A Kinetic Study of Nitric Acid Extraction by Tri-n-octylamine

Xuhong JIA,1 Jun LI2* and Yang JIN2
1 School of Aviation Security, Civil Aviation Flight University of China, Guanghan, Sichuan, 618307, P. R. China
2 Department of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, P. R. China
(Received August 17, 2014; Accepted September 15, 2014)

The importance of recovering nitric acid from wet-process phosphoric acid (WPA) has been growing due to the many advantages that nitric acid has over sulfuric acid for decomposing phosphate rock. Since tri-n-octylamine (TOA) shows good extraction and selectivity for nitric acid, basic research of this topic is required. In this study, the kinetics and mechanism of the extraction of nitric acid with tri-n-octylamine in kerosene has been studied at 25 °C, using a constant interfacial area cell with laminar flow. According to the results of this work, we find that the extraction process is controlled by the diffusion of nitric acid in the aqueous phase and by the chemical reaction taking place at the interface of both phases. The mechanism of the nitric acid extraction with TOA is revealed and the kinetic model is established.

1. Introduction

Phosphoric acid is generally produced by two methods: the wet process and the thermal process. Wet-process phosphoric acid (WPA) can be obtained by the decomposition of phosphate rock with acids (hydrochloric, nitric, sulfuric acids) [1, 2]. Sulfuric acid is most commonly used to decompose the rock because the calcium sulfate precipitated as a by-product is easy to remove. However, as much as 4-5 tonnes of phosphogypsum (PG) will be generated for each tonne of P2O5 produces [3]. Unfortunately, PG is a waste product mainly disposed of in landfills as its use is difficult and expensive [2, 4]. There are about 5 billion tonnes of PG accumulated in 50 countries and the amount is growing at a rate of 100–200 million tonnes per year [5]. The amount of PG is so great that it will occupy many hectares and can seriously damage the environment. This great shortcoming can be avoided by dissolving phosphate ore with nitric acid for the main by-product calcium nitrate, can be used as a nitrogen fertilizer [6].

Owing to the low energy consumption and good selectivity, solvent extraction can be used for the recovery of nitric acid from the soluble salts solutions [1, 7, 8]. According to our previous studies [6], tri-n-octylamine (TOA) is an effective extractant to separate nitric acid from the WPA to produce phosphoric acid. The thermodynamics and the chemical reaction mechanism of the extraction of nitric acid by TOA has been studied [9,12]. Yet, the kinetics of nitric acid extraction using TOA as extractant has not been reported, especially in the presence of phosphoric acid.

The aim of this work is to study the kinetics of extraction of nitric acid with TOA. The controlling step of the extraction reaction rate is identified. The location of the reaction is determined, and a method for increasing the extraction rate is established.
2. Experimental section

2.1 Materials and apparatus

TOA (mass fraction > 0.99) and kerosene were provided by Sichuan Jingcui Co., Ltd., China and were used without any further purification. Nitric acid (mass fraction=0.68) and phosphoric acid (mass fraction=0.85) were supplied by Kelong Co., China. All of the reagents were of analytical grade. The water used in the experiments was deionized.

The constant interfacial area cell with laminar flow, 0.25 m in length, 0.06 m in width, 0.12 m in height, was home-made (Figure 1). The electronic thermostat water bath (model HH-1) was provided by Jintan Hongke Instrument factory, China. The variable speed electric agitator (model S312) was produced by Shanghai Meiyingpu Instrument Manufacturing Co., Ltd, China. The compact automatic titrator (916 Ti-Touch) was produced by Metrohm AG. The electronic analytical balance (model BSA224S) was produced by Sartorius.

![Figure 1. Schematic diagram of the home-made constant interfacial area cell with laminar flow: 1-Aqueous phase input/Sampling hole; 2-Down thrust stirring paddle; 3-Interfacial plate; 4,5- Flow deflector; 6-Organic phase input; 7-Up thrust stirring paddle.](image)

2.2 Procedures

The constant interfacial area cell, as shown in Figure 1, was used to obtain kinetic data in this work. It was made of Pyrex glass and had an interfacial area of (about 32.45 cm²) and two chambers of equal volumes (126.75 cm³). The upper chamber was filled with the organic phase and the lower one was filled with the aqueous phase. The two stirring paddles with reversed blades were symmetrically located with respect to the interface, and the stirrers were driven in the range of 100-800 rpm by using a variable speed electric agitator. The temperature of the system was maintained constant by circulating water at 25°C through the electronic thermostat water bath.

Known concentration mixtures of nitric acid and phosphoric acid were prepared as aqueous phases and TOA and kerosene were prepared as organic phases. The aqueous phase and organic phase were respectively injected into the cell via the inputs shown in figure 1. Then the two same speed agitators were started simultaneously. As the count-current extraction was performed, samples were periodically taken from the aqueous phase and then assayed for residual nitric acid concentration. The nitric acid and phosphoric acid concentrations in both phases were measured by potentiometric titration and the quinoline
phosphomolybdate gravimetric method [10], respectively. The densities of the aqueous phase $\rho$ were measured with Ostwald-Sprengel pycnometers using the method described elsewhere [11]. All of the experiments were carried out at least twice, and the average values were taken as the results. The relative deviations were 0.1 % for phosphoric acid and nitric acid.

2.3 Theoretical approach

According to the reported study [12], the TOA extraction mechanism for nitric acid is

\[
\begin{align*}
\text{HNO}_3^{\text{(a)}} + \text{TOA}^{\text{(o)}} & \rightarrow K_1 \quad \text{TOA} \cdot \text{HNO}_3^{\text{(o)}} \quad (1) \\
\text{HNO}_3^{\text{(a)}} + \text{TOA} \cdot \text{HNO}_3^{\text{(o)}} & \leftrightarrow K_2 \quad \text{TOA} \cdot \text{HNO}_3^2 \cdot \text{HNO}_3^{\text{(o)}} \quad (2)
\end{align*}
\]

where $K_1 = \left[\text{TOA} \cdot \text{HNO}_3^{\text{(o)}}\right]/\left[\text{TOA} \cdot \text{HNO}_3^{\text{(o)}}\right]$, $K_2 = \left[\text{TOA} \cdot \text{HNO}_3^2 \cdot \text{HNO}_3^{\text{(o)}}\right]/\left[\text{TOA} \cdot \text{HNO}_3^{\text{(o)}}\right]$, in which square brackets denote molar concentrations and the subscripts $\text{o}$ and $\text{a}$ denote the organic and aqueous phases (the same below), respectively. Because $K_1 \left(3 \times 10^6\right)$ is much larger than $K_2 \left(0.19\right)$ [12], the reaction described as equation (2) can be neglected. So the process of nitric acid extraction with TOA can be succinctly described as follows:

\[
\begin{align*}
\text{HNO}_3^{\text{(a)}} + \text{TOA}^{\text{(o)}} & \rightarrow \frac{k_f}{k_b} \quad \text{TOA} \cdot \text{HNO}_3^{\text{(o)}} \quad (3)
\end{align*}
\]

where $k_f$ and $k_b$ are the forward and backward reaction rate constants.

The extracting reaction rate $R$ is [13]

\[
R = \frac{V}{A} \cdot \frac{d[HNO_3^{\text{(a)}}]}{dt} = \frac{V}{A} \cdot \frac{d[HNO_3^{\text{(a)}}]_a}{dt} = k_f [HNO_3^{\text{(a)}}]_a - k_b [HNO_3^{\text{(a)}}] \quad (4)
\]

where $A$ is the contact area for both phases; $V$ is the volume of the organic/aqueous phase. Using $a_i$, $a_e$ and $a_t$ to represent the initial concentration, equilibrium concentration and the concentration at time $t$, equation (4) can be rewritten as

\[
R = \frac{V}{A} \cdot \frac{d(a_t - a_i)}{dt} = \frac{V}{A} \cdot \frac{da_t}{dt} = k_f a_i - k_b (a_t - a_i) \quad (5)
\]

when the extraction process reaches equilibrium, the extraction rate $R=0$, $a_i=a_e$

\[
R = k_f a_i - k_b (a_t - a_i) = k_f a_e - k_b (a_t - a_e) = 0 \quad (6)
\]

so

\[
k_b = \frac{a_e}{a_i - a_e} k_f \quad (7)
\]

by substitution of equation (7) into equation (5), we get

\[
R = \frac{1}{a_t - a_e} \cdot \frac{d(a_t - a_i)}{dt} = -\frac{da_t}{dt} = \frac{A}{V} \cdot \frac{a_i}{a_t - a_e} k_f \quad (8)
\]

Since the boundary condition is $a_i=a_t$ when $t=0$, on integrating equation (8) from $t=0$ to $t=t$, we get

\[
\frac{a_t - a_e}{a_i} \ln \frac{a_t - a_e}{a_t - a_e} = \frac{A}{V} k_f t = \frac{a_i - a_e}{a_i} Y \quad (9)
\]
similarly

$$\frac{a_e}{a_i} \ln \frac{a_i-a_e}{a_i-a_e} = \frac{A}{V} k_{b} t = \frac{a_e}{a_i} Y$$

(10)

where $Y$ is defined to be $Y=\ln(a_i-a_e)/(a_i-a_e)$. Since the feed solution obtained from decomposing the phosphate rock with nitric acid contained about 30% wt. of nitric acid and 19% wt. of phosphoric acid [6], the mixture of acids prepared for the aqueous phase contained 29.18% wt. (5.77 mol·L$^{-1}$) of nitric acid ($a_i$) and 18.19% wt. (2.31 mol·L$^{-1}$) of phosphoric acid. The value of $a_e$ was measured when the extraction reached equilibrium.

From a dot of $Y$ against $t$, we should get a straight line passing through the origin. The $k_f$ and $k_b$ values can be calculated from the slope of the line. Then $R$ can be calculated from equation (8). Hence, the relationship between the extraction rate and the factors influencing it could be determined.

3. Results and Discussion

3.1 Determination of the relationship between $Y$ and $t$

In order to obtain an accurate extraction rate equation, the relationship between $Y$ and $t$ must be determined first. In this work, concentrations of nitric acid in aqueous phase at different times ($a_i$) were investigated. The experiments were carried out under the following conditions: extraction temperature = 25°C, stirring speed = 500 rpm, interfacial area = 32.45 cm$^2$, nitric acid concentration = 5.77 mol·L$^{-1}$, phosphoric acid concentration=2.31 mol·L$^{-1}$, TOA concentration=0.90 mol·L$^{-1}$. $Y$ can be calculated from the above definition and the relationship between $Y$ and $t$ is plotted in Figure 2.

![Figure 2. Relationship between $Y$ and extraction time.](image-url)
As seen from Figure 2, we get a straight line passing through the origin. This result shows that the theoretical approach given in section 2.3 is correct.

3.2 Effect of agitation speed on the extraction kinetics

The effects of agitation at different speeds (100, 200, 300, 400, 500, 600, 700 and 800 rpm) on the extraction rate \( R \) and initial extraction rate \( R_i \) of nitric acid have been investigated under the following conditions: extraction temperature = 25°C, interfacial area = 32.45 cm\(^2\), nitric acid concentration = 5.77 mol·L\(^{-1}\), phosphoric acid concentration = 2.31 mol·L\(^{-1}\), TOA concentration = 0.90 mol·L\(^{-1}\). The results are shown in Figure 3 and Figure 4.

Figure 3 shows that the initial extraction rate of nitric acid increases linearly with increasing agitation speed from 100 to 500 rpm. However, \( R_i \) increases sharply with a further increase in agitation speed. Figure 4 shows an analogous variation trend over the whole extraction time studied. The cause of this phenomenon is that the mass transfer coefficient is a linear correlation of the agitation speed when the phase contact interface is stable. When the agitation speed exceeds 500 rpm, the stability of the interface is broken and the flow pattern is no longer laminar, the contact area of both phases increases sharply. From this, we can deduce the extraction process is controlled by diffusion or by chemical reaction and diffusion jointly [14]. An agitation speed of 500 rpm was chosen for the rest of the experiments.

![Figure 3. Effect of agitation speed on the initial extraction rate.](image-url)
3.3 Determination of the diffusion resistance area

In order to determine the diffusion resistance area, the concentration of nitric acid in the aqueous phase with increasing extraction time was investigated under the following three conditions: the organic phase is stirred only, the aqueous phase is stirred only and both phases are stirred. The experiments were carried out at 25°C, 500 rpm, 32.45 cm² of interfacial area, 5.77 mol·L⁻¹ of nitric acid, 2.31 mol·L⁻¹ of phosphoric acid, 0.90 mol·L⁻¹ of TOA. The results are plotted in Figure 5.

Figure 4. Effect of agitation speed on the extraction rate.

Figure 5. Effect of stirring on the extraction of nitric acid.
From Figure 5, we find that the rate of decrease in the nitric acid concentration in the aqueous phase is similar when we stir both phases or stir the aqueous phase only. However, the nitric acid concentration declines very slowly compared with the two other cases when only the organic phase is stirred. This phenomenon indicates that the diffusion resistance is mainly in the aqueous phase. Therefore, the extracting reaction could only take place in the aqueous phase or of the interface and could not take place in the organic phase [15].

3.4 Effect of the temperature on the extraction kinetics

The effect of temperature on the extraction kinetics can be obtained by plotting the $k_t$ values against the reciprocal of the absolute temperature $1/T$. The results in Figure 6 give straight line indicating that this extraction reaction obeys the Arrhenius equation

$$k_t = A e^{\frac{E_a}{RT}}$$

where $E_a$ is the apparent activation energy, $R$ is the universal gas constant (8.314 J·mol$^{-1}$·K$^{-1}$), $T$ is the absolute temperature (K) and $A$ is the pre-exponential factor. The experiments were carried out at different temperatures (15, 25, 35, 45, 55°C) under the following conditions: stirring speed = 500 rpm, interfacial area = 32.45 cm$^2$, nitric acid concentration = 5.77 mol·L$^{-1}$, phosphoric acid concentration = 2.31 mol·L$^{-1}$, TOA concentration = 0.90 mol·L$^{-1}$.

The value of $E_a$ is calculated from the slope of this line and found to be 28.35 kJ·mol$^{-1}$, indicating that the extraction of nitric acid in the investigated system is jointly controlled by chemical reaction and diffusion [16, 17]. The enthalpy of activation ($\Delta H^*$) and the entropy of activation ($\Delta S^*$) at 298.15 K is calculated from eq (8) [18,19] and eq (9) [18], respectively.
\[ \Delta H^* = E_a - RT \]  
(12)

\[ k_f = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{\Delta H^*}{RT}} \]
(13)

where \( N \) is the Avogadro number \( (6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}) \) and \( h \) is Planck’s constant \( (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \). The value of \( \Delta H^* \) and \( \Delta S^* \) are found to be 25.87 kJ·mol\(^{-1}\) and -208.03 J·mol\(^{-1}\)·K\(^{-1}\). The large negative value of \( \Delta S^* \) indicates that the structure of the extracted nitric acid is more or less ordered.

3.5 Effect of the interfacial area on the extraction kinetics

The effect of interfacial area on the extraction rate was studied to determine whether the chemical reaction takes place in the bulk phase or at the interface. For the first case, the rate of extraction is independent of the interfacial area, while for the second the extraction rate depends on the interfacial area \([18, 20]\). In this work, the effect of different interfacial areas \((14.75, 23.60, 32.45 \text{ and } 41.30 \text{ cm}^2)\) on the initial extraction rate of the nitric acid was investigated under the following conditions: extraction temperature = 25°C, stirring speed = 500 rpm, nitric acid concentration = 5.77 mol·L\(^{-1}\), phosphoric acid concentration = 2.31 mol·L\(^{-1}\), TOA concentration = 0.90 mol·L\(^{-1}\). The result is shown in Figure 7.

![Figure 7. Effect of interfacial area on the initial extraction rate of nitric acid.](image)

As seen in Figure 7, a straight line is obtained by plotting \( R_i \) against the corresponding interfacial area. This indicates that the extraction rate of nitric acid is dependent on the variation of the interfacial area and the rate controlling reaction takes place at the interface.

3.6 Effect of the nitric acid and TOA concentration on the extraction rate

The effects of a nitric acid concentration range from 1.72 to 8.07 mol·L\(^{-1}\) with constant phosphoric acid concentration \((2.31 \text{ mol} \cdot \text{L}^{-1})\) and TOA concentration \((0.90 \text{ mol} \cdot \text{L}^{-1})\) and for a TOA concentration...
range from 0.45 to 2.25 mol·L⁻¹ with constant nitric acid concentration (5.77 mol·L⁻¹) and phosphoric acid concentration (2.31 mol·L⁻¹) were studied in this work. The experiments were carried out under the following conditions: extraction temperature = 25°C, stirring speed = 500 rpm, interfacial area = 32.45 cm². The relationships of \( R_i \) with regard to the nitric acid and TOA concentrations from non-linear fitting are plotted in Figure 8 and Figure 9, respectively.

From Figure 8 and Figure 9, we can see that \( R_i \) increases with increasing TOA concentration and nitric acid concentration. The \( R_i \) value is proportional to the TOA concentration to the 0.925th power and nitric acid concentration to the 0.993th power.

![Figure 8. Effect of TOA concentration on the initial extraction rate.](image)

![Figure 9. Effect of nitric acid concentration on the initial extraction rate.](image)
3.7 Determination of the extraction mechanism

According to the results presented above, we can summarize that the extraction process is jointly controlled by diffusion and chemical reaction. The main diffusion resistance is in the aqueous phase and the extracting reaction takes place at the interface of both phases. Therefore, the mechanism of nitric acid extraction by TOA can be described as follows:

a. The nitric acid molecules (ion pairs of H⁺ and NO₃⁻) in the aqueous phase diffuse from the bulk phase to the boundary layer.

\[
\text{HNO}_3(a) \xrightarrow{k^-} \text{HNO}_3(ia) \quad \text{slow} \quad (14)
\]

b. The TOA molecules in the organic phase diffuse from the bulk phase to the boundary layer.

\[
\text{TOA}(o) \xrightarrow{k^+} \text{TOA}(io) \quad \text{fast} \quad (15)
\]

c. The nitric acid molecules and the TOA molecules meet at the interface, and then react chemically to form the extracted complex HNO₃·TOA.

\[
\text{HNO}_3(ia) + \text{TOA}(io) \xrightarrow{k^+} \text{HNO}_3\cdot\text{TOA}(i) \quad \text{slow} \quad (16)
\]

d. The HNO₃·TOA molecules pass through the organic phase boundary layer and then diffuse into the bulk organic phase.

\[
\text{HNO}_3\cdot\text{TOA}(i) \leftrightarrow \text{HNO}_3\cdot\text{TOA}(o) \quad \text{fast} \quad (17)
\]

where the subscripts a, o, i, ia and io denote the bulk aqueous phase, bulk organic phase, interface, aqueous phase boundary layer and organic phase boundary layer, respectively. \( k^- \) is the apparent transfer coefficient of nitric acid in the aqueous phase. The \( k^+ \) and \( k^- \) values are the forward and backward reaction rate constants at the interface. The extraction rate is controlled by steps (14) and (16). The diffusion or reaction rates for equations (14) to (17) can be described as follows:

equation (14) is a slow process, so

\[
-\frac{d[HNO_3]}{dt} = k([HNO_3]_a - [HNO_3]_{ia}) \quad (18)
\]

equation (17) is a fast process, so

\[
[\text{TOA}]_o = [\text{TOA}]_i \quad (19)
\]

equation (18) is a slow reaction process, so

\[
\frac{d[HNO_3\cdot\text{TOA}]}{dt} = k^+[HNO_3]_{ia} [\text{TOA}]_o - k^-[HNO_3\cdot\text{TOA}]_i \quad (20)
\]

equation (15) is a fast process, so

\[
[HNO_3\cdot\text{TOA}]_i = [HNO_3\cdot\text{TOA}]_o \quad (21)
\]

from equation (8), we get

\[
-\frac{d[HNO_3]}{dt} = \frac{d[HNO_3\cdot\text{TOA}]}{dt} \frac{RA}{V} \quad (22)
\]

solving the simultaneous equations described by eq (18), (19), (20), (21), and (22), we get

\[
R = \frac{kk^+[\text{TOA}]_o[HNO_3]_a - kk^-[HNO_3\cdot\text{TOA}]_o}{k^+[\text{TOA}]_o + k} \times \frac{V}{A} \quad (23)
\]
when $t \to 0$, we obtain $[\text{HNO}_3]_a \to [\text{HNO}_3]_{a,0}$, $[\text{TOA}]_o \to [\text{TOA}]_{o,0}$, $[\text{HNO}_3\cdot\text{TOA}]_o \to 0$. Thus, equation (23) can be reduced to

$$R = \frac{kk' [\text{TOA}]_{o,0} [\text{HNO}_3]_{a,0}}{k' [\text{TOA}]_{o,0} + k} \times \frac{V}{A}$$

(24)

defining $K = \frac{kV}{A}$, $K^+ = \frac{k^+ V}{A}$, equation (24) can be reduced to

$$R = \frac{[\text{HNO}_3]_{a,0}}{K + \frac{1}{K^+ [\text{TOA}]_{o,0}}}$$

(25)

where the subscripts $a,0$, and $o,0$ denote the mole concentration at the beginning of the extracting reaction.

By means of a non-linear regression analysis of the experimental data obtained from section 3.6 using the Levenberg-Marquardt algorithm, we get $K = 4.86 \times 10^{-4}$ m·s$^{-1}$ and $K^+ = 2.99 \times 10^{-5}$ L·mol$^{-1}$·m·s$^{-1}$. The value of $K$ is about 16 times greater than $K^+$, indicating that the mass transfer rate in the aqueous phase is much larger than the chemical reaction rate at the interface.

The results of the calculated and experimental values obtained from the investigated conditions are listed in Table 1. The quality of the correlation is measured by the root-mean-square error (RMSE).

<table>
<thead>
<tr>
<th>$C_{\text{HNO}_3}$</th>
<th>$C_{\text{TOA}}$</th>
<th>$R_{\text{exp}}$</th>
<th>$R_{\text{cal}}$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.77</td>
<td>0.45</td>
<td>7.96</td>
<td>7.55</td>
<td></td>
</tr>
<tr>
<td>5.77</td>
<td>0.9</td>
<td>14.53</td>
<td>14.71</td>
<td></td>
</tr>
<tr>
<td>5.77</td>
<td>1.35</td>
<td>21.21</td>
<td>21.49</td>
<td>2.33</td>
</tr>
<tr>
<td>5.77</td>
<td>1.8</td>
<td>27.73</td>
<td>27.95</td>
<td></td>
</tr>
<tr>
<td>5.77</td>
<td>2.25</td>
<td>34.3</td>
<td>34.08</td>
<td></td>
</tr>
<tr>
<td>1.72</td>
<td>0.9</td>
<td>4.52</td>
<td>4.38</td>
<td></td>
</tr>
<tr>
<td>3.44</td>
<td>0.9</td>
<td>8.77</td>
<td>8.77</td>
<td></td>
</tr>
<tr>
<td>6.82</td>
<td>0.9</td>
<td>17.68</td>
<td>17.38</td>
<td></td>
</tr>
<tr>
<td>8.07</td>
<td>0.9</td>
<td>20.49</td>
<td>20.57</td>
<td></td>
</tr>
</tbody>
</table>

In the table, $C$ stands for the mole concentration and $R$ is the extraction rate. Subscripts exp. and cal. denote experimental and calculated values, respectively. RMSE is the root-mean-square error.

### 4. Conclusions

Kinetics and mechanism for the extraction of nitric acid from nitric and phosphoric acid mixtures with TOA in kerosene has been investigated at 25°C using a constant interfacial area cell with laminar flow. On the basis of this study, the following conclusions can be summarized.

1. The extraction process is controlled jointly by the diffusion of nitric acid in the aqueous phase and chemical reaction taking place at the interface of the both phases.
The mechanism of nitric acid extraction with TOA is as follows: the nitric acid molecules in the aqueous phase and the TOA molecules in the organic phase diffuse firstly from the bulk phases to the boundary layer. Then, the nitric acid molecules and the TOA molecules react chemically to form the extracted complex $\text{HNO}_3 \cdot \text{TOA}$. Finally, the $\text{HNO}_3 \cdot \text{TOA}$ molecules pass through the organic phase boundary layer and diffuse into the bulk organic phase to complete the extraction process.

The extraction kinetic model for the extraction of nitric acid with TOA is established.

References