

Study on Mg²⁺ removal from ammonium dihydrogen phosphate solution by solvent extraction with di-2-ethylhexyl phosphoric acid

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Abstract—The extraction of Mg²⁺ from ammonium dihydrogen phosphate (MAP) solution by extractant (D2EHPA) and its mixture, including acidic extractant (HEHPEHE), alkaline extractant (TOA) and neutral extractant (TBP) respectively, is investigated. The good extraction selectivity of Mg²⁺ with D2EHPA from ammonium dihydrogen phosphate solution is verified, which is found to be associated with the cation exchange and chelation capability of D2EHPA on the basis of its molecular structure. The related thermodynamic data are also obtained in terms of experimental results as follows: the extraction enthalpy is 2.659×10^{-2} (J·mol⁻¹·K⁻¹), the free energy is 1.501×10^3 (J·mol⁻¹) and the entropy is 4.441 (J·mol⁻¹). Meanwhile, the major influencing factors, such as the initial pH, the initial concentration of extractant, phase ratio and the extraction temperature on the extraction ratios of Mg²⁺, are studied, and the optimal process conditions are obtained. As shown in the extraction experiments for practical MAP solution, superior grade MAP can be obtained by three levels of extraction under optimal condition.

Key words: Extraction Process, Di(2-ethylhexyl)phosphoric Acid, MAP

INTRODUCTION

Ammonium dihydrogen phosphate (MAP) is widely used for flame retardant and drip-irrigation fertilization, but highly pure MAP is mainly manufactured using thermal-process phosphoric acid in the past. The cost of thermal-process phosphoric acid is very high. Since many of the yellow-phosphorus manufacturing factories are closed owing to high energy consumption and environment concerns, the price of yellow phosphorus, as a basic raw material of thermal-process phosphoric acid, becomes higher and higher. Thereby, more attention has been paid to the low cost of wet-process phosphoric acid (WPA) by researchers in recent years. However, some undesirable impurities such as Fe³⁺, Al³⁺, Mg²⁺, once in WPA will lower the quality of MAP products. To circumvent the problems, the WPA should be purified to obtain the superior grade MAP. It is well-known that most of the metal ions can be removed by adjusting the pH of the solution (usually 4). But there are still some Mg²⁺ left in the solution; the remnant Mg²⁺ can cause formation of troublesome water-insoluble substances in the following concentration and crystallization process. The main ingredients of water-insoluble substance are recognized as magnesium-containing phosphate. It is therefore of great importance to remove the Mg²⁺ before concentrating the neutralized MAP solution.

The current work studied the extraction capability of the cationic extractant, di-2-ethylhexyl phosphoric acid (D2EHPA) for the separation of Mg²⁺ and other impurities from MAP solution. D2EHPA, as an effective extractant has been widely used for the extraction of zinc, beryllium, copper, vanadium, indium, gallium, cadmium, and rare earth elements [1-7]. The main influencing factors, such as the initial pH, the initial concentration of extractant,

phase ratio and the extraction temperature are investigated to obtain the optimal process conditions for the extraction process. Lastly, the extraction experience is also carried out for the practical MAP solution under the optional process conditions to evaluate the effectiveness of D2EHPA extractant.

EXPERIMENTAL

1. Materials and Equipment

The solvent used in this work is kerosene. D2EHPA and HEHPEHE (AR grade) employed as an extractant were purchased from Luo yang Zhongda Chemical Company (China). TOA and TBP (AR grade) were purchased from Ke Long Chemical Company (China). Pure water was produced by an Aquapro water machine (ABZ1-1001-P) in our laboratory.

2. Parameters Influencing the Extraction Process

To study the removal efficiency of Mg²⁺ and the advantages of the extraction process, it is necessary to investigate various parameters that could affect the process to obtain the optimal conditions. These parameters include the D2EHPA volume content, the reaction temperature, the phase volume ratio, the stirring speed, the stirring time, and the initial pH of MAP solution, and soon.

3. Determination of Mg²⁺ Ion

The concentration of Mg²⁺ is determined by atomic absorption spectrophotometry (GF3000).

RESULTS AND DISCUSSION

Extraction efficiency (E) is defined as follows:

$$E = \frac{M_{(i)}^{Mg^{2+}} - M_{(e)}^{Mg^{2+}}}{M_{(i)}^{Mg^{2+}}} \times 100\% \quad (1)$$

E represents the efficiency of the extraction process;

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Table 1. Influences of extractants

Extractants	Extraction ratio (%)
D2EHPA	61.3
Mixture of D2EHPA and TOA	54.8
Mixture of D2EHPA and TBP	48.5
Mixture of D2EHPA and HEHPEHE	58.3

Solvent: kerosene; R(O/A)=1 : 2; Stirring speed: 450 r/min; Initial Mg^{2+} concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Stirring time: 10 min; Reaction temperature: 70 °C

$M_{(i)}^{Mg^{2+}}$: Mole of Mg^{2+} in initial solution, mol;

$M_{(r)}^{Mg^{2+}}$: Mole of Mg^{2+} in the raffinate, mol.

1. Influences of Extractants

The extraction of Mg^{2+} from MAP solution using various extractants such as D2EHPA and TOA, D2EHPA and TBP, D2EHPA and HEHPEHE, respectively, was carried out. The molar ratio of D2EHPA and other extractant were maintained at 1 : 1. As shown in Table 1, the extraction selectivity of Mg^{2+} with D2EHPA from MAP solution is higher than that of D2EHPA mixtures, indicating that the D2EHPA itself possesses good extraction capability. Therefore, only the D2EHPA was employed as an extractant.

2. Effect of D2EHPA Volume Fraction (%)

Generally, the amount of extractant will increase with the increase in D2EHPA volume concentration in solvent phase, thus resulting in the numbers of free extractant taking participate in the extraction reaction. However, when the D2EHPA concentration increases to a certain value, the extraction efficiency (E) remains almost unchanged, indicating that the extraction reaction will reach equilibrium. The experimental results shown in Fig. 1 are in good agreement with the findings.

3. Effect of Phase Ratio

The ratio of aqueous phase and organic phase has a significant

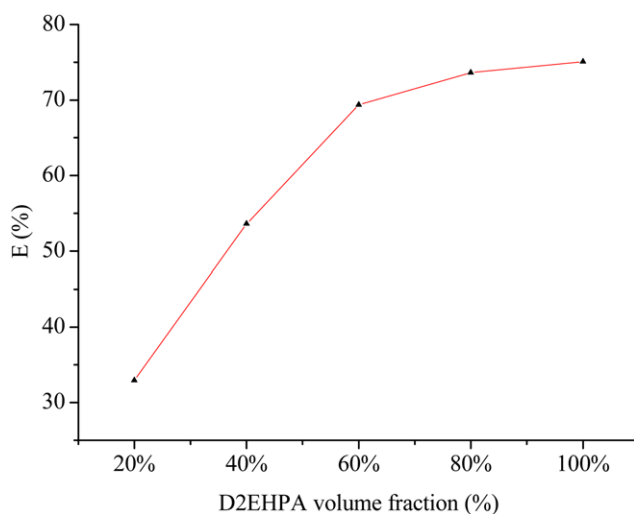


Fig. 1. The relationship of extraction efficiency (E) and D2EHPA volume fraction (%). Solvent: kerosene; R(O/A)=1 : 2; Stirring speed: 450 r/min; Initial Mg^{2+} concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Stirring time: 20 min; Reaction temperature: 70 °C.

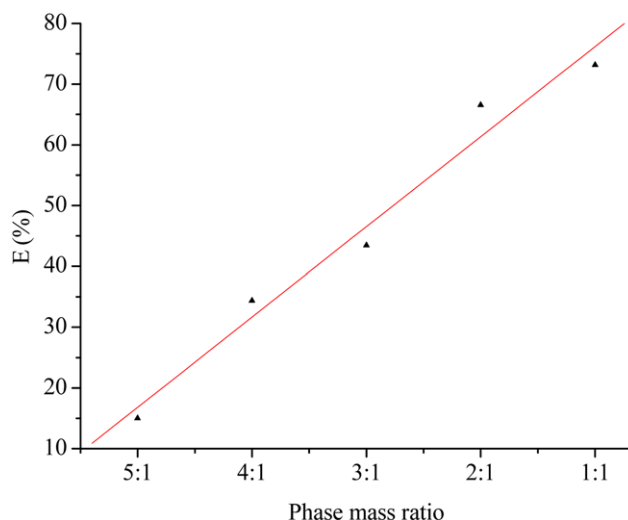


Fig. 2. The dependence of the extraction efficiency (E) on the phase mass ratio. Solvent: kerosene; D2EHPA volume fraction (%): 50%; Stirring speed: 450 r/min; Initial Mg^{2+} concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Stirring time: 20 min; Reaction temperature: 70 °C.

effect on extraction efficiency (E) and entrainment. The effect is studied by changing the ratio of aqueous phase and organic phase from 5 : 1 to 1 : 1. The results in Fig. 2 clearly show that a phase ratio of 1 : 1 gives the best extraction of Mg^{2+} . The result [8] is consistent with the previous findings that for the fixed Mg^{2+} concentration in solution the increase in phase ratio extraction process will enhance the amount of solvent and extractant.

4. Effect of Stirring Speed

As the stirring speed increases, a smaller globule size will lead to a larger transfer interfacial area between the feed and the solvent phase. The increased transfer area allows the extraction to occur at

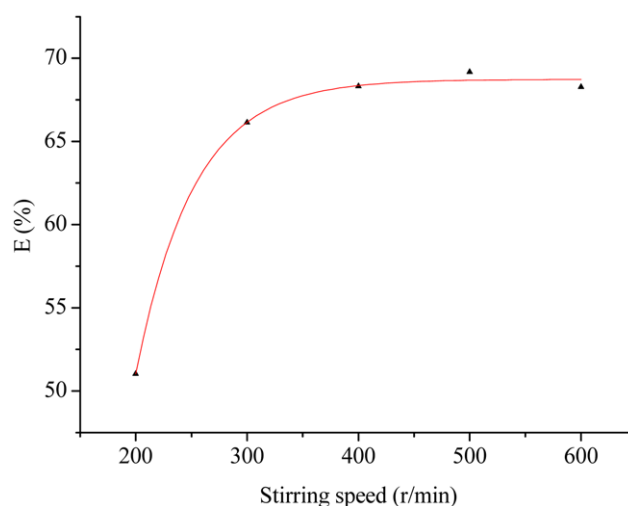


Fig. 3. The relationship of extraction efficiency (E) and the stirring speed. Solvent: kerosene; D2EHPA volume fraction (%): 50%; R(O/A)=1 : 2; Initial Mg^{2+} concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Stirring time: 20 min.

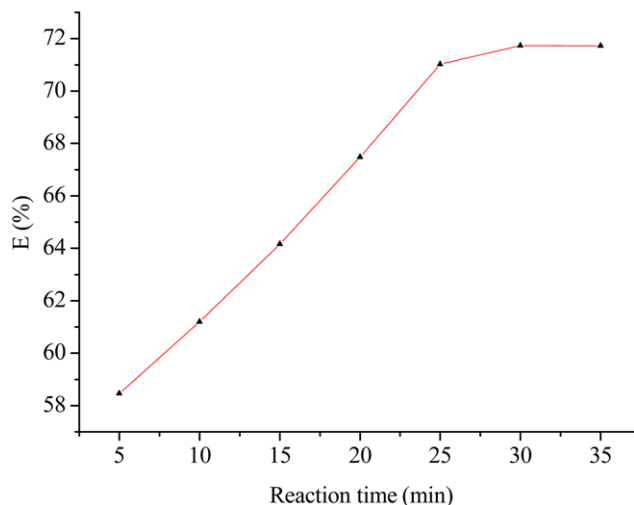


Fig. 4. The dependence of the extraction efficiency (E) on the reaction time. Solvent: kerosene; D2EHPA volume fraction (%): 50%; R(O/A)=1 : 2; Stirring speed: 450 r/min; Initial Mg²⁺ concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Reaction temperature: 70 °C.

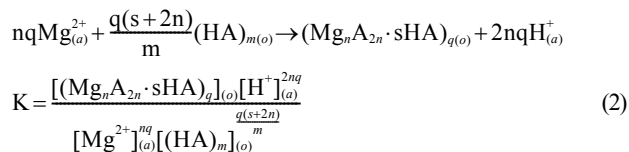
a higher rate. However, the experimental results in Fig. 3 reveal that the stirring speed has little effect on the extraction efficiency (E) when the stirring speed is as high as above 400 r/min. The optimum value for stirring speed is thus found to be 400 r/min.

5. Effect of Reaction Time

The dependence of extraction of Mg²⁺ by emulsification extraction and solvent extraction on reaction time is presented in Fig. 4. Obviously, the extraction ratio (E) of Mg²⁺ increases with the increase of reaction time. The equilibrium for the emulsification extraction of Mg²⁺ can be observed after approximately 30-35 min, indicating that the equilibrium time for emulsification extraction is above 30 min.

6. Effect of Initial pH of MAP Solution

As D2EHPA (HA) contains dissociable H⁺, the mechanism of extracting Mg²⁺ with HA perhaps is consistent with the cation exchange. In general, the extraction reaction can be described as follows:



Where m is the aggregation number of D2EHPA.

Then, the equilibrium constant K is given as

$$[(Mg_nA_{2n} \cdot sHA)_q]_{(o)} = \frac{1}{qn} [Mg^{2+}]_{(a)} \quad (3)$$

And the distribution ratio of Mg²⁺ can be expressed as

$$D = \frac{[Mg^{2+}]_{(o)}}{[Mg^{2+}]_{(a)}} \quad (4)$$

$$\log D = \log K + 2nqpH + \log q$$

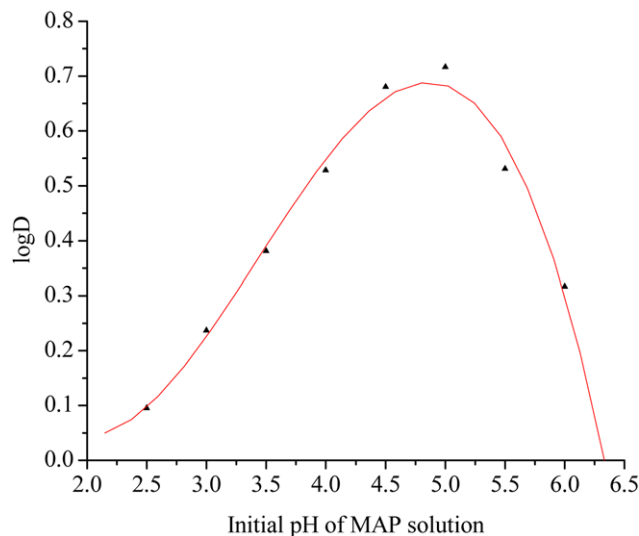


Fig. 5. The extraction distribution ratios (logD) versus the initial pH of MAP solution.

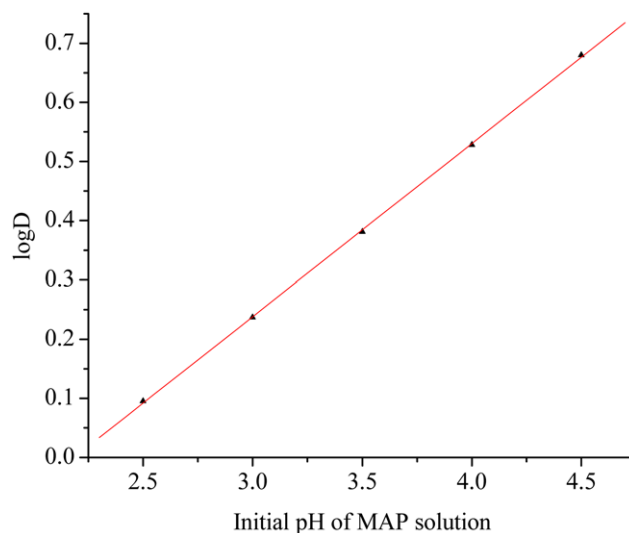


Fig. 6. The extraction distribution ratios (logD) versus the initial pH of MAP solution. Solvent: kerosene; D2EHPA volume fraction (%): 50%; R(O/A)=1 : 2; Stirring speed: 450 r/min; Initial Mg²⁺ concentration: 600 mg/L; Stirring time: 30 min; Reaction temperature: 70 °C.

$$+ \frac{q(s+2n)}{m} \log[(HA)_m]_{(o)} + (nq-1) \log[Mg^{2+}]_{(a)} \quad (5)$$

The plot of logD and pH as shown in Fig. 6 is a straight line with the slope of approximately 0.2923, suggesting 2nq is equal to 0.3. The result indicates the chelating complex of (MgA₂-HA) can be obtained. The mechanism of the extraction of Mg²⁺ with HA is therefore consistent with the cation exchange [10] and chelation. The intercept value is about -0.638, and thus the extraction equilibrium constant K can be calculated as 0.586 on the basis of Eq. (5). As shown in Fig. 5, the extraction distribution ratios (D) of Mg²⁺ increases linearly upon increasing the initial pH of ammonium dihydrogen phosphate solution in the pH range of 2.5 to 5. However, after the solution's pH value increases to 5, attributable to the hydrolysis effect,

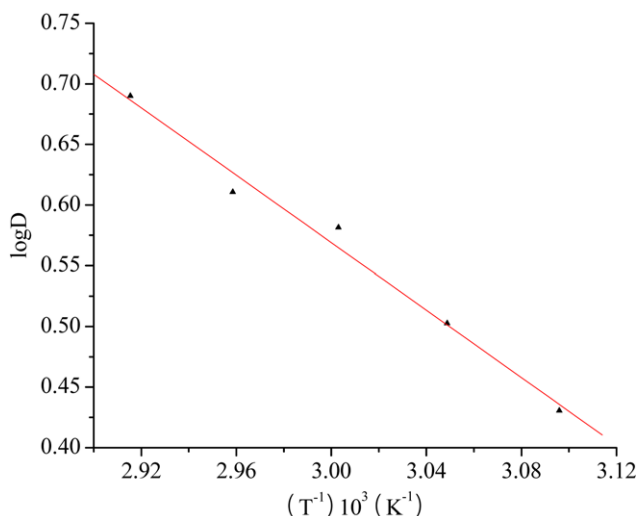


Fig. 7. Change of the extraction distribution ratios ($\log D$) as function of the reaction temperature. Solvent: kerosene; D2EHPA volume fraction (%): 50%; R(O/A)=1 : 2; Stirring speed: 450 r/min; Initial Mg^{2+} concentration: 600 mg/L; Initial pH of ammonium dihydrogen phosphate: 4.5; Stirring time: 30 min.

the extraction rates decreases gradually.

7. Effect of Reaction Temperature

The distribution ratio (D) increases as the temperature rises. Fig. 7 shows the relationship of the extraction distribution ratios and the reaction temperature; obviously, a linear relationship is found between $\log D$ and $10^3 T^{-1}$. Based on the Van't Hoff equation [11], $d \log D / d(1/T) = -\Delta H / (2.303R) + \text{const}$, the ΔH value can be calculated as $2.659 \times 10^2 \text{ (J}\cdot\text{mol}^{-1}\text{)}$, indicating that the extraction of Mg^{2+} with D2EHPA is endothermic. According to the equation of $\Delta G = -RT \ln K$, the ΔG value is obtained as $1.501 \times 10^3 \text{ (J}\cdot\text{mol}^{-1}\text{)}$ where T is equal to 338 K. On the basis of equation $\Delta G = \Delta H - T\Delta S$, the ΔS value is $-4.441 \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\text{)}$, can be calculated.

FIELD STUDY

A kind of practical wet-process phosphoric acid is neutralized to $\text{pH}=4.5$ with ammonia and filtered. The neutralized solution is then extracted under the above mentioned optimal process conditions. And the superior MAP is produced using the extracted solution after the subsequent concentration and crystallization process. Table 2 shows the composition of the final MAP product:

CONCLUSION

Based on the results of removing Mg^{2+} from MAP solution with

solvent extraction with D2EHPA approach, the following specific conclusions can be drawn:

- 1) Solvent extraction with D2EHPA as extraction is an effective method to remove Mg^{2+} from MAP solution.
- 2) The optional process conditions are as follows: The D2EHPA volume fraction: 50%; the reaction temperature: 70°C ; the phase volume ratio (O/A): 1 : 2; the stirring speed: 400 r/min, and the initial pH of $\text{NH}_4\text{H}_2\text{PO}_4$ solution: 4.5.
- 3) The mechanism of the extraction of Mg^{2+} with HA is associated with the cation exchange and chelation.
- 4) The thermodynamic function values of the extraction are as follows: $\Delta H = 2.397 \times 10^2 \text{ (J}\cdot\text{mol}^{-1}\text{)}$; $\Delta G = 3.049 \times 10^3 \text{ (J}\cdot\text{mol}^{-1}\text{)}$ ($T = 338 \text{ K}$); $\Delta S = -10.063 \text{ (J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\text{)}$.

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Table 2. Composition of the MAP

Item	N (%)	P ₂ O ₅ (%)	Fe ³⁺ (%)	Mg ²⁺ (%)	Al ³⁺ (%)	Heavy metal (Pb) %
Mass fraction	≥12	≥61	≤0.0003	≤0.009	≤0.0002	≤0.0005
Item	As (%)	F ⁻ (%)	SO ₄ ²⁻ (%)	pH	H ₂ O (%)	Water-insoluble substance (%)
Mass fraction	≤0.0010	≤0.0010	≤0.0020	4.5-4.8	≤0.2	≤0.05

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