Liquid-liquid extraction of mineral acids using Tri-n-octylamine

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Abstract

The present work reports the extraction behaviors of mineral acids: HClO4, HNO3, HCl and H2SO4 (commonly found in acidic bleed solutions from the hydrometallurgical route of metal extraction processes) by tri-n-octylamine (TOA) dissolved in distilled colorless kerosene. The systems have been investigated as functions of various experimental parameters, such as time, [acid], [TOA], temperature, extraction stage and the organic to aqueous phase volume ratio (O/A). Strippings was also examined. Equilibration time is less than 60 min. The acid concentration in the organic phase at equilibrium is increased with increasing initial acid concentration in the aqueous phase for all systems. However, the is after %extraction decreased with increasing initial acid concentration in the aqueous phase. The % extraction increased remarkably with increasing [TOA] for all cases. Being the ratio of the [acid] in the organic to aqueous phase at equilibrium equal to extraction ratio, D; the log D vs. log [TOA] plot is almost a curve with slope 1 at lower concentration region and with slope ~2 at higher concentration region. The extraction efficiency of TOA varies in the order: HClO4 > HNO3 > HCl > H2SO4. The acid-base-neutralization (extraction) reactions are exothermic with ΔH value much higher than -57 kJ/mol obtainable for of a strong acid - strong base neutralization. The loading capacity of extractant (g per 100 g TOA) for acids varied in the order: HClO4 (30.69) > HNO3 (20.49) > H2SO4 (17.87) > HCl (10.31). On using lower organic to aqueous phase volume ratio (O/A), the organic phase saturated with acid can be obtained on stage-wise extraction. The extracted organic phase, for all systems (excepting H2SO4-system) under investigation, can be stripped effectively in a single stage by 0.10 g eq/L NaOH solution to the extents of more than 96%. However, for H2SO4-system, two-stage stripping will be found effective.

Keywords: Mineral acid; TOA; Extraction; Stripping; Mechanism

Introduction:

Amines, categorized as an organic compounds, area derivative of ammonia and prepared by replacement of one or more hydrogen atoms by organic substituents (Biswas et al., 2017; Roose et al., 2015). Generally, they are bases of broadly varying strengths. Depending on the number of hydrogen atoms of ammonia replaced by radicals, amines are classified. The amine compounds have a lone pair of electrons on the amine nitrogen. It enables amines to contribute in a large variety of reactions as a base or a nucleophile. Amines play a prominent role in the field of extractive metallurgy (Biswas et al., 2017; Das et al., 2014; Gai et al., 2018; Hesford and McKay, 1960). The lone pair of an electron on the nitrogen atom determines the chemistry of aliphatic amines and also by the tendency of the hydrogen atoms bonded to nitrogen to be replaced by other substituents (Biswas et al., 2017; Hesford and McKay, 1960; Saw et al., 2018). Aliphatic amines are stronger bases than ammonia because they convey alkyl substituents. High molecular weight amines form salts with acids, that are less soluble in water but soluble in organic non-polar solvents. This property, combined with the difference in solubility between amine and salt, makes amines good acid acceptors and solvents for gas scrubbing and certain extraction processes. Extraction of various types of organic acids

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\[ \text{Introduction:} \]

Amines, categorized as organic compounds, are acid acceptors and have a lone pair of electrons on the nitrogen atom. This property, along with the difference in solubility between water and organic non-polar solvents, makes amines good acid acceptors.\(^3\)

\[ \text{Materials and methods} \]

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Tri-n-octylamine was collected from Tokyo Kaie Ind., Japan (90%). It was used without further refinement. Distilled colorless kerosene was used to dilute TOA to constitute the organic phase. All other chemicals were of reagent grade and used without further purifications. Kerosene was purchased from the local shop. It was distilled at 200-260 °C to collect colorless fraction. The requisite amount of mineral acids (H\(_2\)SO\(_4\), HCl, HClO\(_4\) and HNO\(_3\)) were dissolved separately in 250 mL volumetric flasks to achieve the concentration of 2.0 mol/L for each mineral acid. In most cases, this solution was diluted to obtain test solutions for the present investigations.

\[ \text{Analytical} \]

The concentration of mineral acids was determined by simple acid-base titration with standardized NaOH solution using 4-nitro phenol as indicator. Sometimes analyses were justified by pH-metric titration involving standardized NaOH solution(Bassette et al., 1979). A Mettler Toledo (MP 220) pH-meter was used for pH measurement. Wherever necessary, anhydrous Na\(_2\)CO\(_3\) was used for pH adjustment of the aqueous phase.

\[ \text{Procedure for extraction} \]

Except for the temperature dependence, all studies were performed at (298±1) K using a thermostatic water bath. Equal aliquots (20 mL) of aqueous and organic phases were taken in a 100 mL stoppered bottle and shaken well, in the thermostatic water bath. For equilibration, a predetermined time of 60 min was used. After equilibration, phases were settled and separated by a separating funnel. The aqueous phase was then titrated to obtain the concentration of mineral acids (H\(_2\)SO\(_4\), HCl, HClO\(_4\) and HNO\(_3\)). The distribution ratio (D) was then calculated using the following relation (superscripts ‘o’ and ‘A’ represent organic and aqueous phases, respectively and subscript ‘(ini)’ and ‘(eq)’ represent initial and equilibrium states):

\[ D = \frac{c^o_{(eq)}}{c^A_{(eq)}} = \frac{(c^A_{(ini)} - c^A_{(eq)})}{c^A_{(eq)}} \] (1)

\[ \text{Procedure for loading} \]

An aliquot of the organic phase (20 mL 0.20 mol/L TOA) was repeatedly contacted for 60 min in each stage with a fresh aqueous solution for each mineral acid at 298 K. After each stage, extracted acids concentrations were estimated by the titrimetric method to calculate the cumulative concentration of each mineral acid in the organic phase.

\[ \text{Results and discussion} \]

In all four investigated systems, distribution of acids is completed within 30 min. However, in subsequent experiments, shaking for 1 h is allowed to ensure equilibration at various experimental conditions.

\[ \text{Effect of concentration of mineral acids on their extractions by tri-n-octylamine} \]

The effect of the variation of initial acid concentration on the equilibrium acid concentration in the organic phase and the percentage of extraction are shown in Table I for H\(_2\)SO\(_4\), HCl, HNO\(_3\) and HClO\(_4\) acid systems. In all cases, \([\text{Acid}]_{(eq, o)}\) increased with increasing \([\text{Acid}]_{(ini, A)}\) as expected. In the case of sulphuric acid, the equilibrium H\(_2\)SO\(_4\) concentration in the organic phase levels off at \([H_2SO_4]_{(ini, A)} = 0.13 \text{ mol/L; whence,}[\text{TOA}]_{(ini, A)}\) of 0.20 mol/L being used. This indicates the saturation of 0.20 mol/L TOA by H\(_2\)SO\(_4\). In other cases, \([\text{Acid}]_{(eq, o)}\) is increased regularly up to the studied region (no
saturation is observed even by using initial [Acid] of 1.0 mol/L in the aqueous phase).

The percentage extraction is decreased gradually with increasing [Acid]_{ini,A}. A 100% extraction of H$_2$SO$_4$ at [H$_2$SO$_4$]$_{ini,A}$ of 0.05 mol/L is decreased to only 13% extraction at [H$_2$SO$_4$]$_{ini,A}$ of 1 mol/L. If acid concentration in the aqueous phase is kept low, more than 90% extraction is possible for all acids investigated. In cases of HCl, HNO$_3$ and HClO$_4$, the % extraction at 1 mol/L [Acid]$_{ini,A}$ are 20%, 23% and 21.6%. At any [Acid]$_{ini,A}$, the extractability increases in the order: H$_2$SO$_4$<HCl<HClO$_4$<HNO$_3$.

**Table I. Variation of equilibrium acid concentration in the organic phase and % extraction with initial acid concentration in the aqueous phase.** [TOA] = 0.20 mol/L, Equilibration time = 60 min, O/A = 1 (O = 20 mL), Temperature = (298 ± 1) K

<table>
<thead>
<tr>
<th>[Acid]$_{ini,A}$, mol/L</th>
<th>[Acid]$_{eq,o}$, mol/L</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$SO$_4$</td>
<td>HCl</td>
</tr>
<tr>
<td>0.05</td>
<td>0.050</td>
<td>0.045</td>
</tr>
<tr>
<td>0.10</td>
<td>0.095</td>
<td>0.087</td>
</tr>
<tr>
<td>0.15</td>
<td>0.120</td>
<td>0.138</td>
</tr>
<tr>
<td>0.20</td>
<td>0.125</td>
<td>0.152</td>
</tr>
<tr>
<td>0.30</td>
<td>0.130</td>
<td>0.175</td>
</tr>
<tr>
<td>0.40</td>
<td>0.130</td>
<td>0.188</td>
</tr>
<tr>
<td>0.50</td>
<td>0.130</td>
<td>0.194</td>
</tr>
<tr>
<td>1.00</td>
<td>0.130</td>
<td>0.200</td>
</tr>
</tbody>
</table>

**Table II. Variation of equilibrium acid concentration in the organic phase and % extraction with initial TOA concentration in the organic phase.** [Acid]$_{ini,A}$ = 0.50 mol/L, Equilibration time = 60 min, O/A = (O = 20 mL), Temperature = (298±1) K

<table>
<thead>
<tr>
<th>[TOA]$_{ini,o}$, mol/L</th>
<th>[Acid]$_{eq,o}$, mol/L</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$SO$_4$</td>
<td>HCl</td>
</tr>
<tr>
<td>0.05</td>
<td>0.033</td>
<td>0.062</td>
</tr>
<tr>
<td>0.10</td>
<td>0.069</td>
<td>0.120</td>
</tr>
<tr>
<td>0.15</td>
<td>0.106</td>
<td>0.159</td>
</tr>
<tr>
<td>0.20</td>
<td>0.130</td>
<td>0.194</td>
</tr>
<tr>
<td>0.30</td>
<td>0.193</td>
<td>0.250</td>
</tr>
<tr>
<td>0.40</td>
<td>0.221</td>
<td>0.284</td>
</tr>
<tr>
<td>0.50</td>
<td>0.262</td>
<td>0.333</td>
</tr>
<tr>
<td>0.70</td>
<td>0.333</td>
<td>0.417</td>
</tr>
<tr>
<td>1.00</td>
<td>0.409</td>
<td>0.450</td>
</tr>
</tbody>
</table>

The percentage extraction is decreased gradually with increasing [Acid]$_{ini,A}$. A 100% extraction of H$_2$SO$_4$ at [H$_2$SO$_4$]$_{ini,A}$ of 0.05 mol/L is decreased to only 13% extraction at [H$_2$SO$_4$]$_{ini,A}$ of 1 mol/L. If acid concentration in the aqueous phase is kept low, more than 90% extraction is possible for all acids investigated. In cases of HCl, HNO$_3$ and HClO$_4$, the % extraction at 1 mol/L [Acid]$_{ini,A}$ are 20%, 23% and 21.6%. At any [Acid]$_{ini,A}$, the extractability increases in the order: H$_2$SO$_4$<HCl<HClO$_4$<HNO$_3$.

**Effect of extractant concentration on the extraction of mineral acids**

Table II shows the variation of equilibrium acid concentration in the organic phase with initial [TOA]. The equilibrium acid concentration and % extraction increase with increasing initial TOA concentration in the organic phase. When initial acid concentration of 0.50 mol/L is
used, the \([\text{H}_2\text{SO}_4]_{eq,o}\) increases from 0.033 (at \([\text{TOA}]_{ini,o}\) = 0.05 mol/L) to 0.409 (at \([\text{TOA}]_{ini,o}\) = 1.0 mol/L). Similarly, \([\text{HCl}]_{eq,o}\), \([\text{HNO}_3]_{eq,o}\) and \([\text{HClO}_4]_{eq,o}\) increase from 0.062 to 0.45, 0.08 to 0.465 and 0.068 to 0.465; respectively, for same \([\text{TOA}]_{ini,o}\), variation as in the case of \(\text{H}_2\text{SO}_4\). The percentage extraction of acids also increases regularly with increase in \([\text{TOA}]_{ini,o}\): 6.6% \(\text{H}_2\text{SO}_4\), 12.4% \(\text{HCl}\), 16% \(\text{HNO}_3\) and 13.4% \(\text{HClO}_4\) acid extractions at \([\text{TOA}]_{ini,o}\) of 0.05 mol/L are increased to 81.8% \(\text{H}_2\text{SO}_4\), 90% \(\text{HCl}\), 93% \(\text{HNO}_3\) and 92% \(\text{HClO}_4\) acid extractions at \([\text{TOA}]_{ini,o}\) of 1 mol/L.

The \(\log D\) vs. \(\log ([\text{TOA}]_{ini,o}\text{ mol/L})\) plots for four acid systems investigated are presented in Fig. 1. Plots are curves with asymptotic slope of \(~1\) at lower concentration region and of \(~2\) at higher concentration region. In higher concentration region i.e. in surplus of \(\text{TOA}\), acids are solvated by two molecules of \(\text{TOA}\); but at scarcity of extractant, acids are solvated by one molecule of \(\text{TOA}\).

The extraction occurs via co-ordinate bond formation between amine and \(\text{H}^+\) of each acid. Thus, in scarcity of extractant, the extraction reactions are:

\[
\text{H}_2\text{SO}_4(A) + \text{TOA}(o) \rightarrow [\text{TOA} \rightarrow \text{H}^+ \text{HSO}_4^-](o) \quad (3)
\]

\[
\text{HX}(A) + \text{TOA}(o) \rightarrow [\text{TOA} \rightarrow \text{H}^+ X^-](o) \quad (4)
\]

and at surplus of extractant, the reactions are

\[
\text{H}_2\text{SO}_4(A) + 2 \text{TOA}(o) \rightarrow [(\text{TOA} \rightarrow \text{H}^+) \text{SO}_4^{2-}](o) \quad (5)
\]

\[
\text{HX}(A) + 2 \text{TOA}(o) \rightarrow [(\text{TOA} \rightarrow \text{H}^+) \text{X}^- \text{TOA}](o) \quad (6)
\]

**Effect of temperature on the extraction of mineral acids**

The vant’t Hoff plots (\(\log D\) vs. \((1/T) \times 10^3\), K\(^{-1}\)) are shown in Fig 2. The extraction ratio decreased with increasing temperature, and the straight-line relationship in mentioned plots holds for each system under investigation. For \(\text{H}_2\text{SO}_4\), \(\text{HCl}\), \(\text{HClO}_4\) and \(\text{HNO}_3\) system the slopes obtained are \(1.27 \times 10^3\), \(1.34 \times 10^3\), \(1.34 \times 10^3\) and \(1.34 \times 10^3\), respectively. As...
the slope is equal to $-\Delta H/2.303R$ and the values of $\Delta H$ appear for the $\text{H}_2\text{SO}_4$, $\text{HCl}$, $\text{HClO}_4$ and $\text{HNO}_3$ systems as $-24.32$, $-25.65$, $-25.65$, $-25.65$ kJ/mol, respectively.

The acid-base neutralization ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$) is usually exothermic with $\Delta H$ value of $\sim -57$ kJ/mol for neutralization of a strong acid by a strong base. However, the neutralization for present investigated systems is Lewis type (no water being formed, instead co-ordination bond between $\text{H}^+$ and $\text{N}$ of TOA being formed). Moreover, solvation takes place at surplus of extractant and so the extraction process appears as exothermic with $\Delta H$ value of $-27$ kJ/mol and not $-57$ kJ/mol.

The loading result for $\text{H}_2\text{SO}_4$ indicates that at the saturated condition, the extraction occurs via Eq. (3) and (5). It appears that 70% extraction occurs via Eq. (5), where TOA:$\text{H}_2\text{SO}_4$ is 2:1. The rest 30% extraction occurs via Eq. (3), where TOA:$\text{H}_2\text{SO}_4$ is 1:1 or 2:2. Therefore, overall TOA:$\text{H}_2\text{SO}_4$ ratio becomes $2:(1 \times 0.7 + 2 \times 0.3)$, i.e. $2:1.3$ (experimentally obtained). As 1.0 L of 0.20 mol/L TOA can extract 0.129 mol/L $\text{H}_2\text{SO}_4$; 1.0 L of 1.0 mol/L TOA can extract 0.645 mol/L $\text{H}_2\text{SO}_4$. In other words, 353.67 g TOA can extract 0.645 mol/L $\text{H}_2\text{SO}_4$; or 100 g TOA can extract only 0.1824 mol/L $\text{H}_2\text{SO}_4$, i.e. 17.87 g $\text{H}_2\text{SO}_4$.

![Graph](image)

**Fig. 2.** Effect of temperature on the extraction of mineral acids by TOA dissolved in distilled kerosene. $[\text{H}_2\text{SO}_4]_{\text{ini}} = 0.098$ mol/L, $[\text{HCl}]_{\text{ini}} = 0.089$ mol/L, $[\text{HClO}_4]_{\text{ini}} = 0.102$ mol/L, $[\text{HNO}_3]_{\text{ini}} = 0.098$ mol/L, [TOA] = 0.15 mol/L, Equilibrium time $= 60$ min, O/A = 1 (O=20 mL)

**Loading of TOA solution by mineral acids**

Aqueous phase is repeatedly equilibrated with fresh extractant and each such operation is a stage. Fig. 3 represents the cumulative [acid]$_{\text{org}}$ mol/L vs. stage number plot. It is observed that the organic phase is almost saturated with the mineral acids under investigation at about 4th contact.

Therefore, the loading capacity of TOA for $\text{H}_2\text{SO}_4$ is 17.87 g $\text{H}_2\text{SO}_4$/100 g TOA.

At saturation level, 0.20 mol/L TOA can load 0.20 mol/HCl; so, the TOA to HCl ratio is 1:1. So, the reaction occurs via Eq. (4). If (TOA. HCl), TOA is formed initially via Eq. (6), this species extracts more HCl at deficiency of TOA in the system as illustrated below:

\[
\text{(TOA . HCl) + TOA} \rightarrow 2 \text{TOA} \cdot \text{HCl}
\] (7)
As 0.20 mol/L TOA solution can extract 0.20 mol/L HCl at saturation level, 353.67 g TOA could extract 36.45 g HCl; which is equivalent to the extraction of 10.31 g HCl per 100 g TOA. In other words, the loading capacity of TOA towards HCl is 10.31 g HCl/100 g TOA in comparison to 17.87 g H₂SO₄/100 g TOA.

The cumulative [HClO₄]ₐₒ increases gradually with the phase contact number but levels off at the 4th contact. 0.20 mol/L TOA can extract 0.129 mol/L H₂SO₄; 1.0 L of 1.0 mol/L TOA can extract only 0.1824 mol/L HCl, i.e. 17.87 g H₂SO₄/100 g TOA.

The organic phase is almost saturated with HNO₃ at the 4th contact like in the other cases; when 0.20 mol/L TOA solution is repeatedly contacted with fresh 0.10 mol/L HNO₃ solution at O/A = 1 in each contact. It is seen that 0.20 mol/L TOA can extract as much as 0.23 mol/L HNO₃. This result provides the loading capacity of the extractant as 20.49 g HNO₃ per 100 g TOA.

As the mole ratio of TOA to HNO₃ is 1/1.15, in addition to reaction represented by Eq. (4) for HCl, the following reaction also occur in conjunction:

\[ 2\text{HNO}_3 (\alpha) + \text{TOA} (\alpha) \rightarrow (\text{TOA} \rightarrow \text{H}^+\cdot\text{NO}_2^- \cdots \text{HNO}_3 (\alpha) \)  \]  (9)

**Effect of phase volume ratio (O/A) on the extraction of mineral acids**

At O/A = 1, 0.10 mol/L TOA extracts ~90%, ~83%, 98% and 94% H₂SO₄, HCl, HClO₄ and HNO₃, respectively. However, the % extraction at O/A = 0.50, 0.20 and 0.10 mol/L TOA are 53, 23 and 13% for H₂SO₄; 65, 41 and 21% for HCl; 88, 36
and 20% for HClO₄; and 88, 41 and 21% for HNO₃, as shown in Fig. 4. It is realized to use lower O/A ratio and adopt stage-wise extractions for more extraction of acids.

**Stripping of extracted acids**

Strippings of acids obtained in the organic phase during extractions at O/A = 1/5 have been investigated by 0.15 mol/L NaOH solutions at 303 K while phase contact time of 1 h being allowed. The stripping results are tabulated in Table III. indicates that NaOH solution is a very efficient reagent to strip off HCl, HClO₄ and HNO₃ from the organic phase. In the case of H₂SO₄ system, two-stage stripping might be required for almost quantitative regeneration of TOA. A typical stripping reaction is shown below:

\[
\text{TOA} \cdot \text{HCl} \text{ (o)} + \text{NaOH} \text{ (a)} \rightarrow \text{TOA} \text{ (o)} + \text{NaCl} \text{ (a)} + \text{H₂O} \text{ (o)} \]  (10)

On quantitative utilization of NaOH used in stripping, the stripped salt solutions can be evaporated to crystallize out value-added pure crystals of either Na₂SO₄, NaCl, NaClO₄ or NaNO₃. On passing the stripped solution through a cation exchanger, the acids may be regenerated from these salts.

**Table III. Stripping of acid-extracted organic phase by NaOH solution. Extraction condition: [Acid]₀ = 0.05 mol/L, [TOA] = 0.10 mol/L, O/A = 1/5, Temperature = 303 K, Equilibration / Shaking time = 60 min. Stripping condition: [NaOH]₀ = 0.15 mol/L, O/A = 1, Temperature = 303 K, Equilibration / Shaking time = 60 min**

<table>
<thead>
<tr>
<th>Acid</th>
<th>[NaOH]₀ (eq.), mol/L</th>
<th>[NaOH]₀ (eq.), mol/L</th>
<th>% Stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>0.046</td>
<td>0.104</td>
<td>86.67</td>
</tr>
<tr>
<td>HCl</td>
<td>0.056</td>
<td>0.094</td>
<td>98.95</td>
</tr>
<tr>
<td>HClO₄</td>
<td>0.044</td>
<td>0.106</td>
<td>96.36</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.046</td>
<td>0.104</td>
<td>99.04</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of volume ratio (O/A) on the percentage extraction of mineral acids by TOA dissolved in distilled kerosene. [H₂SO₄]₀ = 0.051 mol/L, [HCl]₀ = 0.046 mol/L, [HClO₄]₀ = 0.06 mol/L, [HNO₃]₀ = 0.051 mol/L, [TOA] = 0.10 mol/L, Temperature = 303 K, Equilibration / Shaking time = 60 min. O = 20 mL, A is varied as 20 mL, 40 mL, 100 mL and 200 mL. % Ex. = \( \frac{D}{D + \frac{V_A}{V_o}} \times 100 \)
It is, therefore, recommended to extract $\text{H}_2\text{SO}_4 / \text{HCl} / \text{HClO}_4 / \text{HNO}_3$ in the bleed solution of a hydrometallurgical process by concentrated TOA at low O/A (if necessary stage-wise) and strip the extracted phase by a concentrated $\text{NaOH}$ solution at high O/A ratio (if necessary stage-wise) to get an aqueous solution containing highly concentrated solutions of $\text{Na}_2\text{SO}_4 / \text{NaCl} / \text{NaClO}_4 / \text{NaNO}_3$. From these solutions, the value-added compounds can be isolated on crystallization. Therefore, the environmental protection and the isolation of value-added products are the benefits to be obtained from the hydrometallurgical acidic bleed solution as suggested from this study.

**Conclusion**

Following conclusions have been drawn from the system under investigation:

TOA can extract mineral acid ($\text{H}_2\text{SO}_4$, $\text{HCl}$, $\text{HClO}_4$ and $\text{HNO}_3$) by solvated ion pair formation mechanism.

From the extractant dependency the value of solvation number has been obtained at lower and higher concentration regions as 1 and 2, respectively.

Temperature dependency study shows the system under investigation is exothermic. The $\Delta H$ value for $\text{H}_2\text{SO}_4$, $\text{HCl}$, $\text{HClO}_4$ and $\text{HNO}_3$ is -24.32, -25.65, -25.65 and -25.65 kJ/mol, respectively.

The loading capacities of TOA for $\text{H}_2\text{SO}_4$, $\text{HCl}$, $\text{HClO}_4$ and $\text{HNO}_3$ are 17.87 g $\text{H}_2\text{SO}_4$/100 g TOA, 10.31 g $\text{HCl}$/100 g TOA, 30.69 g $\text{HClO}_4$/100 g TOA and 20.49 g $\text{HNO}_3$/100 g TOA, respectively.

From the study of phase volume ratio, it is suggested to use stage-wise extractions at lower O/A ratios.

To extract $\text{H}_2\text{SO}_4 / \text{HCl} / \text{HClO}_4 / \text{HNO}_3$ in the bleed solution of a hydrometallurgical process by concentrated TOA at low O/A and strip the extracted phase by a concentrated $\text{NaOH}$ solution at high O/A ratio to achieve an aqueous solution containing highly concentrated solutions of $\text{Na}_2\text{SO}_4 / \text{NaCl} / \text{NaClO}_4 / \text{NaNO}_3$ is recommended. The value-added compounds can be isolated on crystallization from these solutions. Therefore, the environmental protection and the isolation of value-added products are the benefits to be obtained from the hydrometallurgical acidic bleed solution as suggested from this study.

**Acknowledgement**

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