Empirical modelling of U(IV) third phase formation in 30% TBP/n-dodecane system

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Formation of second organic phase due to limiting solubility of tetravalent actinide solvates in organic solvent has been studied in a qualitative manner by several researchers. Quantitative relations for interactions among various solutes for second organic phase formation were not reported in open literature. In this contribution, an empirical model for U(IV) third phase formation in biphasic U(NO$_3$)$_4$-H$_2$O-HNO$_3$-30%TBP/n-dodecane system has been reported. Empirical models were also developed for correlating various third phase characteristics like temperature dependency of third phase formation, volume and concentration of constituents-U(IV) and TBP. Performance of the reported models has been compared with models previously reported.

For mutual separation of uranium and plutonium in contemporary salt-free PUREX flowsheets, it is customary to use a reducing agent (U(NO$_3$)$_4$ or hydroxylamine nitrate) to reduce Pu(IV) to Pu(III) and utilise practical inextractibility of latter in the organic solvent. In reprocessing campaigns, due to several operational reasons, consumption of U(IV) (or any other reductant) is observed several times of that required stoichiometrically. It was reported that during the extraction of tetravalent actinide (i.e. U(IV), Pu(IV) and Th(IV)), organic phase was to split into two phases whenever concentration of solvate exceeded it’s solubility limit in the solvent$^1$. Thus for high plutonium flowsheet having U(IV) based partitioning, quantitative knowledge of limiting organic concentration of U(IV) is required for safe design of partitioning step.

Siddall$^1$ discussed third phase formation in Th(IV) extraction from HNO$_3$ solutions with 30% TBP-Ultrasene solvent. Mills and Logan$^2$ reported third phase formation and reported solubility limits for Th(IV), Pu(IV) and U(IV) under limited conditions. Horner$^4$ mentioned that limiting organic concentration of Pu(IV) could be correlated to aqueous acidity, total nitrate salting strength or total ionic strength of the aqueous phase. Kolariks$^5$ discussed the formation and characteristics of third phase in U(IV), Pu(IV) and Th(IV) extraction. Detailed qualitative information about third phase formation in U(IV) and Pu(IV) was presented$^6,17$ in different diluents including dodecane, Hyfrane and odourless kerosene. For U(IV) third phase formation in biphasic U(NO$_3$)$_4$-H$_2$O-HNO$_3$-30%TBP/n-dodecane system, polynomial models were suggested$^8$ for estimation of third phase characteristics e.g., volumes and concentrations of constituents of the third phase and light organic phases. Their models were of type,

\[
V_3, V_L, C_i = A_0 + A_1 [H] + A_2 [U] + A_3 [H] [U]
+ A_4 [H]^2 + A_5 [U]^2 + A_6 [H]^2 [U]^2
\] ...

(1)

where $V_3$, $V_L$ and $C_i$ are volumes of third phase, light organic phase and concentration of $i_{th}$ species in specified phase respectively. [H] and [U] are nitric acid and U(IV) concentrations. Several models based on initial aqueous concentrations, equilibrated aqueous concentrations and gross organic concentrations were discussed and related constants were reported. Gross organic concentrations were calculated by volume averaging over third phase concentrations and light organic phase concentrations as,

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\[ C_G = \left( \frac{V_3 \cdot C_3 + V_L \cdot C_L}{V_3 + V_L} \right) \]  \hspace{1cm} (2)

where \( C_G, C_3 \) and \( C_L \) are concentrations in un-split organic phase, third phase and light organic phase. \( V_3 \) and \( V_L \) are volumes of third phase and light organic phase respectively. Tachimori et al.\(^9\) reported models similar to that of Ami et al.\(^8\). In this kind of approach, to determine whether a third phase will form under operating conditions, one needs to calculate related third phase and light organic phase parameters to obtain \( \text{LOC} \) of U(IV) and to compare with organic U(IV) concentration.

Recently, a power-law type relation for Pu(IV) third phase formation has been reported\(^10\). Using published data, another model for temperature dependency of Pu(IV) third phase formation was reported by Kumar and Koganti\(^10\). Based on similar lines, U(IV) third phase formation has been modelled and reported here.

**Discussion**

**Models for U(IV) LOC and it’s temperature dependency**

It is assumed that the third phase is formed from splitting of overloaded organic phase. If U(IV) solvate solubility limits are exceeded, the organic phase is to split into two phases- heavy phase (termed as third phase, rich in TBP and U(IV)) and lean phase (rich in diluent and lean in TBP). U(IV) concentrations in the third phase after this split may depend upon concentrations in the un-split organic phase, temperature and free TBP. In the present work, it was postulated to be a function of concentrations of U(IV) and HNO\(_3\) in the un-split phase (here after referred as gross organic phase) at constant temperature. It was observed that the experimental data could be correlated as a power law relation

\[ [\text{U(IV)}_{\text{org}}]_{298.15} = 0.3498 [\text{U(IV)}_{\text{aq}}]^{0.6821} \times [\Sigma \text{NO}_3]^{-0.6450} \]  \hspace{1cm} (3)

Fig.1 represents the comparison between the predicted values of gross organic concentrations of U(IV) and the actual experimental values of Ami et al.\(^8\). For Eq. 3, mean error and standard deviation were 0.44% and 9.46% respectively.

It is established that third phase formation is accompanied with entropy change and LOC is a strong function of temperature. Here, U(IV) limiting organic concentration at different temperatures was correlated as an arrhenius function involving gross organic acidity. The slopes of \( (1/T-1/298.15) \) versus \( \ln(\text{U(IV)}_{\text{org}}/\text{U(IV)}_{\text{org}}[298.15]) \) were found to be a function of aqueous acid concentration. The empirical equation could be written as

\[ [\text{U(IV)}_{\text{org}}]_t = [\text{U(IV)}_{\text{org}}]_{298.15 \text{K}} e^{-D \left( \frac{1}{t} - \frac{1}{298.15} \right)} \]  \hspace{1cm} (4)

where

\[ D = 306.60 + 2401.0 [H_{\text{aq}}] - 599.30 [H_{\text{aq}}]^2 \]

\[ + 46.50 [H_{\text{aq}}]^3 \]  \hspace{1cm} (5)

For a data set compiled from the earlier results\(^5\)\(^6\), mean error and standard deviation were 0.36% and 8.53% respectively. Parity plot shown in Fig.2 represents this comparison.
Correlation for U(IV) concentration in the third phase

Gonda and Oka\(^1\) observed that Pu(IV) concentration in third phase could be expressed as,

\[
[\text{Pu}_{sp}] = a y_H y_{Pu} \quad \ldots (6)
\]

Data set for Pu(IV) system in this case consisted of only three points and this relation could not be extended to other third phase systems. In our opinion, if an empirical equation could represent a general relation holding good for U(IV), Pu(IV) and Th(IV) third phase systems, it may indicate the possible mechanism for formation of the third phase from overloaded organic phase. A simple mechanism for formation of third phase could be assumed on the basis of split of overloaded organic phase for Pu(IV), U(IV) and Th(IV) systems,

\[
[M(IV)]_{\text{Gross}} + [\text{HNO}_3]_{\text{Gross}} \leftrightarrow \text{Third Phase} + \text{Light Phase} \quad \ldots (7)
\]

Incidentally it was observed that for the most of the experimental runs reported by Ami et al.\(^2\), U(IV) concentration in light organic phase was very small as compared to that in third phase. In addition, tetravalent uranium solvate was found to dominate the third phase as compared to nitric acid solvates on weight percent basis. Kolarik\(^3\) reported that for a wide range of TBP moles per g-atom of metal nitrate in the whole system, amount of acid solvate was 1-2% (w/w) as compared to that of U(IV) solvate which ranged between 65% to 51% (w/w) of the third phase. Thus if contributions from the light organic phase as well as from HNO\(_3\) (in the third phase) are neglected (although this assumption may have some inherent error) a parameter may be defined as

\[
K_p^{l(IV)} = \frac{[\text{U(IV)}]_{\text{Org}}^{\text{Third Phase}}}{[\text{U(IV)}]_{\text{Org}}^{\text{Gross}}[\text{HNO}_3]_{\text{Org}}^{\text{Gross}}} \quad \ldots (8)
\]

An exponential relation was observed between this parameter \(K_p\) and nitric acid concentration in the gross organic phase as shown in Fig.3. It was correlated by least-square analysis as

\[
K_p^{l(IV)} = 19.7527 e^{(2.2039 [\text{HNO}_3]_{\text{Gross}})} \quad \ldots (9)
\]

U(IV) concentrations in third phase were back-calculated from numerical estimates of \(K_p\). For U(IV) third phase average and standard deviations from measured values were 1.07% and 14.42% respectively. A fair agreement between predicted and experimental values was observed.

Correlation for volume of the third phase

Reported experimental third phase volume could be correlated by following empirical polynomial model with first level interactions

\[
V_{3p} = a_0 + \sum_{i=1}^{3} a_i x_i + \sum_{i=1}^{3} b_i x_i^2 + \sum_{i=1, j=1, i\neq j}^{3} c_{ij} x_i x_j \quad \ldots (10)
\]
Table 2—Comparison with models reported by Ami et al.8

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Standard Deviation from models of Ami et al.8</th>
<th>Standard Deviation from models reported in the present work</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(IV) limiting organic concentration</td>
<td>20.93% for 25 points.</td>
<td>9.46% for 42 points.</td>
<td>Results of Ami et al. from Fig. 9d</td>
</tr>
<tr>
<td>U(IV) third phase temperature dependency</td>
<td>Not applicable</td>
<td>8.53%</td>
<td>Ami’s model valid at 298.15 K</td>
</tr>
<tr>
<td>Volume of the third phase</td>
<td>11.50%</td>
<td>8.60%</td>
<td>Ami’s model 3</td>
</tr>
<tr>
<td>U(IV) concentration in third phase</td>
<td>11.15%</td>
<td>14.42%</td>
<td>—</td>
</tr>
<tr>
<td>TBP concentration in third phase</td>
<td>3.36%</td>
<td>2.78%</td>
<td>—</td>
</tr>
</tbody>
</table>

Percent deviation = 100 * (measured - experimental) / experimental

Term x stands for molar concentration. These coefficients have been listed in Table 1. For this equation mean error and standard deviation from measured data were 0.77% and 8.60% respectively.

$\frac{[\text{TBP}]_{3p}}{[\U(IV)]_{3p}} = 10.1535 \ e^{-1.4548 \ [\U(IV)]_{3p}}$

TBP concentrations were back calculated and a close agreement between predicted and experimentally observed values was observed. For Eq. 11, mean and standard deviations were 0.033% and 2.78%

Performance of all the models reported above is compared with previously reported models of Ami et al.8 in Table 2. It is observed that for most of the models reported in the present work, statistical parameters were better as compared to models reported by Ami et al.

**Conclusion**

Quantitative models were reported for U(IV) third phase formation in 30% TBP/n-dodecane system. The first empirical model for U(IV) LOC incorporated the interaction of U(IV) concentration and acidity variation at 298.15 K. The second empirical model related U(IV) LOC at other temperatures (278-303K) to that at 298 K. Third phase characteristics like U(IV) and TBP concentrations in third phase and it’s volume were also modelled. Performance of these quantitative models was better than that of earlier reported models.
Nomenclature

- $H_{aq}$: Aqueous acid concentration (mol L⁻¹)
- $K_p$: Pseudo-equilibrium parameter for split of organic phase
- LOC: Limiting organic concentration for actinide nitrate solvate
- $M(IV)$: Tetravalent actinide nitrate
- $Pu_{3p}$: Plutonium(IV) concentration in third phase (g L⁻¹)
- $U_{3p}$: Uranium(IV) concentration in third phase (g L⁻¹)
- $r$: Number of TBP moles per g-atom of metal
- TBP: Tri-n-Butyl Phosphate
- $t$: Temperature (K) at which LOC is required

References