}_{50}$  (Co-Zn and Ni-Co) with various organic compositions composed of Cyanex 272 and Ionquest 801.

Organic Concentration (M)		$\text{pH}_{50}$			$\Delta\text{pH}_{50}$	
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 ( $\text{SF}_{\text{Co/Ni}}$ ) under various organic compositions and pH values.

Organic Concentration (M)		$\text{SF}_{\text{Co/Ni}}$			
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.

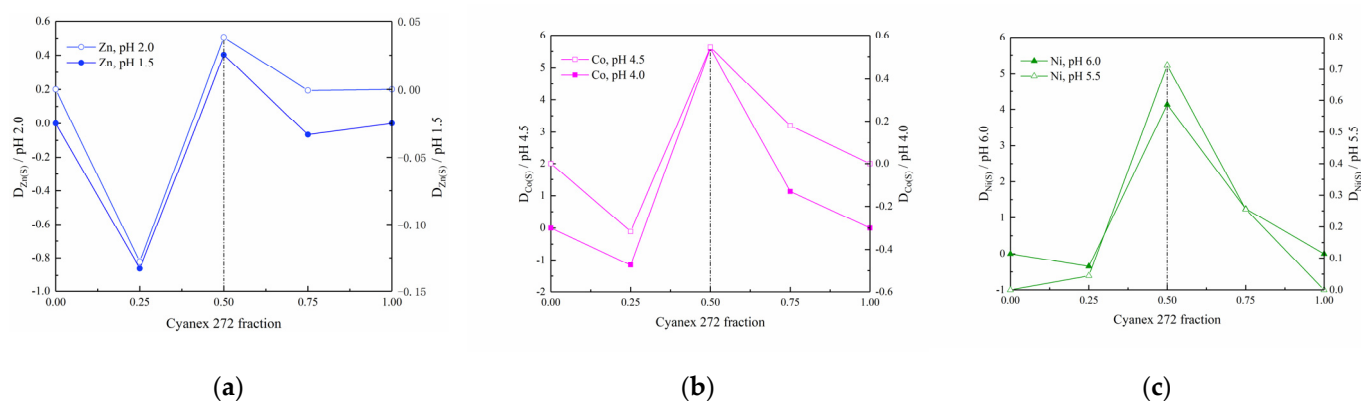
$$SC_M = \frac{D_M}{D_{M(\text{C272})} + D_{M(\text{Ion801})}} \quad (4)$$



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)		$SC_{Zn}$		$SC_{Co}$		$SC_{Ni}$	
Cyanex 272	Ionquest 801	pH = 1.5	pH = 2.0	pH = 4.5	pH = 5.5	pH = 5.5	6.0
0.4	0	1.00	1.00	1.00	1.00	1.00	1.00
0.3	0.1	1.00	0.94	1.34	1.29	4.74	4.03
0.2	0.2	1.10	1.17	1.49	1.80	2.86	3.44
0.1	0.3	0.73	0.73	0.81	0.90	1.03	0.96
0	0.4	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 Ionquest 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 Ionquest 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 Ionquest 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. Ionquest 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 Ionquest 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 Ionquest 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 Ionquest 801, separation factors over thousands were also obtained when low Ionquest 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 Ionquest 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 Ionquest 801. The mixture of Cyanex 272 and Ionquest 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 Ionquest 801 concentration. The synergistic species was determined to have the form of  $M(AB)$ .

**Author Contributions:** Conceptualization, Z.Z. and J.L. Methodology, Z.Z. Software, W.L. Validation, J.Z. and Z.X. Investigation, Z.Z. Resources, Z.Z. Data curation, J.Z. and Z.X. Writing-original draft preparation, W.L. and Z.Z. Writing-review and editing, W.L., J.L., and Z.Z. Project administration, J.Z. Funding acquisition, Z.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (51774260, 51804289, 51904286, 21908231), Beijing Natural Science Foundation (2202053), Key Program of Innovation Academy for Green Manufacture, and Chinese Academy of Sciences (Grant No. IAGM-2019-A15), Key Research Program of Frontier Sciences of Chinese Academy of Sciences (Grant No. QYZDJ-SSW-JSC021), and CAS Interdisciplinary Innovation Team.

**Institutional Review Board Statement:** The study did not involve humans or animals.

**Informed Consent Statement:** The study did not involve humans or animals.

**Data Availability Statement:** This study did not report any data and the data presented in this study are available on request from the corresponding author.

**Acknowledgments:** The authors would like to acknowledge the financial support by all the funders.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Lewis, A.E. Review of metal sulphide precipitation. *Hydrometallurgy* **2010**, *104*, 222–234. [\[CrossRef\]](#)
2. Zhu, Z.W.; Pranolo, Y.; Zhang, W.S.; Cheng, C.Y. Separation of cobalt and zinc from concentrated nickel sulphate solutions with Cyanex 272. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 75–81. [\[CrossRef\]](#)
3. Mishra, R.K.; Rout, P.C.; Sarangi, K.; Nathsrma, K.C. Solvent extraction of zinc, manganese, cobalt and nickel from nickel laterite bacterial leach liquor using sodium salts of TOPS-99 and Cyanex 272. *Trans. Nonferrous Met. Soc. China* **2016**, *26*, 301–309. [\[CrossRef\]](#)

4. Senapati, D.; Chaudhury, G.R.; Sarma, P.V.R.B. Purification of nickel sulphate solutions containing iron, copper, cobalt, zinc and manganese. *J. Chem. Technol. Biotechnol.* **1994**, *59*, 335–339. [\[CrossRef\]](#)
5. Kursunoglu, S.; Ichlas, Z.T.; Kaya, M. Solvent extraction process for the recovery of nickel and cobalt from Caldag laterite leach solution: The first bench scale study. *Hydrometallurgy* **2017**, *169*, 135–141. [\[CrossRef\]](#)
6. Ichlas, Z.T.; Ibana, D.C. Process development for the direct solvent extraction of nickel and cobalt from nitrate solution: Aluminum, cobalt, and nickel separation using Cyanex 272. *Int. J. Miner. Metall. Mater.* **2017**, *24*, 37–46. [\[CrossRef\]](#)
7. Donegan, S. Direct solvent extraction of nickel at Bulong operations. *Miner. Eng.* **2006**, *19*, 1234–1245. [\[CrossRef\]](#)
8. Crundwell, F.K.; Moats, M.S.; Ramachandran, V.; Robinson, G.; Davenport, W.G. Hydrometallurgical Production of High-Purity Nickel and Cobalt. In *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*; Elsevier: Radarweg, The Netherlands, 2011.
9. Parhi, P.K.; Padhan, E.; Palai, A.K.; Sarangi, K.; Nathsarma, K.C.; Park, K.H. Separation of Co (II) and Ni (II) from the mixed sulphate/chloride solution using NaPC-88A. *Desalination* **2011**, *267*, 201–208. [\[CrossRef\]](#)
10. Li, Y.; Zhang, L.H.; Guo, S.H.; Zhang, L.B. Extraction and separation of cobalt from nickel by P507 microemulsion liquid membrane. *Nonferrous Met. Eng.* **2016**, *6*, 40–44.
11. Liu, M.X.; Shen, Y.Y.; Shao, Q.T.; Wu, Z.M.; Zhong, S.H. Study on mixed phase disengagement of cobalt and nickel by extraction with P 507. *Biol. Chem. Eng.* **2016**, *2*, 1–3.
12. Wang, J.K.; Gao, K.; Xu, W.X.; Wang, Z.J.; Guo, R.; Zhou, Y.; Li, J. Study on extraction and separation of nickel and cobalt with P 507. *Nonferrous Met.* **2018**, *8*, 19–22.
13. Wu, J.H.; Dong, B.; Zhang, X.P.; Ye, F.C.; Wang, H.J.; Ji, H.W.; Guo, F.Y.; Qiu, S.W.; Liu, Z.D. Solvent extraction of Cu, Zn, Co from nickel sulphate solution applying P507. *Nonferrous Met. Sci. Eng.* **2018**, *9*, 19–24.
14. Flett, D.S. Cobalt-Nickel separation in hydrometallurgy: A review. *Chem. Sustain. Dev.* **2004**, *12*, 81–91.
15. Flett, D.S. Solvent extraction in hydrometallurgy: The role of organophosphorus extractants. *J. Organomet. Chem.* **2005**, *690*, 2426–2438. [\[CrossRef\]](#)
16. Thakur, N.V. Extraction studies of base metals (Mn, Cu, Co and Ni) using the extractant 2-ethylhexyl 2-ethylhexyl phosphonic acid, PC 88A. *Hydrometallurgy* **1998**, *48*, 125–131. [\[CrossRef\]](#)
17. Tsakiridis, P.E.; Agatzini-Leonardou, S. Simultaneous solvent extraction of cobalt and magnesium in the presence of nickel from sulfate solutions by Ionquest 801. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1236–1243. [\[CrossRef\]](#)
18. Zhu, Z.W.; Zhang, J.; Yi, A.F.; Su, H.; Wang, L.N.; Qi, T. Magnesium removal from concentrated nickel solution by solvent extraction using Cyanex 272. *Int. J. Miner. Process. Ext. Metall.* **2019**, *4*, 36–43.
19. Preston, J.S.; du Preez, A.C. Solvent extraction of nickel from acidic solutions using synergistic mixtures containing pyridinecarboxylate esters, Part 1: Systems based on organophosphorus acids. *J. Chem. Technol. Biotechnol.* **1996**, *66*, 86–94. [\[CrossRef\]](#)
20. Cheng, C.Y.; Barnard, K.R.; Zhang, W.S.; Zhu, Z.W.; Pranolo, Y. Recovery of nickel, cobalt, copper and zinc in sulphate and chloride solutions using synergistic solvent extraction. *Chin. J. Chem. Eng.* **2016**, *24*, 237–248. [\[CrossRef\]](#)
21. Sulaiman, R.N.R.; Othman, N. Synergistic green extraction of nickel ions from electroplating waste via mixtures of chelating and organophosphorus carrier. *J. Hazard. Mater.* **2017**, *340*, 77–84. [\[CrossRef\]](#)
22. Sun, Q.; Yang, L.M.; Huang, S.T.; Xu, Z.; Wang, W. Synergistic solvent extraction of nickel by 2-hydroxy-5-nonylacetophenone oxime mixed with neodecanoic acid and bis(2-ethylhexyl) phosphoric acid: Stoichiometry and structure investigation. *Miner. Eng.* **2019**, *132*, 284–292. [\[CrossRef\]](#)
23. Zhao, J.M.; Shen, X.Y.; Deng, F.L.; Wang, F.C.; Wu, Y.; Liu, H.Z. Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. *Sep. Purif. Technol.* **2011**, *78*, 345–351. [\[CrossRef\]](#)
24. Liu, M.R.; Zhou, G.Y.; Wen, J.K. Separation of divalent cobalt and nickel ions using a synergistic solvent extraction system with P507 and Cyanex272. *Chin. J. Process Eng.* **2012**, *12*, 415–419.
25. Liu, T.C.; Chen, J.; Li, H.L.; Li, K.; Li, D.Q. Further improvement for separation of heavy rare earths by mixtures of acidic organophosphorus extractants. *Hydrometallurgy* **2019**, *188*, 73–80. [\[CrossRef\]](#)
26. Quinn, J.E.; Soldenhoff, K.H.; Stevens, G.W.; Lengkeek, N.A. Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures. *Hydrometallurgy* **2015**, *157*, 298–305. [\[CrossRef\]](#)
27. Dreisinger, D.B.; Cooper, W.C. The solvent extraction separation of cobalt and nickel using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester. *Hydrometallurgy* **1984**, *12*, 1–20. [\[CrossRef\]](#)
28. Devi, N.B.; Nathsarma, K.C.; Chakravorty, V. Separation and recovery of cobalt (II) and nickel (II) from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272. *Hydrometallurgy* **1998**, *49*, 47–61. [\[CrossRef\]](#)
29. Tait, B.K. Cobalt-nickel separation: The extraction of cobalt (II) and nickel (II) by Cyanex 301, Cyanex302 and Cyanex 272. *Hydrometallurgy* **1993**, *32*, 365–372. [\[CrossRef\]](#)
30. Sarangi, K.; Reddy, B.R.; Das, R.P. Extraction studies of cobalt (II) and nickel (II) from chloride solutions using Na-Cyanex 272: Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. *Hydrometallurgy* **1999**, *52*, 253–265. [\[CrossRef\]](#)
31. Ahmadipour, M.; Rashchi, F.; Ghafarizadeh, B.; Mostoufi, N. Synergistic effect of D2EHPA and Cyanex 272 on separation of zinc and manganese by solvent extraction. *Sep. Sci. Technol.* **2011**, *46*, 2305–2312. [\[CrossRef\]](#)
32. Begum, N.; Bari, F.; Jamaludin, S.B.; Hussin, K. Solvent extraction of copper, nickel and zinc by Cyanex 272. *Int. J. Phys. Sci.* **2012**, *7*, 2905–2910.

- 
33. Innocenzi, V.; Veglio, F. Separation of manganese, zinc and nickel from leaching solution of nickel-metal hydride spent batteries by solvent extraction. *Hydrometallurgy* **2012**, *50*, 50–58. [[CrossRef](#)]
  34. Devi, N.B.; Nathasarma, K.C.; Chakravorty, V. Sodium salts of D2EHPA, PC-88A and Cyanex-272 and their mixtures as extractants for cobalt (II). *Hydrometallurgy* **1994**, *34*, 331–342. [[CrossRef](#)]
  35. Darvishia, D.; Haghsheenas, D.F.; Alamdari, E.K.; Sadrnezhad, S.K.; Halali, M. Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. *Hydrometallurgy* **2005**, *77*, 227–238. [[CrossRef](#)]
  36. Renny, J.S.; Tomasevich, L.L.; Tallmadge, E.H.; Collom, D.B. Method of Continuous Variations: Applications of Job Plots to the Study of Molecular Associations in Organometallic Chemistry. *Angew. Chem. Int. Ed.* **2013**, *52*, 11998–12013. [[CrossRef](#)] [[PubMed](#)]