An extended Setschenow model for aqueous solubility of TBP in 5-100% TBP/n-dodecane-nitric acid-water biphasic system at 298.2 K

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Reported experimental data on aqueous solubility of Tri-n-Butyl Phosphate (TBP) in 5-100% TBP/n-dodecane-nitric acid-water biphasic system at 298.2 K was analyzed by least-squares technique and an extended Setschenow model was proposed for correlating the same. Database could be correlated with a standard deviation of about 7%. A further extension was proposed for presence of multiple solutes (extracting/non-extracting).

Aqueous solubility of a non-electrolyte in the presence of an electrolyte was studied by Setschenow1. It was observed that the solubility could be correlated by the empirical relation,

$$\log \frac{S^0}{S} = k_s C_s$$

(1)

The relation is valid for low salt concentrations. At higher concentrations, usually a power series in concentration is used. Eq. (1) has been related to the theory of salt-effect by Long and McDevit2 and Gordon3.

TBP is the solvent for solvent extraction step of PUREX process, used for separation of uranium and plutonium from spent nuclear fuel. In the PUREX process, usual TBP concentration is 30% on a volume basis. In the Interim-23 process, for the separation of U-233 from irradiated thorium, 5% TBP is used as solvent. Use of Setschenow equation for aqueous solubility of 100% TBP was reported by Higgins et al.4. Setschenow constants were calculated for 14 electrolytes (non-extracting with TBP). Related literature was discussed by Leroy3 and Burger5. Burger also noted that for Tri-n-Butyl Phosphate percentage less than 100% (TBP diluted with a diluent, aliphatic paraffin or otherwise), the aqueous solubility was affected by the interaction between the diluent and TBP.

In the literature, meager information is available on models available for aqueous solubility of TBP in wide conditions. Belousov and Zakharova7 correlated aqueous solubility of TBP in the HCl solutions. Kunoo et al.8 investigated aqueous solubility of 100% TBP in presence of Pu(NO3)4 and nitric acid. Setschenow type models reported may be given as,

$$\log \left( \frac{S^0}{S} \right) = 6.0 C_{Pu(IV)}$$

(2)

Eq. (2) was valid only in the range of Pu(NO3)4 concentration of 0-0.1 mol/L. In the presence of nitric acid and Pu(NO3)4, data were correlated as,

$$\log (S) = -2.8 - 0.15 C_{HNO_3} + 6.0 C_{Pu(IV)}$$

(3)

Nitric acid concentrations were 1-8 mol/L and Pu(NO3)4 concentrations were 0-0.1 mol/L.

Recently Geetha et al.9 reported aqueous solubility of 5%, 20% and 30% TBP in nitric acid solutions at ambient temperature (assumed to be 298.2±2 K). Diluent was n-dodecane. Any model for solubility was not reported.

Discussion

It was observed that the recently reported data9 on solubility of 5, 20, 30% TBP along with data4,6-11 of 100% TBP could be predicted well with sufficient accuracy by the empirical equation,

$$\ln \left( \frac{S^0}{S} \right) = \sum_{i=1}^{3} k_i C^i_{HNO_3} + \left( A_0 + \sum_{i=1}^{3} A_i C^i_{TBP} \right)$$

+ b_0 C_{HNO_3} C_{TBP}

(4)

The database is listed in Table 1. Least-square determined constants of Eq. (4) are listed in Table 2. Eq. (4) is essentially an extended form of the basic
Table 1—Database for aqueous solubility of TBP

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Reference</th>
<th>Tri-n-Butyl Phosphate % in organic phase</th>
<th>Aqueous acidity, mol/L</th>
<th>No. of points</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alcock et al.</td>
<td>100%</td>
<td>0.11</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Burger and Forsman</td>
<td>100%</td>
<td>0.79 - 9.61</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Geetha et al.</td>
<td>5, 20 and 30</td>
<td>1 - 9*</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Higgins et al.</td>
<td>100%</td>
<td>0.05 - 3.09</td>
<td>8</td>
</tr>
</tbody>
</table>

* Data were reported in the range of 1-14 mol/L.

Table 2—Constants of Eq. (3)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>5.3321 x 10^-2</td>
</tr>
<tr>
<td>$k_2$</td>
<td>2.9013 x 10^-2</td>
</tr>
<tr>
<td>$k_3$</td>
<td>-2.4354 x 10^-2</td>
</tr>
<tr>
<td>$A_0$</td>
<td>1.2934</td>
</tr>
<tr>
<td>$A_1$</td>
<td>-1.8945</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1.0287</td>
</tr>
<tr>
<td>$A_3$</td>
<td>-1.6720 x 10^-3</td>
</tr>
<tr>
<td>$B_j$</td>
<td>2.3324 x 10^-2</td>
</tr>
</tbody>
</table>

Fig. 1—Variation of aqueous solubility of TBP with varying acidity at 298.2 K. O- 5%TBP; □- 20% TBP; ▲-30%TBP (all three from Geetha et al.9), ●- 100% TBP (Alcock et al.10), ■-100%TBP (Higgins et al.4), ▲-100% TBP (Burger and Forsman11).

Setschenow equation. As nitric acid concentration ranged between 0-10 mol/L, higher order terms were added to the basic equation. The terms inside brackets in the R.H.S. of Eq. (4) are of purely empirical nature and for dealing with the varying concentration of TBP in the organic phase (ranging between 5% to 100%). Since Tri-n-Butyl Phosphate extracts the nitric acid into the organic phase, the last term of Eq. (4) was introduced to take care of the interaction between TBP and the solute (nitric acid). The mean and standard deviations for 52 experimental points were 0.27% and 7.46% respectively. Fig.1 shows variation of aqueous solubility of Tri-n-Butyl Phosphate with varying acidity and varying Tri-n-Butyl Phosphate concentration in the organic phase. Fig.2 is a Setschenow plot. It shows that the slope of aqueous acidity versus $\ln(S/S_0)$ varies with acidity in a highly non-linear fashion, thus the use of higher order terms in Eq. 4 is justified.

In presence of $N$ electrolyte solutes (extracting/non-extracting), the Eq. (4) may be extended as

$$\ln \frac{S}{S_0} = \sum_{j=1}^{N} \left( \sum_{i=1}^{n} k_{ij} C_j^i \right) + \left( A_0 + \sum_{i=1}^{3} A_i C_{TBP}^i \right) + \sum_{j=1}^{N} b_{ij} C_j C_{TBP} \quad \ldots (5)$$
If a particular solute is not extracted into the organic phase, its associated interaction parameter should be set to zero. Since data of Kuno et al. were available only as published graph and manual digitization was prone to errors, they could not be used. Authors believe that Eq. (5) can represent data on aqueous solubility of Tri-n-Butyl Phosphate with a sufficient accuracy.

Few data on temperature dependency of Tri-n-Butyl Phosphate solubility exist in literature. Results of Kuno et al. showed that at constant acidity, the slopes of Arrhenius plots (1/T vs. ln(S^o/S)) were functions of aqueous Pu(IV) concentration. It appears that the slopes of Arrhenius plot could be related to the concentrations of various species in a non-linear fashion. Since available data are necessarily limited, additional experimental results are needed to test this hypothesis.

Conclusion

Reported experimental data on aqueous solubility of Tri-n-Butyl Phosphate in 5-100% Tri-n-Butyl Phosphate/n-dodecane-nitric acid-water biphasic system at 298.2 K could be modeled satisfactorily by means of an extended Setschenow equation. An extension was proposed for presence of multiple solutes (extracting/non-extracting).

Nomenclature

\[ A = \text{empirical coefficients} \]
\[ B = \text{interaction parameter} \]
\[ C = \text{concentration of solute, mol/L} \]
\[ K = \text{Setschenow coefficients} \]
\[ N = \text{number of solutes} \]
\[ S = \text{aqueous solubility} \]
\[ S^o = \text{reference aqueous solubility} \]
\[ T = \text{temperature, k} \]

\[ TBP = \text{Tri-n-Butyl Phosphate} \]

References