



## Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE)

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### ABSTRACT

The inner synergistic extraction of [tricaprylmethylammonium][sec-octylphenoxy acetate] ([A336][CA-12]) is studied for cobalt and nickel separation. Distribution ratios of [A336][CA-12] for  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  are by far higher than those of tricaprylmethylammonium sulfate ([A336] $_2\text{SO}_4$ ), sec-octylphenoxy acetic acid (CA-12), mixture of [A336] $_2\text{SO}_4$  and CA-12 at the acidities from  $1 \times 10^{-5} \text{ mol L}^{-1}$  to  $1 \times 10^{-3} \text{ mol L}^{-1}$ . The synergy coefficients of [A336][CA-12] for  $\text{Co}^{2+}$  are higher than the synergy coefficients of [A336][CA-12] for  $\text{Ni}^{2+}$ , which can be used for the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  separation. Some thermodynamic properties of the inner synergistic extraction using [A336][CA-12] for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are also studied, such as influence of temperature, thermodynamic functions, extraction mechanism, separation factors and stripping properties.

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### 1. Introduction

Cobalt and nickel are concomitant metal elements. It is difficult to obtain pure cobalt and nickel compounds because their similar physicochemical properties. With the ever-increasing need of cobalt and nickel in alloy, battery and catalyst [1–3], much effort has been devoted for developing their separation technology, such as liquid membrane [4], microemulsion extraction [5], hollow fiber membrane [6], electro dialysis [7] and reversed micelle [8]. It worth well noted that cobalt and nickel are hazardous metals, lots of industrial activities concerning the contaminants pose a threat to ecosystems [9]. As a result, their enrichments seem to be necessarily for ecosystem monitoring and pollution control. Up till now, many achievements for cobalt or nickel enrichment have been made in the field of solid-phase extraction [10], cloud point extraction [11], salting out liquid–liquid extraction [12], nanoparticle preconcentration [13], adsorption [14,15]. Solvent extraction is one of the most popular methods for cobalt and nickel separation and enrichment [16,17]. In the numerous methods mentioned above, separation and enrichment abilities are important factors for evaluating potential application value of a method. As an effective method for increase extraction efficiency and selectivity, synergistic extraction has been studied for many years because the theoretical and applicative importance [18,19]. Using synergistic effect of two extractants, distribution ratios of their mixture can be obviously enhanced than those of their individual contributions. As

for synergistic extraction of  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$ , many contributions have been reported on those topics [20,21].

Ionic liquids (ILs) are a class of organic salts that are liquids at room temperature. Discrete cations and anions of ILs can be individually customized. The tunable synthesis contributes to preparing a wide range of ILs with different properties. Numerous applications of ILs have been published on electrochemistry, biological uses, analytics, separation, catalysis, physical chemistry and engineering [22–24]. Since the different properties of ILs compared to volatile organic compounds (VOCs), the former are found to have unique behavior in solvent extraction. Some IL-based extraction systems reveal higher extraction efficiencies than VOC-based extraction systems, which have brought IL-based extraction considerable attention since 2000s [25–27]. Recently, task-specific ionic liquid (TSIL) has become a developmental trend of IL. The TSILs contain functional groups in their cation and/or anion and they can be “tailor-made” prepared for specific processes. TSILs are not only used just as solvents but also used as liquid functional materials. In our recent papers, the application of Bif-ILEs for metal ions separation using extraction [28] and adsorption [29] have been studied. In this paper, we prepare [A336][CA-12] whose cation and anion originate from quaternary ammonium salt and organocarboxylic acid. The cation and anion of [A336][CA-12] reveal obvious inner synergistic effect for  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  extraction. The inner synergistic effect is something like traditional synergistic effect produced by two extractants. It is named ‘inner synergistic effect’ because the effect comes from cation and anion of bifunctional IL. To our knowledge, the inner synergistic extraction of  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  using Bif-ILE has not been mentioned in any other paper. Trioctylmethylammonium chloride (A336) [30] and sec-octylphenoxy acetic acid

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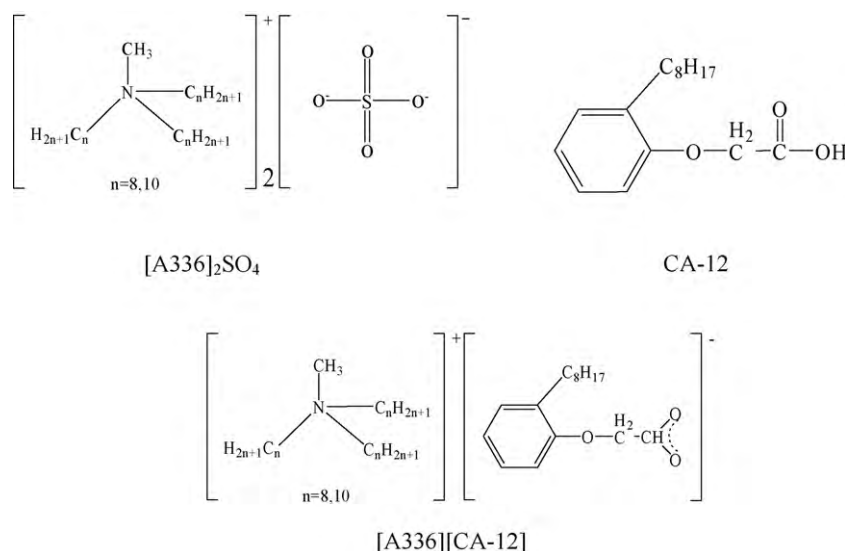


Fig. 1. Structures of [A336]<sub>2</sub>SO<sub>4</sub>, CA-12 and [A336][CA-12].

(CA-12) [19] are widely used in solvent extraction and the inner synergistic effect of [A336][CA-12] may be provided with promising application potentiality for Co<sup>2+</sup>, Ni<sup>2+</sup> enrichment and separation.

## 2. Experimental

### 2.1. Materials

A336 was purchased from Aldrich. CA-12 was kindly supplied by Tianjin Xiandai Chemical Plant (China). Cobalt sulfate, nickel sulfate, sulphuric acid and sodium sulfate were purchased from Beijing BEIHUA Fine Chemicals Co.. Stock solutions of Co<sup>2+</sup> and Ni<sup>2+</sup> were prepared by dissolving their sulfates (99.9%) in DI water. Isopropanol was purchased from Sinopharm Chemical Reagent Co. Ltd., which was distilled before its use. [A336]<sub>2</sub>SO<sub>4</sub> and [A336][CA-12] were prepared using acid/base neutralization method as described in our recent paper [31]. The structures of [A336]<sub>2</sub>SO<sub>4</sub>, CA-12 and [A336][CA-12] are given in Fig. 1. The other chemicals are analytical grade reagents.

### 2.2. The preparation of [A336]<sub>2</sub>SO<sub>4</sub> and [A336][CA-12]

#### 2.2.1. Tricaprylmethylammonium hydroxide ([A336][OH])

Sodium alkoxide was prepared by combining 6.39 g (0.278 mol) sodium and 125 mL isopropanol for 3 h. 112.36 g (0.278 mol) A336 was dissolved in 500 mL isopropanol, and then added dropwise into the isopropanol solution containing sodium alkoxide. The solution was stirred for 4 h at 50 °C. The mixture was centrifuged at 8000 rpm for 10 min to remove the white precipitate of sodium chloride. Then the filtrate was shaken with equal volume of DI water for half an hour to get [A336][OH] by the hydrolysis of [A336][OR]. The yield of [A336][OH] prepared was 88.42%.

#### 2.2.2. [A336]<sub>2</sub>SO<sub>4</sub>

[A336]<sub>2</sub>SO<sub>4</sub> was prepared by the addition of 200 mL [A336][OH] (0.12 mol L<sup>-1</sup>) and 1.09 mL H<sub>2</sub>SO<sub>4</sub> (10 mol L<sup>-1</sup>) (mole ratio is 2.2:1). The mixture was vigorously agitated for 12 h at 50 °C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotary evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336]<sub>2</sub>SO<sub>4</sub> was indicated to be 78.82%.

<sup>1</sup>H NMR: 0.844–0.866 (t), 1.245–1.276 (m), 1.763–1.81 (m), 3.851 (s), 1.139–4.163 (m), 7.674 (s), 7.74 (s), 9.094 (s). <sup>13</sup>C NMR:

61.15, 48.94, 32.23, 32.14, 30.08, 29.94, 29.79, 26.87, 23.05, 22.83, 14.37.

#### 2.2.3. [A336][CA-12]

[A336][CA-12] was prepared by the addition of 290 mL [A336][OH] (0.12 mol L<sup>-1</sup>) and 11.02 g of CA-12 (mole ratio is 1.1:1). The mixture was vigorously agitated for 12 h at 50 °C under reflux and left to settle. After a while, an aqueous layer formed at the bottom. The upper phase was poured into a vacuum rotary evaporator (353 K, 20 mbar, 60 min) to remove residual water and isopropanol. The final yield of [A336][CA-12] was indicated to be 71.57%.

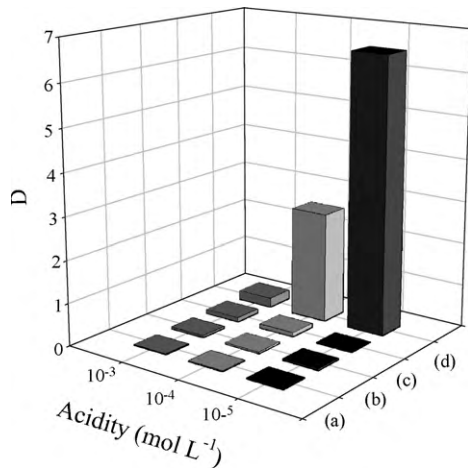
<sup>1</sup>H NMR: 0.664–0.710 (m), 0.719–0.7640 (m), 1.057–1.175 (m), 1.185–1.251 (m), 1.341–1.465 (m), 1.633–1.712 (m), 3.400 (s), 3.602–3.611 (m), 4.793–4.847 (m), 6.868–6.986 (m), 7.031–7.054 (m), 7.088 (s), 7.150–7.163 (m). <sup>13</sup>C NMR: 173.04, 128.70, 137.99, 126.73, 120.05, 115.45, 115.41, 70.36, 61.58, 48.38, 32.19, 32.04, 29.86, 29.84, 29.66, 29.61, 29.53, 29.46, 26.84, 23.04, 22.97, 22.72, 14.41, 14.38, 14.34.

### 2.3. Methods

To confirm the structure and purity of [A336]<sub>2</sub>SO<sub>4</sub> and [A336][CA-12], <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> with an AV 600 NMR spectrometer (Bruker, Switzerland). A model pHs-3C pH meter (Leici, China), calibrated daily with 4.01 and 6.86 standard buffer solutions, was used for measuring pH values of the aqueous phase. The concentrations of metal ions in aqueous phase were determined using an iCAP 6000 inductively coupled plasma spectroscopy (Thermo, USA), and the concentration of metal ions in organic phase were calculated by mass balance.

### 2.4. Extraction and stripping experiments

In the extraction experiments, 4 mL of aqueous phase and 4 mL of toluene containing extractant were mixed and shaken in equilibrium tubes using a mechanical shaker for 60 min at 298 K, which was sufficient for equilibrium. Sodium sulfate was used to keep constant ionic strength during extraction. The mixtures were then centrifuged for 3 min to enhance phase separation. For stripping of metal ion, 4 mL of loaded phase with metal ion was taken and contacted with 4 mL of H<sub>2</sub>SO<sub>4</sub> solution, followed by vigorous shaking to reach equilibrium. The extraction efficiency *E*, distribution ratio *D*,



**Fig. 2.** The  $\text{Co}^{2+}$  distribution ratios of  $[\text{A336}]_2\text{SO}_4$ , CA-12 and  $[\text{A336}][\text{CA-12}]$ . (a)  $[\text{A336}]_2\text{SO}_4$ ; (b) CA-12; (c) mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12; (d)  $[\text{A336}][\text{CA-12}]$ .  $1/2 [[\text{A336}]_2\text{SO}_4] = [\text{CA-12}] = [[\text{A336}][\text{CA-12}]] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ .

synergy coefficient  $R$ , separation factor  $SF$  and stripping efficiency  $S$  are defined as follows:

$$E\% = \frac{[M]_t - [M]_a}{[M]_a} \times 100 \quad (1)$$

$$D = \frac{[M]_t - [M]_a}{[M]_a} \quad (2)$$

$$R = \frac{D_{ab}(D_{a+b})}{D_a + D_b} \quad (3)$$

$$SF = \frac{D_1}{D_2} \quad (4)$$

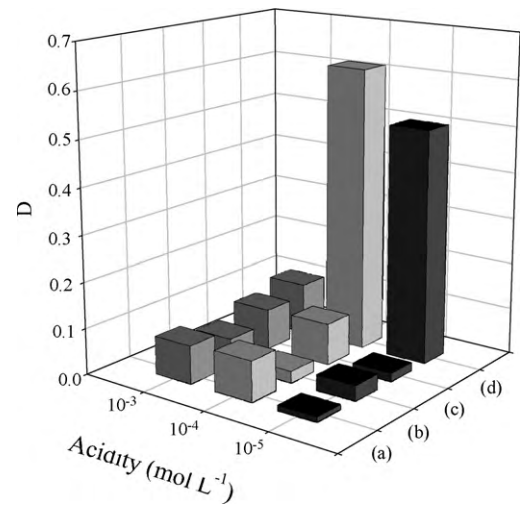
$$S\% = \frac{[M]_{\text{aq},a}}{[M]_{\text{org},t}} \times 100 \quad (5)$$

where  $[M]_t$  and  $[M]_a$  represent the initial and final concentration of metal ion in aqueous phase;  $D_a$  is the distribution ratio of CA-12,  $D_b$  is the distribution ratio of  $[\text{A336}]_2\text{SO}_4$ ,  $D_{ab}$  is the distribution ratio of  $[\text{A336}][\text{CA-12}]$ ,  $D_{a+b}$  is the distribution ratio of mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12, all of them for the same metal;  $D_1$  and  $D_2$  are the distribution ratio of metal 1 and 2;  $[M]_{\text{aq},a}$  is equilibrium concentration of metal ion in stripping acid and  $[M]_{\text{org},t}$  is initial concentration of metal ion in organic phase, respectively.

### 3. Results and discussion

#### 3.1. Inner synergistic effect of $[\text{A336}][\text{CA-12}]$ for $\text{Co}^{2+}$ and $\text{Ni}^{2+}$

The distribution ratios of  $[\text{A336}][\text{CA-12}]$  are compared with those of  $[\text{A336}]_2\text{SO}_4$  and CA-12. As can be seen in Fig. 2, distribution ratios of  $[\text{A336}][\text{CA-12}]$  for Co(II) are by far higher than those of  $[\text{A336}]_2\text{SO}_4$ , CA-12, mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12 at the acidities from  $1 \times 10^{-5} \text{ mol L}^{-1}$  to  $1 \times 10^{-3} \text{ mol L}^{-1}$ . The distribution ratio increase indicates there is a clear inner synergistic effect between cation and anion of  $[\text{A336}][\text{CA-12}]$ . The inner synergistic effect is emphasized at the lower acidity. At the acidity of  $1 \times 10^{-5} \text{ mol L}^{-1}$ , the distribution ratio of  $[\text{A336}][\text{CA-12}]$  for  $\text{Co}^{2+}$  is 6.529, the distribution ratios of  $[\text{A336}]_2\text{SO}_4$ , CA-12, mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12 for  $\text{Co}^{2+}$  is 0.023, 0.037, 0.017, respectively. The comparison reveals that the mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12 do not have the extraction abilities of  $[\text{A336}]_2\text{SO}_4$  and CA-12 for  $\text{Co}^{2+}$ . However, extraction abilities from tricaprylmethylammonium ion ( $[\text{A336}]^+$ ) and sec-octylphenoxy acetic acid group

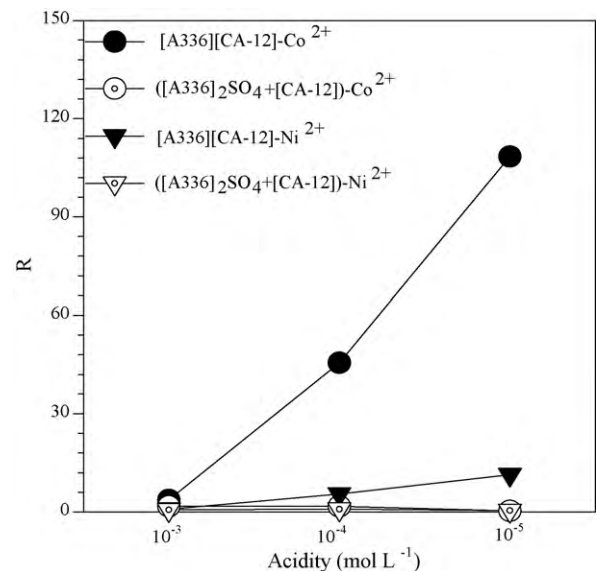


**Fig. 3.** The  $\text{Ni}^{2+}$  distribution ratios of  $[\text{A336}]_2\text{SO}_4$ , CA-12 and  $[\text{A336}][\text{CA-12}]$ . (a)  $[\text{A336}]_2\text{SO}_4$ ; (b) CA-12; (c) mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12; (d)  $[\text{A336}][\text{CA-12}]$ .  $1/2 [[\text{A336}]_2\text{SO}_4] = [\text{CA-12}] = [[\text{A336}][\text{CA-12}]] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Ni}^{2+}] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ .

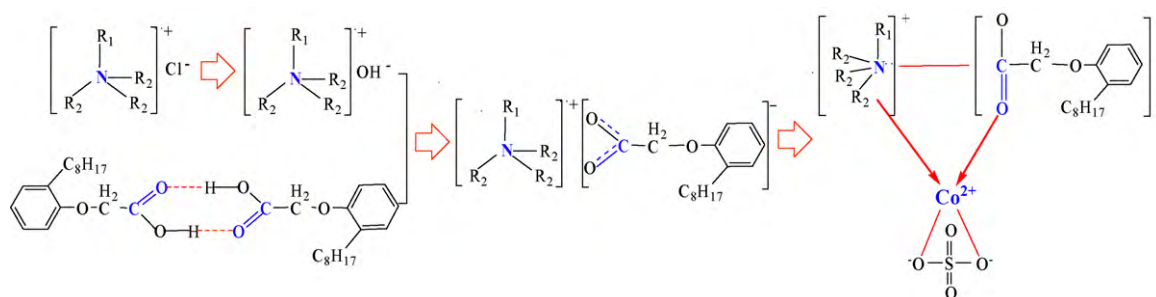
( $[\text{CA-12}]^-$ ) for  $\text{Co}^{2+}$  can be markedly enhanced when they are combined into  $[\text{A336}][\text{CA-12}]$ .

The inner synergistic effect of  $[\text{A336}][\text{CA-12}]$  is not only obviously for  $\text{Co}^{2+}$  but also for  $\text{Ni}^{2+}$ . As revealed in Fig. 3, the distribution ratios of  $[\text{A336}]_2\text{SO}_4$ , CA-12, mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12,  $[\text{A336}][\text{CA-12}]$  for  $\text{Ni}^{2+}$  are 0.011, 0.034, 0.018, 0.506, respectively. The comparison is similar with that for  $\text{Co}^{2+}$ . The mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12 does not result in a synergistic effect, and the  $[\text{A336}][\text{CA-12}]$  has obviously inner synergistic effect. Since inner synergistic effects of Bif-ILE for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  contribute to enhancing extraction abilities of  $[\text{A336}]^+$  and  $[\text{CA-12}]^-$ , the interesting effect is further investigated for enrichment and separation of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  in this study.

To quantify the inner synergistic effect, synergy coefficient is used to measure the effect. As can be seen in Fig. 4, the inner synergistic effects of  $[\text{A336}][\text{CA-12}]$  for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  increase gradually from the acidities of  $1 \times 10^{-3} \text{ mol L}^{-1}$  to  $1 \times 10^{-5} \text{ mol L}^{-1}$ . More-



**Fig. 4.** The synergy coefficients of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  using  $[\text{A336}][\text{CA-12}]$  at different acidities,  $1/2 [[\text{A336}]_2\text{SO}_4] = [\text{CA-12}] = [[\text{A336}][\text{CA-12}]] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Ni}^{2+}] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ , pH 5.25.



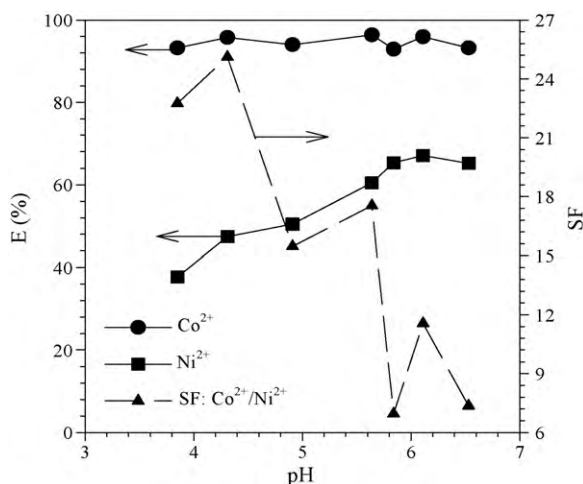
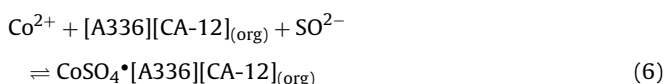
**Scheme 1.** The proposed structure of [A336][CA-12] and its coordination environment with  $\text{Co}^{2+}$ .

over, the synergy coefficients of  $\text{Co}^{2+}$  are by far higher than those of  $\text{Ni}^{2+}$ , for example, the synergy coefficients of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are 108.41 and 11.34 at the acidity of  $1 \times 10^{-5} \text{ mol L}^{-1}$ . The different synergy coefficients offer a possibility for the separation of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ .

As can be seen in Fig. 5, the aqueous acidity has less influence on the  $\text{Co}^{2+}$  extraction from pH values 3.8 to 6.6. However, the extraction efficiencies of  $\text{Ni}^{2+}$  using [A336][CA-12] increase as the acidities are reduced. As a result, the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  can be effectively separated using adjusting aqueous acidity. The pH value of 4.3 is an optimal condition for achieving the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  separation, where the separation factor can be arrived at 25.

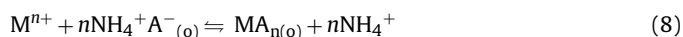
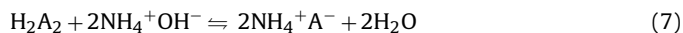
### 3.2. Extraction mechanism

To elucidate mechanism of the inner synergistic extraction, extraction equation of [A336][CA-12] for  $\text{Co}^{2+}$  is exactly determined using slope analysis. The linear relationship between  $\log D_{\text{Co}}$  and  $\log[\text{A336}][\text{CA-12}]$  is obtained with a slope of 1.05 as illustrated in Fig. 6, which reveals the stoichiometry of [A336][CA-12] with  $\text{Co}^{2+}$  is 1:1. According to the principle of charge balance, sulfate radical is believed to be concerned in the extraction to keep charge balance. The extraction mechanism is an ion association mechanism, the extraction equation of  $\text{Co}^{2+}$  using [A336][CA-12] can be represented by Eq.(6).

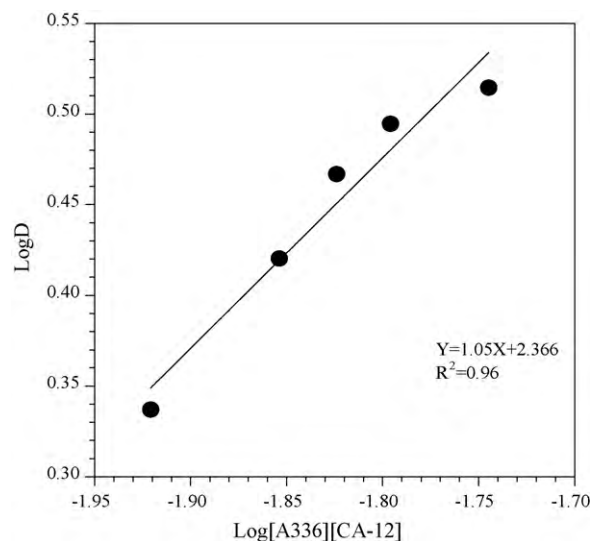


**Fig. 5.** The extraction efficiency and separation factor of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  using mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12 vs. [A336][CA-12] at different acidities,  $1/2 [\text{A336}]_2\text{SO}_4 = [\text{CA-12}] = [\text{A336}][\text{CA-12}] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Ni}^{2+}] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ .

The CA-12 molecules form dimers ( $\text{H}_2\text{A}_2$ ) through intermolecular hydrogen bonding [19]. For increasing extraction ability, CA-12 is always saponified using ammonium hydroxide to break the hydrogen bonds before extraction [32]. By acid–base reaction with ammonium hydroxide Eq. (7), CA-12 can be converted into ammonium salt. As revealed in Eq. (8), the ammonium ion from saponified acidic extractant ( $\text{NH}_4\text{A}$ ) is released into aqueous phase during extraction because the cation exchange between metal ion ( $\text{M}^{n+}$ ) and ammonium ion ( $\text{NH}_4^+$ ) [33,34]. The resulting ammonia-nitrogen wastewater is a serious pollution to environment.



In this study, we develop a novel method to break the dimers in CA-12 using acid–base neutralization between [A336][OH] and CA-12. The prepared [A336][CA-12] is a bifunctional IL. There are electrostatic interaction, van der Waals force, induction interaction between cation and anion of IL [35,36], moreover, [A336]<sup>+</sup> and [CA-12]<sup>-</sup> can complex with  $\text{Co}^{2+}$  by nitrogen donor and carbonyl. The ion–pair interactions mentioned above contribute to the extracting complex stability. As described in Scheme 1, the higher extraction ability of [A336][CA-12] than  $[\text{A336}]_2\text{SO}_4$  and CA-12 can be attributed to two reasons. Firstly, the hydrogen bonds in CA-12 can be broken when [A336][CA-12] is prepared, which contribute to improve the extraction ability of CA-12. Secondly, the stability of extracting complex formed by the reaction of the metal ion and [A336][CA-12] is higher than the reaction formed by the same metal ion and the mixture of  $[\text{A336}]_2\text{SO}_4$  and CA-12. The higher stability

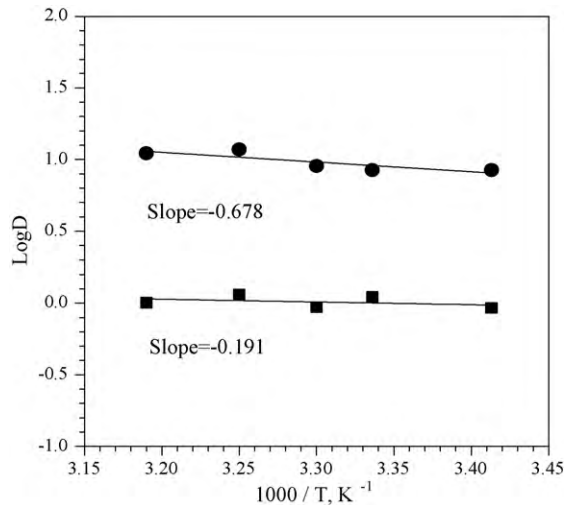


**Fig. 6.** Slope analysis of  $\text{Co}^{2+}$  extraction as a function of [A336][CA-12] concentration,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ .



**Table 1**  
Thermodynamic parameters of Co<sup>2+</sup> and Ni<sup>2+</sup> extraction using [A336][CA-12].

Temp. (K)	Co <sup>2+</sup>			Ni <sup>2+</sup>		
	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/Kmol)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/Kmol)
293	-35.74	-	166.28	-30.35	-	116.06
298	-36.34	-	165.5	-31.33	-	117.41
303	-37.13	12.98	165.38	-31.39	3.657	115.67
308	-38.39	-	166.79	-32.38	-	117
313	-38.89	-	165.71	-32.66	-	116.03

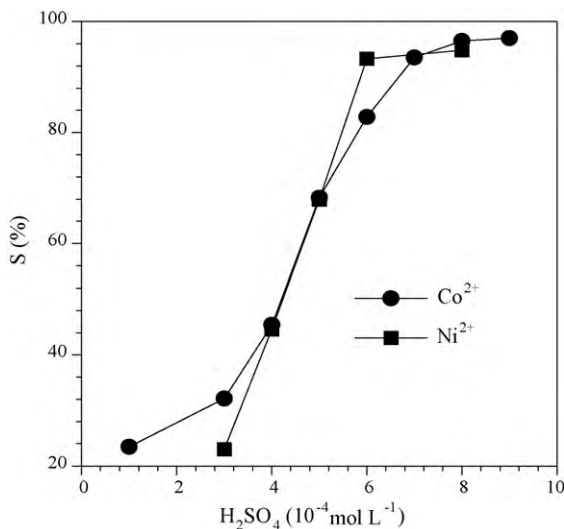


**Fig. 7.** Relationship between  $D_{\text{Co}}$  (●)/ $D_{\text{Ni}}$  (■) and temperature,  $[[\text{A336}][\text{CA-12}]] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Ni}^{2+}] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{Na}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$ , pH 5.25.

of extracting complex can result in higher extraction efficiency. The application of [A336][CA-12] is an alternative to saponified CA-12 which can increase the extraction abilities of [A336]<sup>+</sup> and [CA-12]<sup>-</sup>, and avoid the wastewater from saponification of CA-12.

### 3.3. Influence of temperature

Fig. 7 reveals the effect of temperature change (20–45 °C) on the extraction equilibrium of Co<sup>2+</sup> and Ni<sup>2+</sup>. As shown in Fig. 7, the slopes of  $\log D_{\text{Co}}$  and  $\log D_{\text{Ni}}$  versus  $1000/T$  plots are -0.678 and



**Fig. 8.** The stripping of Co<sup>2+</sup> and Ni<sup>2+</sup> using H<sub>2</sub>SO<sub>4</sub>,  $[[\text{A336}][\text{CA-12}]] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ,  $[\text{Co}^{2+}] = 1.8 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Ni}^{2+}] = 3.7 \times 10^{-3} \text{ mol L}^{-1}$ .

-0.191, respectively. The enthalpy change ( $\Delta H$ ) of extraction can be obtained from the slope of  $\log D$  vs.  $1/T$  using the following Van't Hoff Equation:

$$\log D = -\frac{\Delta H}{2.303R} \frac{1}{T} + C \quad (9)$$

where  $R$  is the gas constant and  $C$  is a constant. Gibbs free energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ ) of the extraction can be calculated as:

$$\Delta G = -RT \ln K_{\text{ex}}(T) = -2.303 RT \log K_{\text{ex}}(T) \quad (10)$$

$$K_{\text{ex}}(T) = \frac{[\text{CoSO}_4 \cdot [\text{A336}][\text{CA-12}]_{\text{org}}]}{[\text{Co}^{2+}]_{\text{aq}} [[\text{A336}][\text{CA-12}]_{\text{org}}] [\text{SO}_4^{2-}]_{\text{aq}}}$$

$$= \frac{D}{[[\text{A336}][\text{CA-12}]_{\text{org}}] [\text{SO}_4^{2-}]_{\text{aq}}} \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (12)$$

Table 1 lists the change of thermodynamic parameters. It is clear that the extraction of Co<sup>2+</sup> and Ni<sup>2+</sup> using [A336][CA-12] are endothermic processes.

### 3.4. Stripping property

Although [A336][CA-12] reveals higher extraction abilities for Co<sup>2+</sup> and Ni<sup>2+</sup>, stripping characteristics are important factors for evaluating its potential application. Stripping of Co<sup>2+</sup> and Ni<sup>2+</sup> are carried out using H<sub>2</sub>SO<sub>4</sub> solution at 25 °C. To strip the loaded Co<sup>2+</sup> or Ni<sup>2+</sup>, a series of experiments are carried out varying H<sub>2</sub>SO<sub>4</sub> solution concentration from  $1 \times 10^{-4} \text{ mol L}^{-1}$  to  $1 \times 10^{-3} \text{ mol L}^{-1}$ . As shown in Fig. 8, the extracted Co<sup>2+</sup> and Ni<sup>2+</sup> using [A336][CA-12] can be fully stripped by adjusting acidity.

## 4. Conclusions

Herein we report the inner synergistic effect of [A336][CA-12] for cobalt and nickel extraction. The effect contributes to obtain enriched solutions of Co<sup>2+</sup> or Ni<sup>2+</sup> because the stronger extraction ability of [A336][CA-12] compared to [A336]<sub>2</sub>SO<sub>4</sub> and CA-12. Moreover, the different synergy coefficients of Co<sup>2+</sup> and Ni<sup>2+</sup> are favorable for their separation. The extraction mechanism of [A336][CA-12] for Co<sup>2+</sup> is indicated to be an ion association mechanism. The extraction of Co<sup>2+</sup> and Ni<sup>2+</sup> using [A336][CA-12] are endothermic processes. The Co<sup>2+</sup> or Ni<sup>2+</sup> extracted can be quantitatively stripped by adjusting H<sub>2</sub>SO<sub>4</sub> solution acidity. The application of [A336][CA-12] is an alternative to the saponification of CA-12 using ammonium hydroxide. The alternative cannot only increase the extraction ability of [A336]<sup>+</sup> and [CA-12]<sup>-</sup>, but also effectively avoid the ammonia-nitrogen wastewater from saponified CA-12. The inner synergistic extraction using [A336][CA-12] is an environment-friendly and high-efficient enrichment/separation protocol for Co<sup>2+</sup> and Ni<sup>2+</sup>. To increase selectivity of Co<sup>2+</sup> and Ni<sup>2+</sup>,

some other separation technologies based on the inner synergistic effect of Bif-ILE, i.e., adsorption and membrane separation, are underway in this lab.

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