



## Research Article

# Synergistic Extraction of Ga(III) from Chloride Solution by Mixture of Cyanex 272 and Alamine 336

Kailun Zhu<sup>1</sup>, Xiaoxi Ding<sup>1</sup>, Jiaxin Jiang<sup>1</sup>, Boning Tian<sup>1</sup>, Qingjie Guo<sup>1,2</sup>, Lingyun Wang<sup>1\*</sup> 

<sup>1</sup>Key Laboratory of Clean Chemical Processing of Shandong Province, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China

<sup>2</sup>State Key Laboratory of High-Efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China  
E-mail: wangly412@qust.edu.cn

**Received:** 21 February 2023; **Revised:** 24 March 2023; **Accepted:** 24 March 2023

**Abstract:** Aiming to select a suitable system for the synergistic solvent extraction of Ga(III), solvent extraction (SX) experiments were carried out by using acidic organo-phosphorous extractants, namely P204, P507 and Cyanex 272, and their mixtures with neutral extractants (TBP, N503) or amine extractants (Alamine 336). Among the studied mixtures, a remarkable synergistic effect for Ga(III) extraction was resulted by the combination of Cyanex 272 and Alamine 336 and the maximal synergistic enhancement coefficient reached 3.11. Compared to the single Cyanex 272, higher equilibrium pH values were observed when mixture of Cyanex 272 and Alamine 336 was employed. The extraction of hydrogen ions by Alamine 336 during the reaction was considered to be responsible for the synergistic extraction, and thus the the extraction of Ga(III) by Cyanex 272 was promoted. Finally, the synergistic extraction stoichiometry of mixture of Cyanex 272 and Alamine 336 for Ga(III) was projected by slope analysis. Ga(OH)A<sub>2</sub> was resulted to be the composition of extracted complexes.

**Keywords:** Ga(III), solvent extraction, synergistic extraction, acidic extractants, amine extractants

## 1. Introduction

Gallium is a rare element of strategic importance and widely employed in various high-technology applications, such as semiconductor materials, solar panels, LED chips. However, there is no independent mineral deposit containing Ga(III) in nature and it is generally found by a very small amount in aluminum ore, zinc ore, iron ore, coal and other rocks.<sup>1</sup> Growing market demand and constrained natural resources may lead to insufficient supply of gallium<sup>2</sup>, the use of efficient technology to recover gallium from secondary resources has become a hot topic nowadays, such as red mud, fly ash, e-waste containing gallium, and soot from the phosphorus plant furnace, etc.<sup>3-6</sup>

Several separation techniques have been proposed to recover Ga(III), such as ion exchange, precipitation, solvent extraction(SX) and so on.<sup>7-10</sup> Compared with other technologies, SX is considered the preferred technology to recover gallium because of its simple operating equipment, low operating time and high economic efficiency, such as high molecular weight amines<sup>11</sup>, neutral extractants<sup>12-14</sup>, carboxylic acids extractants<sup>15</sup> and oximes extractants<sup>16,17</sup>.

Although the neutral extractant has good extraction effect on gallium (tri-n-butyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), mixture of branched chain alkylated phosphine oxides (C923) and bis

(2,4,4-trimethylpentyl) octylphosphine oxide (C925))<sup>18-19</sup> and the recovery effect depended on the acidity of water phase<sup>12</sup>. The excessive usage of acid in the aqueous phases leads to environmental problems.

Acidic organophosphorous compounds like di-(2-ethylhexyl) phosphoric acid (P204)<sup>20</sup>, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507)<sup>21</sup> and bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272)<sup>22</sup> also have been used as extractants to recover and purify Ga(III) from various sources. Although acidic organophosphorus extractants can extract Ga(III) to some extent within a pH range of 2.0~3.0, the extraction ability is greatly limited by the intermolecular hydrogen bonding of the dipolymer. In addition, the H<sup>+</sup> dissociated from acidic organophosphorous extractants caused by cation-exchange mechanism also negatively affect the extractabilities for Ga(III). To destroy the dipolymers and eradicate H<sup>+</sup> in the acidic organophosphorous extractants, the widely used method is to saponify the acidic extractant with alkaline compounds such as NH<sub>3</sub>·H<sub>2</sub>O, NaOH, etc.<sup>23</sup> The saponification procedure can improve extractabilities of acidic extractants by destroying the H<sup>+</sup> and eradicating the dipolymers in the extractants.<sup>24</sup> However, the saponification process consumes more operation cost and releases high salty wastewater into the environment. Therefore, there is a need to explore new extractants or extraction systems for gallium recovery.

The problem can be well solved by mixing two extractants to develop a new synergistic system. The extraction capacity or selectivity of this mixture in a synergistic extractant exceeds the total capacities of the individual components. An aggregate of two or more extractants (acidic/neutral, two acidic, two neutral, basic/neutral, acidic/basic) have been investigated for metal extractions and separations.

Several types of synergistic extractants have been used for Ga(III) recovery in the last decades. For example, Nusen et al. (2016) reported a high extractions percentage of Ga(III) and In(III) obtained by using a combination of Versatic 10 and LIX 63.<sup>25</sup> The synergistic effect of the extractant has a significant effect on In(III) while it has little effect on Ga(III). Choi and Ohashi (2000) found that 2-methyl-8-hydroxyquinoline derivatives (HA) showed better extraction performance for Ga(III) after the addition of 3,5-dichlorophenol (HDCP).<sup>26</sup> The combination of HDCP and complex Ga(III)-HA formed by quantitative calculation is Ga(DCP)<sub>2</sub>·HDCP. In a process developed by Ma et al. (2011), sec-octylphenoxyacetic acid (CA12) was mixed with primary amine N1923 for Ga(III) extraction.<sup>27</sup> The mixtures performed synergistic effects on Ga(III) at low CA12 concentrations and inhibition effect at high CA12 concentrations.

Progress has been made in the research of mixtures of cationic extractants and amine extractants in the field of hydrometallurgy, such as Liu (2014) purified REEs from aqueous solution with Cl<sup>-</sup> with a synergistic extraction system containing Alamine 336 and organophosphoric acid extractants (P204, P507, Cyanex 272).<sup>28</sup> Alamine 336 extracts Ga(III) from acidic extractants more effectively by combining H<sup>+</sup> released from organophosphoric acid extractants. Therefore, aim to improve the extraction capability of Ga(III) by acid extractants, SX experiments were performed by using mixtures of cationic extractants and tertiary amines. Hence in this study, Ga(III) was extracted by solvent extraction using cationic extractants (P204, P507, Cyanex 272) and their mixtures with neutral extractants (TBP, N503) or amine extractants (Alamine 336). For this purpose, the influence of some important parameters such as the properties of extractants, the extractant concentration, and the initial and equilibrium pH of the chloride solution were studied. For the chosen synergistic extraction system, the synergistic enhancement factor R and the reaction mechanism was also discussed.

## 2. Experimental

### 2.1 Materials and reagents

The stock solution containing Ga(III) was prepared by dissolving Ga(NO)<sub>3</sub> (Aladdin Reagents, 99.9%) in deionized water at a concentration of 1 g/L of Ga(III). All the extractants (P204, P507, Cyanex 272, N503, TBP and Alamine 336) were purchased from Kopper Chemical Industry Corp., Ltd., China. The chemical formulas of each type of extractants are reflected in Table 1. Kerosene was used as a diluent and all other reagents used were of analytical reagent grade. Subsequent work solutions were obtained by further dilution of the standardized stock solutions.

**Table 1.** Chemical formulas and structures of the extractants.

| Extractant   | Structure |
|--------------|-----------|
| D2EHPA       |           |
| Acidic PC88A |           |
| Cyanex 272   |           |
| Neutral TBP  |           |
| Neutral N503 |           |
| Amine N235   |           |

\* R is the alkyl groups.

## 2.2 Procedure

Extraction experiments were performed by centrifuging equal volumes (8 ml) of aqueous and organic phases in 20 ml centrifuge tubes for 10 min using a centrifuge (TDL-80-2B model, Shanghai, China). After equilibrium, let stand for 3 min to complete the phase separation of the contents. All the extraction experiments were made at room temperature (10 °C ~ 20 °C). After the split of the phases, the Ga(III) concentration in the aqueous phase was measured by AAS (Purkinje General Instrument Co., LTD, TAS-986 model, Beijing, China). Solution pH was measured using an WIGGENS PH610 meter. Ga(III) concentration in the organic phase was obtained by calculating the Ga(III) concentration in the aqueous phase before and after the extraction. The distribution ratio of Ga(III) (D) was calculated as according to  $D = \frac{[Ga(III)]_{org, eq}}{[Ga(III)]_{aq, eq}}$ , where  $[Ga(III)]_{aq, eq}$  and  $[Ga(III)]_{org, eq}$  are the concentrations of the Ga(III) in the water and organic phases, respectively, at equilibrium. The extraction percentage were calculated by  $Ex\% = \frac{[Ga(III)]_{org, eq}}{[Ga(III)]_{aq, init}} \times 100$ , where  $[Ga(III)]_{aq, init}$  represents the concentrations of the Ga(III) in initial aqueous phase before extraction.

## 3. Results and discussion

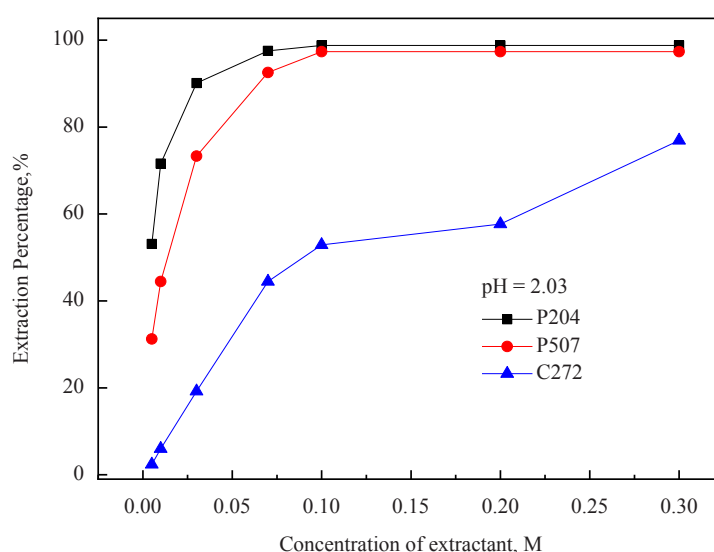
### 3.1 Extraction of Ga(III) by single acidic extractants

#### 3.1.1 Effect of acidic extractants concentration on Ga(III) extractionon

The initial screening experiments were performed to explore the effect of acidic extractants concentration on Ga(III) extractionon. The cationic extractants concentrations (P204, P507 and Cyanex 272) were in the gradient range

of 0.005 M to 0.30 M. The concentration of Ga(III) was 100 ppm and the initial pH was kept at 2.03 in the aqueous solutions.

The plot of the extraction percentage against acidic extractants concentrations is exhibited in Figure 1. The obtained experimental results show that the extraction behavior of Ga(III) with P204 and P507 was almost comparable to each other. In both cases, the Ga(III) percent extraction increased from 29.1 and 52.8 to 98.3 and 99.2 when the P507 and P204 concentrations were increased from 0.005 M to 0.1 M, respectively, and thereafter stabilized up to 0.3 M, respectively. In both cases, the Ga(III) percent extraction sharply from 29.1 to 98.3 and 52.8 to 99.2 with increasing the P507 and P204 concentrations from 0.005 M to 0.1 M and thereafter tend to approach constant with up to 0.3 M, respectively. However, in the case of Cyanex 272, the percent extraction was much smaller than that of P507 and P204. This phenomenon is caused by the different acidity of the extractants and can be explained by their pKa values, which are in the order of the acidity of the three acidic extractants: P204 (pKa = 3.24) > P507 (pKa = 4.51) > Cyanex 272 (pKa = 6.37).<sup>29</sup> In general, a stronger acid extractant can extract more metal at a given pH.



**Figure 1.** Effect of P204, P507, Cyanex 272 concentration on extraction Ga(III) when the initial pH of the solution was 2.03.

**Table 2.** Effect of P204, P507, Cyanex 272 concentration on the equilibrium pH when the initial pH of the solution was 2.03.

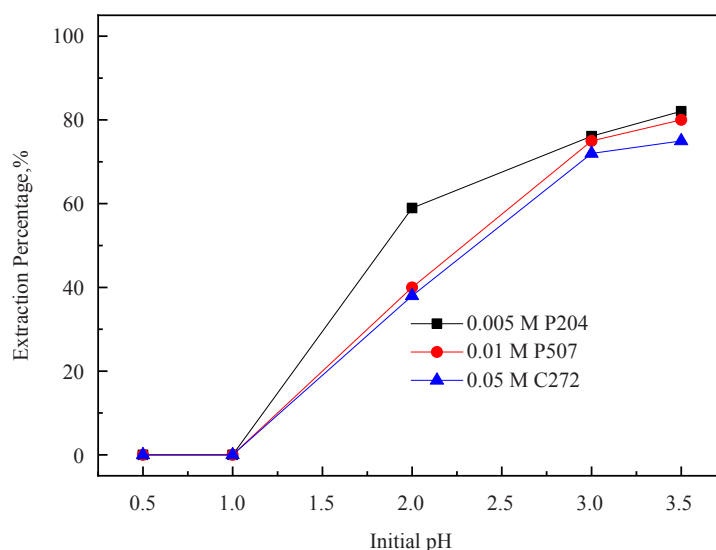
| [Extractant], mol/L | Equilibrium pH |      |            |
|---------------------|----------------|------|------------|
|                     | P204           | P507 | Cyanex 272 |
| 0.005               | 1.95           | 2.01 | 2.03       |
| 0.01                | 1.93           | 2.00 | 2.03       |
| 0.03                | 1.91           | 1.96 | 2.01       |
| 0.07                | 1.91           | 1.94 | 1.99       |
| 0.10                | 1.91           | 1.93 | 1.97       |
| 0.20                | 1.91           | 1.93 | 1.97       |
| 0.30                | 1.91           | 1.93 | 1.95       |

Aim to explore the H<sup>+</sup> release behavior of acidic extractants, the equilibrium pH(Eq pH) was measured after the completion of the extraction under all acidic extractant concentration conditions. As shown in Table 2, the Eq pH decreases with increasing acidic concentration due to the fact that the acidic extractant will extract Ga(III) as a cation exchange mechanism, which releases H<sup>+</sup> into the solution. And the decrease in Eq pH of the solution after extraction was in the order of: P204 > P507 > Cyanex 272.

The above results show that the extraction capability for Ga(III) from the chloride solution by the three acidic extractants follows the order of the acidity by extractants: P204 > P507 > Cyanex 272.

### 3.1.2 Effect of initial pH on the extraction of Ga(III) by acidic extractants

In the SX of Ga(III) by acidic extractant, the H<sup>+</sup> released from the acidic extractant will be transported to the water phase, so the increase in acidity of the water phase will inhibit the SX of Ga(III). So the initial pH of the water phase is vital to the gallium recovery. In the following experiments, acidic extractants (0.005 M P204, 0.01 M P507, 0.05 M Cyanex 272) were chosen to extract Ga(III) from the hydrochloric acid solutions within the initial pH from 0.5 to 3.5. The results are shown in Figure 2, the Ga(III) percent extraction was almost nil at initial pH of 0.5 or 1.0. While, with the increase of the initial pH from 1.0 to 3.5, the Ga(III) percent extraction increased steadily.



**Figure 2.** Effect of initial pH on the extraction of Ga(III) by 0.005 M P204, 0.01 M P507, 0.05 M Cyanex 272.

**Table 3.** Effect of initial pH on the aqueous equilibrium pH using 0.005 M P204, 0.01 M P507, 0.05 M Cyanex 272.

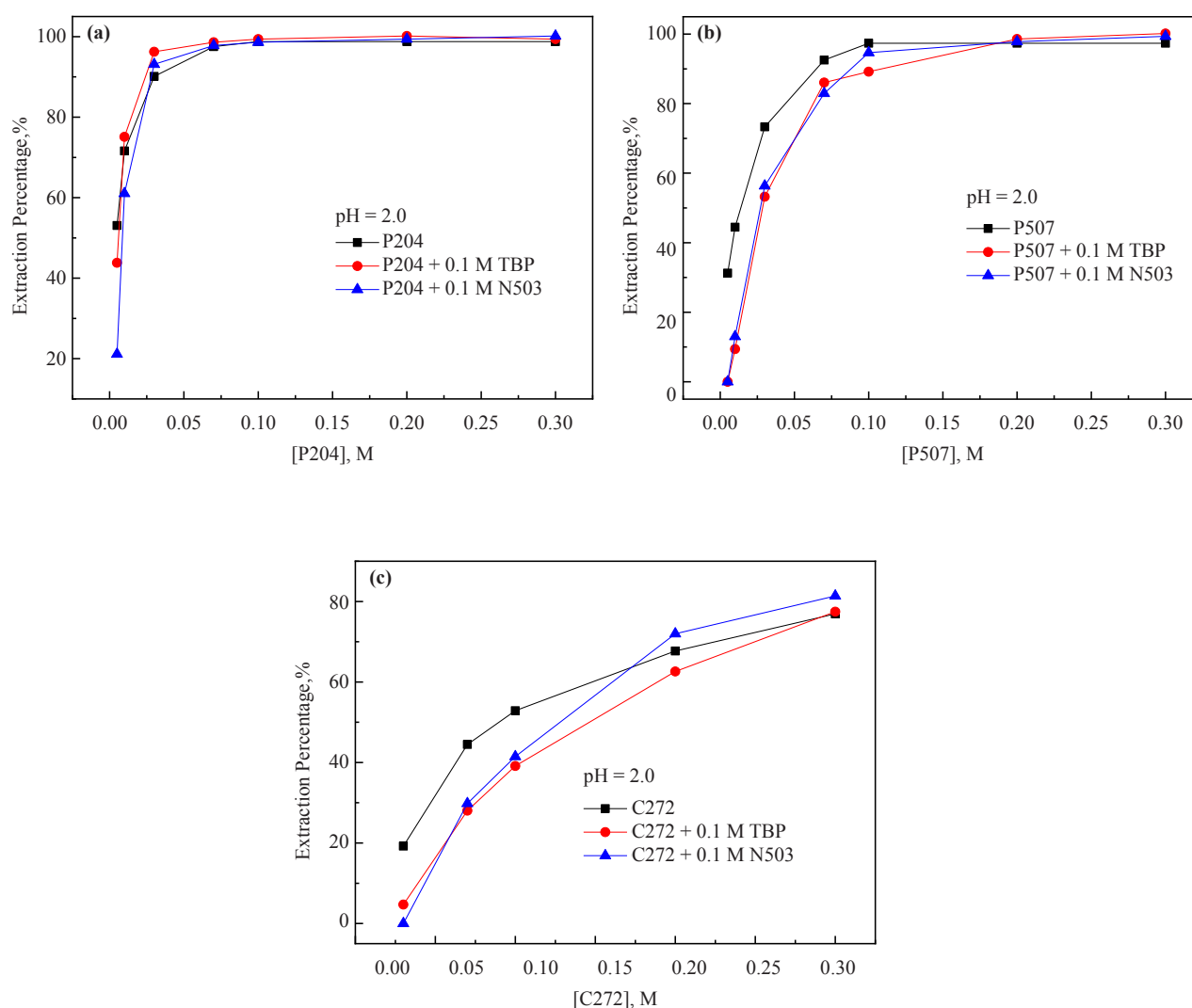
| Initial pH | Equilibrium pH |             |                   |
|------------|----------------|-------------|-------------------|
|            | 0.005 M P204   | 0.01 M P507 | 0.05 M Cyanex 272 |
| 0.5        | 0.5            | 0.5         | 0.5               |
| 1.0        | 1.0            | 1.0         | 1.0               |
| 2.0        | 1.95           | 1.96        | 1.96              |
| 3.0        | 2.53           | 2.55        | 2.56              |
| 3.5        | 3.00           | 2.99        | 2.99              |

In terms of equilibrium pH, the equilibrium pH values observed are lower than the initial pH because of cation exchange mechanism by acidic extractants (Table 3). As the  $H^+$  are releasing from acidic extractant to aqueous phase during the extraction, From Le Chatelier's principle, decreasing the concentration of the  $H^+$  in water phase leads to formation of more extractable complex. Aim to develop new synergistic solvent extraction systems included acidic extractants, the initial pH of the solution for subsequent experiments was chosen to be 2.0.

### 3.2 Solvent extraction of Ga(III) with mixtures of acidic extractants and neutral extractants

#### 3.2.1 Effect of concentration of acidic extractants in the mixtures

Aim to find the synergistic effect, the Ga(III) extraction with the mixtures of acidic extractants (P204, P507, Cyanex 272) and neutral extractants (TBP, N503) was investigated from hydrochloric acid solutions within initial pH 2.0. The neutral extractant concentration in the mixture was always 0.1M, and the concentration gradient of acidic extractant was in the range of 0 ~ 0.005 M (P204) and 0 ~ 0.1 M (P507/Cyanex 272).



**Figure 3.** Extraction of Ga(III) with mixtures of (a) 0.1 M TBP/0.1 M N503 and P204 (b) 0.1 M TBP/0.1M N503 and P507 (c) 0.1 M TBP/0.1 M N503 and Cyanex 272 when the initial pH of the solution was 2.0.

Figure 3 represents that when the concentration range is 0 ~ 0.005 M and 0 ~ 0.1 M by P204 and P507/Cyanex 272, more Ga(III) were extracted by the single acidic extractants than by the mixtures of acidic extractants (P204/P507/Cyanex 272) and neutral extractants (TBP/N503), respectively. Thereafter, as the acidic extractant concentration increases to 0.3 M, the percent extraction by the mixture was comparable than that by single cationic extractant. According to the above experimental data, all the mixture systems did not show significant promotion for the Ga(III) extraction. This appearance might be the interaction between acidic extractants and neutral extractants.<sup>30</sup> There is not enough free acidic extractant to combine with Ga(III) to form complexes when the concentration of acidic extractant is low. Therefore, with increasing acidic extractants concentration, effective concentration of acidic extractants increased.

Effect of the single acidic extractant on the Eq pH of the aqueous phase and the mixtures are represented in Tables S1-S3. Those tables demonstrate that the Eq pH decreases gradually as the amount of acidic extractant in the mixture increases. Comparable behavior was found when extractions were performed with a single acidic extractant. Compared to the single acidic extractants, the combination of neutral extractants and acidic extractants led to higher equilibrium pH values.

### 3.2.2 Effect of concentration of neutral extractants in the mixture

The combination of acidic extractants and neutral extractants is related to the acidity of the acid extractants. Since the acidity of Cyanex 272 is the weakest among the three cationic extractants, so Cyanex 272 was chosen to the subsequent experiments. The effect of TBP and N503 concentrations in the mixture with 0.05 M Cyanex 272 extractants on Ga(III) extraction has been explored at initial aqueous phase pH 2.03 and the results are displayed in Figure 4. Under the set conditions, the percent extraction of Ga(III) by single TBP or N503 is negligible. And in the mixtures, the percent extraction of Ga(III) diminishes from 37.1 to 14.6 and 37.1 to 14.3 with increasing TBP and N503 concentrations from 0 to 1.0 M, respectively. It should be noted that the percent extraction of Ga(III) decreased with increasing concentration of TBP and N503, which might be the interaction between Cyanex 272 and TBP/N503 extractants.

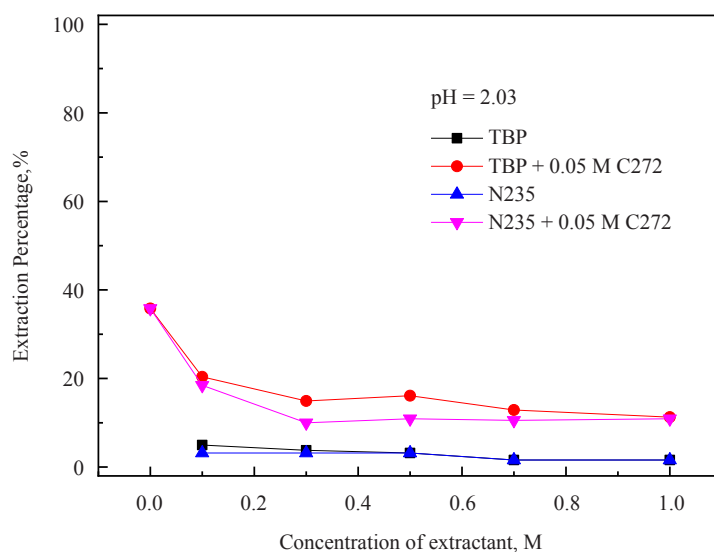


Figure 4. Extraction of Ga(III) with mixtures of TBP/N503 and 0.05 M Cyanex 272 when the initial pH of the solution was 2.03.

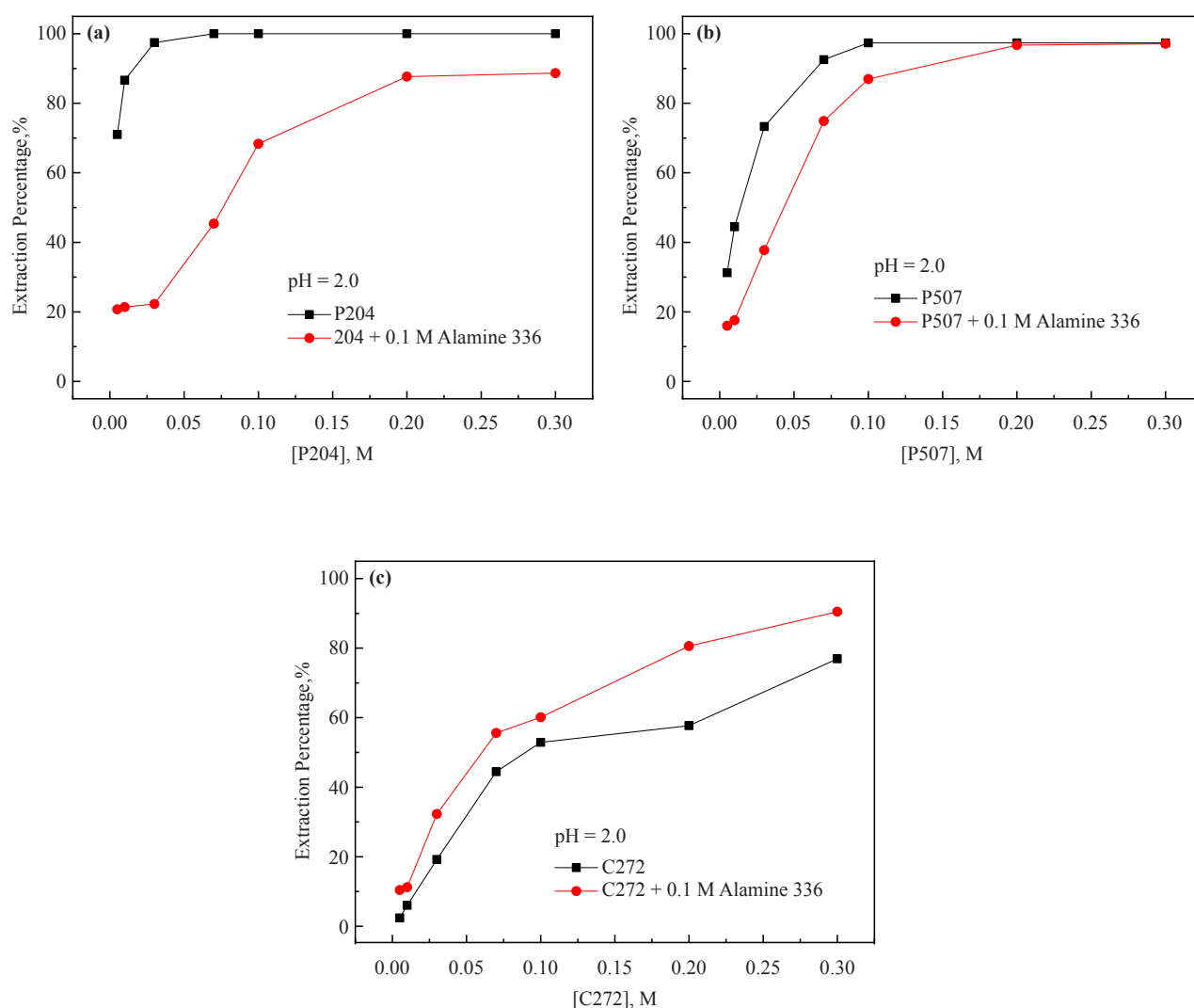
In terms of Eq pH by single neutral extractants, as reflected in Table S4, the Eq pH increased from 2.08 to 3.02 with increasing N503 concentration, whereas the Eq pH maintained constant with increasing TBP concentration. It was demonstrated that N503 can extract acid by forming a strong bond with H<sup>+</sup>. The mixture of 0.05 M Cyanex 272 and N503 caused the Eq pH to increase from 1.96 to 2.37 with increasing N503 concentration from 0 to 1.0 M, while the Eq pH of the mixture of 0.05 M Cyanex 272 and TBP did not change much (Table S4).

The influence of N503 concentration on the Eq pH is somehow interesting. The addition of N503 to Cyanex 272 can extract a large number of  $H^+$ , but can't enhance the percent extraction of Ga(III) compared to single 0.05 M Cyanex 272. It can be speculated that although the acidity of Cyanex 272 is the weaker, but the combination of N503 and Cyanex 272 is strong enough to form ionic compounds.

### 3.3 Solvent extraction of Ga(III) with mixtures of acidic extractants and amine extractants

#### 3.3.1 Effect of concentration of acidic extractants in the mixture

When metal ions are extracted with amine extractants, the amine extractants are protonated by the acid to undergo an anion exchange reaction. Usually, amine extractants bind to  $H^+$  in the aqueous phase and then this binding body is transferred to the organic phase. As a result, the equilibrium pH of the aqueous solution after amine extractant extraction will be higher than the initial pH. Therefore, it can be inferred that the addition of amine extractants to acidic extractants will facilitate the metals extraction.



**Figure 5.** Effect of concentration of acidic extractants in the binary mixtures of (a) P204 (b) P507 (c) Cyanex 272 and 1.0 M Alamine 336 on the extraction of Ga(III) when the initial pH of the solution was 2.0.



For this purpose, mixed extractants of acidic extractants (P204, P507 and Cyanex 272) with amine extractant (Alamine 336) were tested in the following experiments. In the solvent extraction experiments, the concentration of Alamine 336 was kept 1.0 M, but the acidic extractants concentration was varied from 0.005 M to 0.3 M. Although the corresponding data for the single amine extractants are not presented together, the Ga(III) percent extraction with single amine extractant was negligible in our conditions. As shown in Figure 5, the Ga(III) percent extraction increased with increasing the acidic extractant (P204, P507, Cyanex 272) concentration in the mixture. In the case of P204/P507 system, the Ga(III) percent extraction using the mixture is lower than that by single P204/P507. However, the mixture of Cyanex 272 and 1.0 M Alamine 336 led to higher percent extraction than single Cyanex 272, which means that the addition of Alamine 336 into Cyanex 272 have synergistic extraction effect on the extraction of Ga(III) have obvious synergistic extraction. In addition, the synergistic enhancement factor, R, can be obtained according to  $(R = D_{\text{mix}} / [D_{\text{Cyanex 272}} + D_{\text{Alamine 336}}])$ .<sup>31</sup> The highest value of synergistic enhancement factor calculated at 0.3 M Cyanex 272 and 1.0 M Alamine 336 is 3.11 (Table 4).

**Table 4.** Synergistic enhancement coefficients (R) of Ga(III) with mixtures of acidic extractants and 1.0 M Alamine 336.

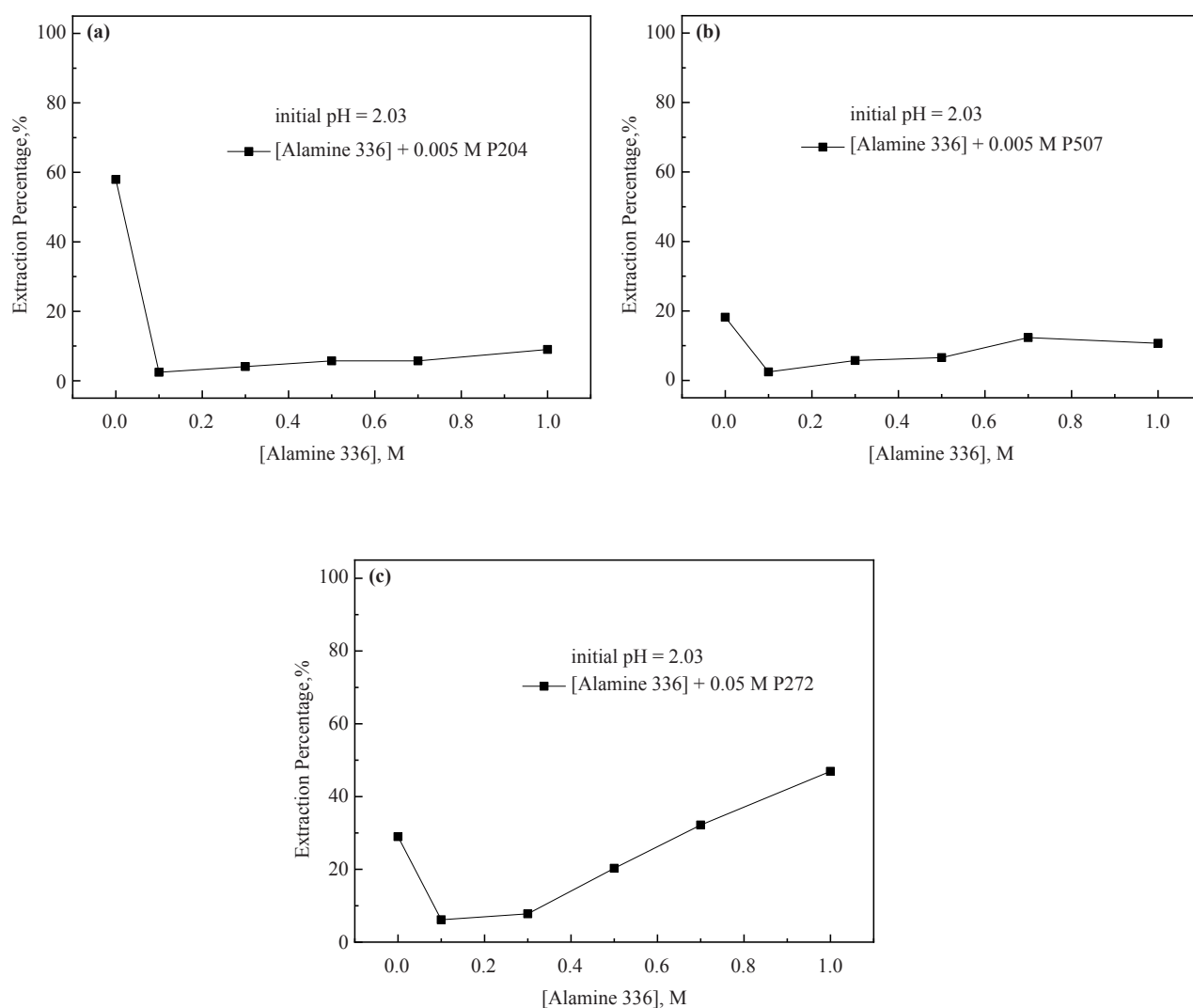
| $D^I$ , extractant I (Alamine 336), (1.0 M) | Concentration of extractant II (Cyanex 272) (M) | $D^{II}$ | $D^{I+II}$ | $D^I + D^{II}$ | R    |
|---|---|----------|------------|----------------|------|
| 0.05  | 0.005   | 0.02     | 0.12       | 0.07           | 1.47 |
| 0.05  | 0.01  | 0.06     | 0.13       | 0.11           | 1.07 |
| 0.05  | 0.03  | 0.24     | 0.29       | 0.29           | 0.98 |
| 0.05  | 0.07  | 0.80     | 0.81       | 0.85           | 0.94 |
| 0.05  | 0.10  | 1.12     | 1.23       | 1.27           | 1.04 |
| 0.05  | 0.20  | 1.36     | 4.16       | 1.41           | 2.93 |
| 0.05  | 0.30  | 3.33     | 10.50      | 3.38           | 3.11 |

**Table 5.** Effect of acidic extractants concentration on the equilibrium pH using mixture of P204/P507/Cyanex 272 + 1.0 M Alamine 336 when the initial pH of the solution was 2.0.

| [Acidic Extractant], mol/L | Equilibrium pH |                            |             |                            |                   |                                  |
|----------------------------|----------------|----------------------------|-------------|----------------------------|-------------------|----------------------------------|
|                            | Single P204    | [P204] + 1.0 M Alamine 336 | Single P507 | [P507] + 1.0 M Alamine 336 | Single Cyanex 272 | [Cyanex 272] + 1.0 M Alamine 336 |
| 0.005                      | 1.95           | 2.26                       | 2.00        | 2.28                       | 2.03              | 2.32                             |
| 0.01                       | 1.93           | 2.28                       | 2.00        | 2.27                       | 2.03              | 2.25                             |
| 0.03                       | 1.91           | 2.32                       | 1.96        | 2.29                       | 2.01              | 2.25                             |
| 0.07                       | 1.91           | 2.39                       | 1.94        | 2.31                       | 1.99              | 2.25                             |
| 0.10                       | 1.91           | 2.36                       | 1.93        | 2.32                       | 1.97              | 2.26                             |
| 0.20                       | 1.91           | 2.33                       | 1.93        | 2.30                       | 1.97              | 2.25                             |
| 0.30                       | 1.91           | 2.01                       | 1.93        | 2.15                       | 1.95              | 2.22                             |

During the extraction of metal with the mixtures of amine extractants and acidic extractant, some reactions can occur simultaneously, such as the formation of amine salt, protonation reaction of amine extractants and cation exchange reaction of  $H^+$ . The Eq pH values of the aqueous phase by single P204/P507/Cyanex 272 and by the mixture of P204/P507/Cyanex 272 and 1.0 M Alamine 336 are represented in Table 5. It can be seen, the equilibrium pH of the mixtures is higher than that of single P204/P507/Cyanex 272. The formation of amine salts is the result of the reaction between the acidic extractant and the amine extractant, which will lead to a decrease in the effective concentration of the acidic extractant. The acidity of Cyanex 272 is weaker than P204/P507, so the weaker interaction between Cyanex 272 and Alamine 336 can be obtained. In addition, the Alamine 336 by protonation reaction to extracting  $H^+$  dissociated from acidic extractant during the extraction process. Thus, the synergistic effect of the mixture of Cyanex 272 and Alamine 336 can be attributed to extract  $H^+$  by Alamine 336.

### 3.3.2 Effect of concentration of Alamine 336 in the mixtures



**Figure 6.** Extraction of Ga(III) with mixtures of Alamine 336 and 0.005 M P204/0.005 M P507/0.05 M Cyanex 272 when the initial pH of the solution was 2.03.

Under the above tested experimental conditions, the mixture of Cyanex 272 and Alamine 336 shows synergistic

effect. Aim to explore the effect of the Alamine 336 concentration in the mixture of acidic extractants and Alamine 336 on extraction Ga(III), the Alamine 336 concentration was varied from 0 to 1.0 M. It can be seen in Figure 6, a small amount of Ga(III) (lower than 15%) was extracted using the mixture of P204/P507 with Alamine336 and the percent extraction of the mixture was lower than by single P204/P507. The mixture system of Alamine 336 and Cyanex 272 showed higher extraction ability for Ga(III) compared to the two Alamine 336 mixture systems mentioned above. It is significant to highlight here that in the Cyanex 272 and Alamine 336 mixture systems, the higher the concentration of Alamine 336, the higher the Ga(III) percent extraction. The percent extraction at 0.05 M Cyanex 272 + 1.0 M Alamine 336 is higher than that by single 0.05 M Cyanex 272. The synergistic enhancement factors ( $R = 2.33$ ) can be obtained.

**Table 6.** Effect of Alamine 336 concentration on the equilibrium pH using mixture of Alamine 336 + 0.005 M P204/0.005 M P507/0.05 M Cyanex 272 when the initial pH of the solution was 2.0.

| [Alamine 336], mol/L | Equilibrium pH                     |                                    |   |
|----------------------|------------------------------------|------------------------------------|---|
|                      | [Alamine 336]<br>+<br>0.005 M P204 | [Alamine 336]<br>+<br>0.005 M P507 | [Alamine 336]<br>+<br>0.05 M Cyanex 272 |
| 0.0                  | 1.95                               | 2.00                               | 2.01                                    |
| 0.1                  | 2.24                               | 2.25                               | 2.21                                    |
| 0.3                  | 2.57                               | 2.56                               | 2.51                                    |
| 0.5                  | 2.92                               | 2.87                               | 2.76                                    |
| 0.7                  | 3.19                               | 3.18                               | 3.02                                    |
| 1.0                  | 3.53                               | 3.48                               | 3.23                                    |

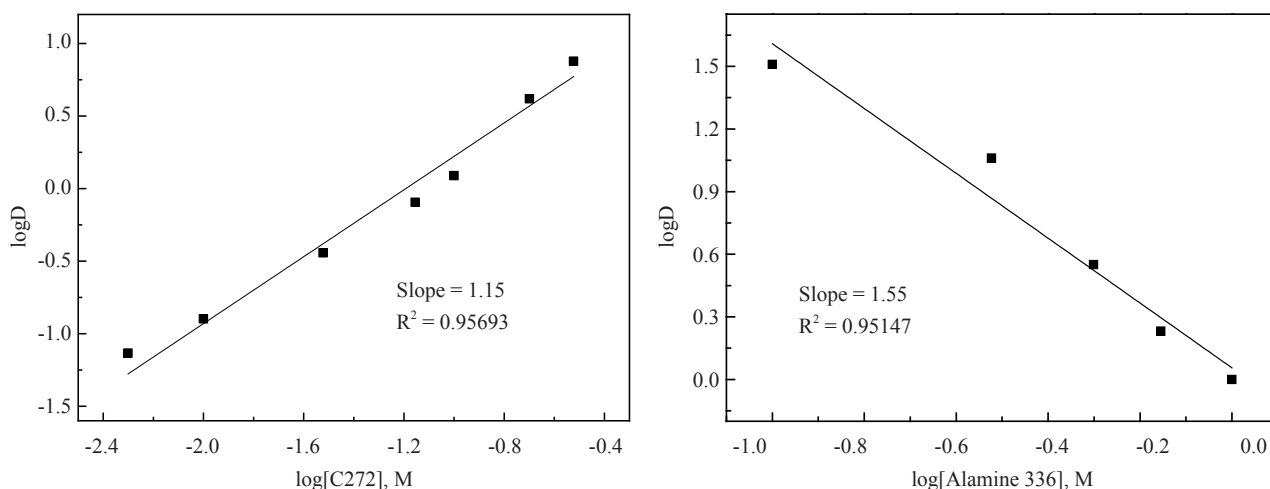
Table 6 shows the Eq pH, it is evident that the mixture of P204/P507/Cyanex 272 and Alamine 336 caused to higher Eq pH than single P204/P507/Cyanex 272. As the same as the mixture of P204/P507 and N503, the addition of Alamine 336 to P204/P507 can extract a large number of  $H^+$ , but Ga(III) the percent extraction was not improved. This may be attributed to the interactions between P204/P507 and Alamine 336 led to the effective concentration of P204/P507 is insufficient. In case of Cyanex 272 system, the combination of Alamine 336 to Cyanex 272 enhanced the extraction of Ga(III). Therefore, the increase of the Eq. pH implies that the interaction between Cyanex 272 and Alamine 336 is weaker and some of  $H^+$  dissociated from acid extractants are extracted into the organic phase by Alamine 336 during the solvent extraction. Hence, the mixture of Cyanex 272 and Alamine 336 showed the best synergism among the tested mixture.

### 3.4 Mechanism of extraction

The synergistic extraction stoichiometry of Ga(III) mixtures with Cyanex 272 and Alamine 336 was investigated by slope analysis. The results are shown in Figure 7, giving two straight lines with a slope of about 1.0 and 2.0 for  $\log[\text{Cyanex 272}]$  and  $\log[\text{Alamine 336}]$ , respectively. Suggesting that 1 mol Cyanex 272 and 2 mol Alamine 336 are involved during the transfer of 1 mol Ga(III) in the extraction reaction. Furthermore, Cyanex 272 is predicted to exist as a dipolymer in the organic phase<sup>32</sup>. From the above experimental results, references and charge balance theory, the synergistic solvent extraction of Ga(III) using mixtures of Cyanex 272 and Alamine 336 can be represented as in:

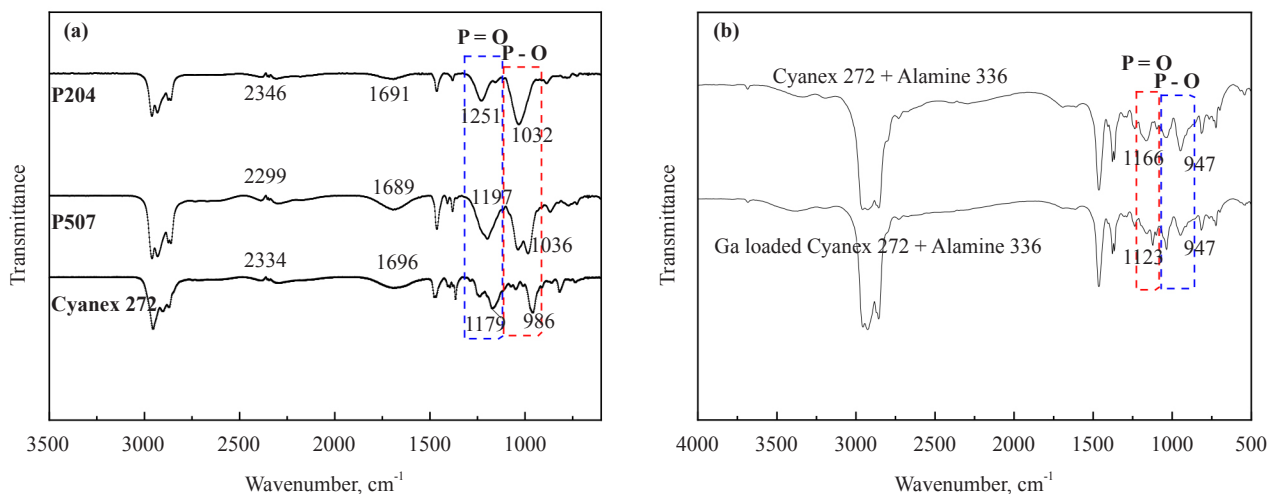


Where  $H_2A_2$  refers to Cyanex 272 and  $R_3N$  refers to Alamine 336.



**Figure 7.** Log-log plot of distribution ratio versus concentration of Cyanex 272/Alamine 336. Aq: 100 ppm Ga(III), initial pH = 2.03.

The change of characteristic bands in the FT-IR spectra of extractant was investigated to reflect the strength of the interaction in an extractant mixture. The structures of the prepared mixture of Cyanex 272 + Alamine 336 and the mixture system loaded with Ga(III) were further determined by FT-IR spectroscopy in Figure 8. For comparison, the respective FT-IR spectra of single P204, P507 and Cyanex 272 were also recorded. In Figure 8(a), the spectra curves for single P204, P507 and Cyanex 272 show typical of stretching vibration of P = O group at 1251, 1197, and 1179  $cm^{-1}$  respectively, and P - O characteristic bands at 1032, 1036 and 986  $cm^{-1}$  respectively.



**Figure 8.** FT-IR spectra of (a) single P204, P507 and Cyanex 272 and (b) mixtures of Cyanex 272 + Alamine 336 and Ga loaded Cyanex 272 + Alamine 336.

A comparison of spectra of single Cyanex 272 and mixture of Cyanex 272 and Alamine 336 reveals that shifts of P = O band from 1180 to the low-frequency range of 1166  $cm^{-1}$ , and P - O band of 986 to 947  $cm^{-1}$  took place. The change

of frequencies confirmed the interaction between Cyanex 272 and Alamine 336. As shown in Figure 8(b), the stretching vibration of P = O shifted from 1166 cm<sup>-1</sup> in initial organic solution to 1123 cm<sup>-1</sup> in Ga(III) loaded organic solution. The difference clearly indicates that Ga(III) were extracted by Cyanex 272 and the interaction between P = O in Cyanex 272 and Ga(III) was strong.

## 5. Conclusions

The current work is focusing on the synergistic extraction of Ga(III) from hydrochloric solutions in the initial pH 2.0. Acidic extractants (P204, P507, Cyanex 272) and its mixture with neutral extractants (TBP, N503) and amine extractant (Alamine 336) have been investigated. Firstly, the initial screening experiments was showed that the extraction capability for Ga(III) by the single acidic extractants follows P204 > P507 > Cyanex 272 and the H<sup>+</sup> releasing from acidic extractant to aqueous phase during the extraction of Ga(III). Compared with single acidic extractants system, significant synergism was observed with the mixture of Cyanex 272 and Alamine 336 on extraction of Ga(III) and the highest synergistic factor value reached 3.11 under the concentration of 0.3 M Cyanex 272 and 1.0 M Alamine 336. The equilibrium pH values increased with the addition of Alamine 336 in the mixture system. It indicated that the H<sup>+</sup> released from acidic extractants during the extraction process could be combined by Alamine 336 by protonation reaction. On the other hand, the molecular formed acidic extractants also could be bonded with Alamine 336 by hydrogen-bond interaction. As extractant with stronger acidity, P204 and P507 combined with Alamine 336 more stable compared with Cyanex 272. Thus led to the effective concentration of P204/P507 is insufficient, and therefore the extraction efficiency of Ga(III) by P204 and P507 decreased after Alamine 336 was added. Finally, a synergistic extraction reaction was proposed, and the extracted species was found to be Ga(OH)A<sub>2</sub> based on the slope analysis. The proposed synergistic extraction system of the extraction of Ga(III) would be a promising hydrometallurgical process to separate and enrich gallium.

## Acknowledgements

The authors would like to appreciate the financial support of the Foundation of State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering (2022-K24), Talent Fund for Province and Ministry Co-construction Collaborative Innovation Cent of Eco-Chemical Engineering Chemical Engineering (STHGYX2216 ) and the Shandong Provincial Natural Science Foundation (ZR2022MB111).

## Conflict of interest

The authors declare no competing financial interest.

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## Appendix

**Table S1.** Effect of P204 concentration on the equilibrium pH using mixture of P204 + 0.1 M TBP/N503 when the initial pH of the solution was 2.0.

| [P204], mol/L | Equilibrium pH |                    |                     |
|---------------|----------------|--------------------|---------------------|
|               | Single P204    | [P204] + 0.1 M TBP | [P204] + 0.1 M N503 |
| 0.005         | 1.95           | 1.96               | 2.02                |
| 0.01          | 1.93           | 1.94               | 1.98                |
| 0.03          | 1.91           | 1.92               | 1.94                |
| 0.07          | 1.91           | 1.91               | 1.93                |
| 0.10          | 1.91           | 1.91               | 1.91                |
| 0.20          | 1.91           | 1.91               | 1.91                |
| 0.30          | 1.91           | 1.91               | 1.90                |

**Table S2.** Effect of P507 concentration on the equilibrium pH using mixture of P507 + 0.1 M TBP/N503 when the initial pH of the solution was 2.0.

| [P507], mol/L | Equilibrium pH |                    |                     |
|---------------|----------------|--------------------|---------------------|
|               | Single P507    | [P507] + 0.1 M TBP | [P507] + 0.1 M N503 |
| 0.005         | 2.00           | -                  | -                   |
| 0.01          | 2.00           | 2.01               | 2.02                |
| 0.03          | 1.96           | 1.97               | 1.97                |
| 0.07          | 1.94           | 1.95               | 1.97                |
| 0.10          | 1.93           | 1.94               | 1.95                |
| 0.20          | 1.93           | 1.94               | 1.95                |
| 0.30          | 1.93           | 1.94               | 1.94                |

**Table S3.** Effect of Cyanex 272 concentration on the equilibrium pH using mixture of Cyanex 272 + 0.1 M TBP/N503 when the initial pH of the solution was 2.0.

| [Cyanex 272], mol/L | Equilibrium pH    |                          |                           |
|---------------------|-------------------|--------------------------|---------------------------|
|                     | Single Cyanex 272 | [Cyanex 272] + 0.1 M TBP | [Cyanex 272] + 0.1 M N503 |
| 0.005               | 2.03              | -                        | -                         |
| 0.01                | 2.03              | -                        | -                         |
| 0.03                | 2.01              | 2.03                     | 2.05                      |
| 0.07                | 1.99              | 2.00                     | 2.03                      |
| 0.10                | 1.97              | 1.98                     | 2.03                      |
| 0.20                | 1.97              | 1.98                     | 2.00                      |
| 0.30                | 1.95              | 1.96                     | 1.98                      |

**Table S4.** Effect of TBP/N503 concentration on the equilibrium pH using mixture of TBP/N503 + 0.05 M Cyanex 272 when the initial pH of the solution was 2.0.

| [Neutral Extractant], mol/L | Equilibrium pH |                           |             |                            |
|-----------------------------|----------------|---------------------------|-------------|----------------------------|
|                             | Single TBP     | [TBP] + 0.05 M Cyanex 272 | Single N503 | [N503] + 0.05 M Cyanex 272 |
| 0                           | -              | 1.96                      | -           | 1.96                       |
| 0.1                         | 2.03           | 1.99                      | 2.08        | 2.03                       |
| 0.3                         | 2.03           | 2.00                      | 2.19        | 2.10                       |
| 0.5                         | 2.03           | 2.01                      | 2.32        | 2.19                       |
| 0.7                         | 2.03           | 2.01                      | 2.52        | 2.30                       |
| 1.0                         | 2.03           | 2.01                      | 3.02        | 2.37                       |